1986

X-ray diffraction characterization of CdTe epitaxial layers on GaAs substrates as a function of temperature

Robert Dean Horning
*Iowa State University*

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X-RAY DIFFRACTION CHARACTERIZATION OF CADMIUM TELLURIDE EPITAXIAL LAYERS ON GALLIUM ARSENIDE SUBSTRATES AS A FUNCTION OF TEMPERATURE

Iowa State University

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X-ray diffraction characterization of CdTe epitaxial layers on GaAs substrates as a function of temperature

by

Robert Dean Horning

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Department: Physics
Major: Solid State Physics

Approved:

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In Charge of Major Work

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Iowa State University
Ames, Iowa
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I. INTRODUCTION

A. Preliminary Remarks

The study of the growth, physical properties, and uses of epitaxial thin films began over 150 years ago. Epitaxy (from the Greek "epi" meaning on, and "taxis" meaning arrangement) means that two single crystals grow together, having a definite relationship between their orientations. Epitaxy was first noticed by minerologists in certain naturally occurring crystals. Frankenheim,\(^1\) in 1836, was the first to artificially reproduce this effect, growing sodium nitrate on calcite with a parallel orientation. Systematic studies of epitaxy were first carried out in the early 1900s, and the field has grown tremendously since then. A more complete historical review of the subject has been given by Pashley.\(^2\)

Significant advances in growth technologies have been made in the last twenty years. Most notably, Metal-Organic Chemical Vapor Deposition (MOCVD, also commonly called Organo-Metallic Vapor Phase Epitaxy, or OMVPE), Molecular Beam Epitaxy (MBE), and numerous variations of these techniques are now able to produce high quality epitaxial films. The growth can be controlled one monolayer at a time. Thus, entirely new "crystals" are being produced, exhibiting new and interesting physical properties. In addition, the large number of potential applications of epitaxial films makes their study valuable from a technological standpoint.
Of particular relevance to this investigation are applications involving epitaxial films of II-VI semiconducting compounds. For example, the alloy $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ($0 \leq x \leq 1$) is the most widely used material for detection of infrared (IR) radiation, and is beginning to find uses in optical communications technology as well. Unfortunately, $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ is soft and very difficult to grow in the form of large, uniform wafers. It is therefore desirable to grow epitaxial layers of this material on a foreign substrate. A suitable substrate should be easily available in large area wafers, relatively inexpensive, and durable. Some additional, but not necessary, features are a small lattice mismatch between substrate and epilayer, a small thermal expansion mismatch, and transparency to IR radiation. Cadmium telluride (CdTe), which has an almost perfect lattice match with $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, has the latter characteristics, but it, too, is brittle and hard to grow in large sizes. Therefore, the technology has shifted toward growing an epitaxial "buffer" layer of CdTe on still another substrate, and the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, or some other II-VI epilayer on top of that. CdTe has been grown on a number of substrates, including sapphire, silicon, InSb, and GaAs. InSb has an excellent lattice match with CdTe, but is no stronger than CdTe. InSb is also opaque to radiation with $\lambda > 0.55 \, \mu\text{m}$. Industry is better equipped for working with Si and GaAs than sapphire, and GaAs has received the most attention. Although it is more brittle than Si, GaAs is much harder than CdTe or
InSb. The thermal expansion coefficients of CdTe and GaAs match reasonably well above room temperature. GaAs is commercially available in high quality, three inch diameter wafers at a relatively low cost. In addition, GaAs is transparent in the two most important IR atmospheric windows: from 3-5 μm and from 8-14 μm. Finally, the emerging technology based on GaAs offers the possibility of using GaAs as an "active" substrate. That is, the processing electronics is contained in the GaAs, and the Hg\(_{1-x}\)Cd\(_x\)Te device is isolated from the substrate by the semi-insulating CdTe buffer layer (this may, or may not ever come about since the present GaAs fabrication methods do not yield consistently reproducible devices). The major disadvantage of GaAs is that it has a large lattice mismatch with CdTe, of Δa/a=14.6% (or 12.8% with respect to the CdTe lattice parameter). The mismatch between CdTe and Si is even larger: 19.4% with respect to Si. It is the combination CdTe on GaAs which is the subject of this report, with the major emphasis being on the CdTe.

B. The Zincblende Structure

Both GaAs and CdTe crystallize in the zincblende structure, shown in Fig. 1. This structure is a face-centered cubic lattice of Ga (Cd) atoms interpenetrated by a fcc lattice of As (Te) atoms. The two lattices are displaced by one quarter of the distance along the body diagonal of the
Fig. 1. The unit cell of the zincblende structure
cube. Each atomic plane perpendicular to the $[0,0,1]$ direction contains two identical atoms. Adjacent planes contain different atoms.

An alternate description more clearly shows the structure along the $[1,1,1]$ axis (Fig. 2). This begins with a close-packed layer of Ga (Cd) atoms, labelled as layer A. A second, identical layer of atoms is placed above this, covering half of the "holes" between the atoms in layer A. This is layer B. Layer C is stacked on layer B so that it covers the remaining holes in layer A. This is then repeated. The •••A B C A B C••• stacking sequence describes the cubic close-packed, or fcc, lattice with the stacking direction being a $<1,1,1>$ direction. To complete the zincblende structure, an As (Te) atom is placed above each Ga (Cd) atom, so that the As (Te) atom is equidistant from its four nearest neighbors. Since the As (Te) layer is closer to the layer above it than to the one below it, as shown in Fig. 3, the structure is polar in the $<1,1,1>$ directions. If a $(1,1,1)$ surface is terminated by Ga (Cd) atoms, it is referred to as a $(1,1,1)A$ surface. If the terminating layer is As (Te) the surface is $(1,1,1)B$. Each atom in this structure is bonded to four atoms of the opposite kind, which sit at the corners of a regular tetrahedron. The bonding is mostly covalent, but since the atoms are not all the same, there is some degree of ionicity present.
Fig. 2. ABC stacking sequence of the close-packed fcc lattice. A \( <1,1,1> \) direction is out of the page. In the zincblende structure, the atoms in the figure are all cations, and one anion would be placed directly above each cation.

Fig. 3. The zincblende structure oriented in a \( <1,1,1> \) direction. This view clearly shows the polar nature of the \{1,1,1\} planes.
C. GaAs and CdTe

GaAs is a III-V semiconductor with a band gap of 1.42 eV. It has a lattice parameter of $a=5.654 \ \text{Å}$ at room temperature. GaAs is available in three inch diameter wafers with dislocation densities less than $10^5 \ \text{cm}^{-2}$ throughout. On a typical wafer, the dislocation density varies as a function of the distance from the center of the wafer. A plot of this has a characteristic "W" shape. At the high points in the "W", the dislocation density is typically $\sim10^5 \ \text{cm}^{-2}$, and is on the order of $10^4 \ \text{cm}^{-2}$ in the low density regions. The major physical properties of GaAs have been reviewed recently by Blakemore.

CdTe has a lattice parameter of $a=6.482 \ \text{Å}$ at room temperature. Under certain conditions, CdTe can be found in a metastable hexagonal phase (the wurtzite structure). The ionic component of the Cd-Te bond is much larger than the ionic component in GaAs. In fact, of all the tetrahedrally bonded semiconductors, CdTe is one of the most ionic, ranking 35th out of 42. In addition, the large atomic numbers of Cd and Te, and the presence of more d-electrons, introduce a metallic character to the bond, reducing the cohesive energy. Thus CdTe is much softer and more brittle than GaAs.

The majority of the defects in bulk CdTe are either small-angle grain boundaries, twin faults, or small inclusions. These nonuniformities are the main reason epitaxial growth techniques are being studied so extensively for CdTe. The close-packed description of the zincblende
structure makes it clear why twinning occurs. As shown in Fig. 4, either a B or a C layer could be placed above an A layer. The nearest neighbor interactions are identical for both configurations. This ambiguity allows the stacking sequence to reverse itself creating a twin fault:

\[ \cdots A B C A B C B A C B A \cdots \]. A twin fault can also be portrayed as a 180° rotation about the \([1,1,1]\) axis. It was hoped that epitaxial CdTe would be free of twinning.

Inclusions are small pockets of impurities. They are usually rich in tellurium, and contain high concentrations of other elements. Inclusions are caused by the presence of impurities and deviations from stoichiometry during crystallization. It has been shown\(^{11}\) that these inclusions affect many of the physical properties of the crystal, and that they migrate over long time periods. In as-grown crystals, these inclusions are less than about 1 \(\mu m\) in size, but during annealing, can grow to 100 \(\mu m\) or more. Epitaxial films are free of these defects. The book by Zanio\(^{12}\) is a very complete review of the properties and applications of CdTe.

D. The CdTe/GaAs Composite System

The history of the epitaxial growth of CdTe on GaAs goes back to 1964. Alferov et al.\(^{13}\) claimed epitaxial growth using a gas transport method involving iodine as a transfer gas. However, no orientations were given, and the monocrystalline nature of the film was determined using only
Fig. 4. A slice through the (1,1,0) plane of a twinned crystal. The [1,1,1] direction is up, showing the \ldots ABC\ldots stacking sequence. Atoms not in this plane are not shown for clarity. The twin can be thought of as a reversal of the stacking sequence or as a rotation by 180° about the [1,1,1] axis.
a metallurgical (optical) microscope. Later, Aitkhozhin and Temirov\textsuperscript{14} obtained single crystal films which were verified by electron diffraction. They obtained parallel epitaxy in all cases. That is, on (0,0,1) oriented substrates the epilayer also had a (0,0,1) orientation, with the [1,0,0] axis of CdTe parallel to the [1,0,0] axis of GaAs in the surface. This is denoted (0,0,1)\parallel(0,0,1) with [1,0,0]\parallel[1,0,0]. They also grew films having the orientation (1,1,1)\parallel(1,1,1) with [\bar{1},1,0]\parallel[\bar{1},1,0].

The first reported growth of CdTe on GaAs using modern growth techniques was by Nishitani et al.,\textsuperscript{7} who used MBE. Since then, successful growth has been reported by a large number of researchers using a variety of methods, mostly MBE and MOCVD. Table 1 is a chronological bibliography of all the successful attempts to date. Four orientations are noted: (i). (0,0,1)\parallel(0,0,1) with [1,0,0]\parallel[1,0,0]; (ii). (1,1,0)\parallel(1,1,0) with [0,0,1]\parallel[0,0,1]; (iii). (1,1,1)\parallel(1,1,1) with [\bar{1},1,0]\parallel[\bar{1},1,0]; and (iv). (1,1,1)\parallel(0,0,1) with [1,1,\bar{2}]\parallel[1,1,0]. This last orientation is rather surprising since the [1,1,1] axis has three-fold symmetry, while the [0,0,1] is an axis of four-fold symmetry. The lattice mismatch between the substrate and epilayer is only 0.7% along the [1,1,\bar{2}] direction of CdTe. Perpendicular to that, in the CdTe [1,\bar{1},0] direction, the lattice mismatch is again 14.6%.

Since the [1,1,1] direction is polar, several groups determined the polarity of the substrate and epilayer.
Table 1. Chronological listing of studies performed on the CdTe/GaAs system

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Krotov et al.\textsuperscript{15} reported that \((1,1,1)\text{A} \) CdTe grew on \((1,1,1)\text{A} \) GaAs, and \((1,1,1)\text{B} \) CdTe on \((1,1,1)\text{B} \) GaAs. They did not say how this polarity was determined. In contrast, Harris et al.,\textsuperscript{41} using an etchant that reacted differently with the A and B faces, found \((1,1,1)\text{A} \parallel (1,1,1)\text{B} \) growth. Hsu and coworkers\textsuperscript{43} used three independent methods to deduce that CdTe grew with the \((1,1,1)\text{B} \) orientation on \((0,0,1) \) GaAs substrates.

The reason why CdTe sometimes grows with a \((1,1,1) \) orientation and other times with a \((0,0,1) \) orientation on \((0,0,1) \) GaAs is not fully understood. Some guidelines have been found, however, for consistently obtaining one or the other orientation. For \((0,0,1) \) growth, the substrate is preheated between ~480°C and 580°C for a short time (2-3 min.). The temperature is then reduced to 300-400°C for CdTe deposition. \((1,1,1) \) growth is obtained by a preheat at ~580°C for ten minutes or more, followed by a slow cooling to the growth temperature. The higher temperature preheat, over a longer time period, desorbs the oxide on the GaAs surface. It was therefore suspected that the presence or absence of an oxide determined the orientation. Otsuka and coworkers\textsuperscript{32} did observe a 10 Å thick layer of something, presumably an oxide, between the substrate and a MBE grown \((0,0,1) \) epilayer using high resolution transmission electron microscopy (HRTEM). No such layer was seen at the interface of a \((1,1,1) \) CdTe epilayer on a \((0,0,1) \) GaAs substrate. An alternate theory, by Feldman et al.,\textsuperscript{40} suggested that the orientation was
influenced by a Ga-As-Te mixed phase at the interface. This phase, they said, was produced by the higher "sticking coefficient" of Te. In either case, a clean GaAs surface results in (1,1,1) epitaxy, and a surface oxide or mixed phase yields (0,0,1) growth. Surface contamination is inherent in MOCVD because it is not a high vacuum process. The (1,1,1)|| (0,0,1) orientation therefore would not be expected to grow easily, and has only been reported very recently.\textsuperscript{54} Recently, Faurie et al.\textsuperscript{48} experimented on very carefully cleaned substrates. They found that even when the oxide layer was less than one monolayer, (0,0,1) growth resulted. When this oxide was completely absent, a preheat at the lower temperature produced a polycrystalline film having both the (1,1,1) and (0,0,1) orientations. This implies that the oxide is not the only deciding factor, although it plays an important role. These conclusions were corroborated by attempts to grow Cd$_{1-x}$Zn$_x$Te on (0,0,1) GaAs.\textsuperscript{42} For $x<0.10$, both orientations could be grown, but for $x>0.15$, only the (0,0,1) orientation was possible. The addition of zinc reduces the lattice parameter of the epilayer, increasing the lattice mismatch for the (1,1,1) orientation, but reducing it for the (0,0,1) orientation. It appears, therefore, that a defect layer of some sort is the most important factor in obtaining (0,0,1) growth. Other mechanisms are also involved but it is not clear what they are.

Twin faults have been observed in epilayers having the
(1,1,1) orientation. Epilayers are free from twinning, although microtwins have been observed by HRTEM extending about 100 Å from the interface into the epilayer.

In almost all cases reported, an initial characterization of the electronic structure is done using photoluminescence (PL). Two peaks are generally seen in the PL spectra. One is at 1.58 eV and is due to radiative transitions from excitonic states just below the CdTe conduction band edge. The full width at half maximum (FWHM) of this peak is an indicator of the impurity concentration and defect density in the film. The second peak is very broad and is centered at ~1.42 eV. The exact nature of the state associated with this second peak is not known, but it is related to a defect trap. The ratio of the intensity of the 1.42 eV peak to that of the 1.58 eV peak is a measure of the density of defects.

Unfortunately, PL is not a quantitative measure of crystal quality, and it is only sensitive to the top 50-100 Å of the layer. It is also insensitive to low angle grain boundaries and twins because these defects are typically much larger than the minority carrier diffusion length in CdTe.

**E. Motivation**

This report describes x-ray diffraction studies on three epilayers, and on bulk GaAs and CdTe for comparison purposes. All three epilayers were grown by MOCVD on commercial GaAs wafers. Two of them had the (0,0,1)||(0,0,1) orientation and
the other had the (1,1,1)||(1,1,1) orientation.

X-ray diffraction is well suited for this type of investigation. X-rays scatter from the electrons in the crystal, and the interaction is strong enough that a diffraction pattern can be obtained easily from an epilayer less than one micron thick. On the other hand, x-rays are penetrating enough that diffraction from the substrate is also recorded. The substrate is invisible in electron diffraction experiments when the epilayer is thicker than 10-15 Å. X-rays probe the bulk of the sample, so the measured quantities are averages over the entire epilayer. Techniques like Auger depth profiling and TEM can measure some properties as a function of depth, but these methods are destructive. X-ray diffraction is not. A relatively new technique called grazing incidence diffraction has been used to determine structural properties as a function of depth in a few materials and could be used on this system also.

Our x-ray measurements were done as a function of temperature. Temperature dependent measurements are important for several reasons. First, most devices that would be made on this composite substrate would be operated at 77 K. Structural characterization at this temperature is therefore essential. Second, besides the stress from the lattice parameter mismatch, the thermal expansion mismatch between CdTe and GaAs will introduce additional stress. Finally, since photoluminescence is usually done at 77 K or
lower, it is important to compare this with structural measurements at the same temperature. With the stresses present in this system, it is impossible to predict how the sample will change between room temperature and the lower temperatures.

The remainder of this dissertation is organized as follows. The theory of x-ray diffraction will first be developed. An emphasis is placed on the assumptions behind the equations derived, and the physical meaning of those equations. This is followed by a discussion of the experimental equipment and methods. The experimental results are divided into sections covering bulk GaAs, bulk CdTe, two (0,0,1) CdTe on (0,0,1) GaAs samples, and a (1,1,1) CdTe on (1,1,1) GaAs sample. Each section is concluded by a discussion of the most important results and their physical meaning. The final conclusions combine the results of the individual sections.
II. X-RAY DIFFRACTION: THEORY

A. Crystal Structure and Perfection

A crystal is a periodic array of atoms. The basic unit is the unit cell. Only a simple cubic lattice will be considered here, with a lattice parameter $a$ and volume $V = a^3$. The unit cells are displaced from the origin by lattice vectors $R$, which can be written

$$R = a(n_x x + n_y y + n_z z). \quad [1]$$

$n_x$, $n_y$, and $n_z$ are integers, and $x$, $y$, and $z$ are the Cartesian unit vectors. For convenience, it will be assumed that $0 \leq n_x < N_x$, $0 \leq n_y < N_y$, and $0 \leq n_z < N_z$. The total number of unit cells is $N_x N_y N_z = N$.

The atoms are at the positions $r_j$ with respect to the origin of the unit cell. In the zincblende structure (space group $F\bar{4}3m$) there are eight atoms. Four are cations (Ga in GaAs and Cd in CdTe) at the positions $(0,0,0)$, $(a/2,a/2,0)$, $(a/2,0,a/2)$, and $(0,a/2,a/2)$. The four anions are displaced from the cation positions by $(a/4,a/4,a/4)$. Note that although the zincblende structure is based on a fcc lattice with two atoms per lattice point, it is taken here as a simple cubic Bravais lattice with eight atoms per lattice point.

The reciprocal lattice is the set of points, at the
ends of the vectors $H$, which satisfy the condition $\exp(H \cdot R) = 1$, for all $R$. The reciprocal lattice of a simple cubic lattice is a simple cubic lattice with lattice parameter $2\pi/a$. Therefore

$$H = \frac{2\pi}{a}(hx + ky + lz)$$

[2]

where $h$, $k$, and $l$ are integers. It is well known that the reciprocal lattice of a fcc lattice is a body-centered cubic lattice with lattice parameter $4\pi/a$. These reciprocal lattice points are only a subset of those defined by equation 2, yet both sets can be used to describe the reciprocal lattice for the zincblende structure. The apparent discrepancy will be resolved later when it is shown that the structure factors associated with the additional reciprocal lattice vectors are identically zero. The extra points do not exist in one picture, and they have a structure factor of zero in the other, but the physical result is the same.

The perfection of a crystal is the extent to which it approaches the ideal case of equation 1. Two extremes are defined for single crystals. The first is the perfect crystal, which obeys equation 1 on a macroscopic length scale. Perfect crystals contain very few defects (less than $10^5$ cm$^{-2}$ in the context of x-ray diffraction). The opposite extreme is the ideally mosaic crystal. This is composed of many small, perfect crystal domains (mosaic blocks) which are
slightly misoriented with respect to each other. The misorientation is due to small angle grain boundaries, large numbers of point defects, and other inhomogeneities. A crystal with a defect density of about $10^8 \text{ cm}^{-2}$ or more can be considered ideally mosaic. If the defect density is between $10^5$ and $10^8 \text{ cm}^{-2}$, the crystal will be somewhere between the two extremes.

B. Diffraction by a Crystal

There are many excellent books on the subject of x-ray diffraction. Those by James, Cullity, and Warren have been especially helpful. The treatment here is, of course, limited to those topics necessary for understanding the analysis and results of the experiments. First, radiation scattered by a point charge will be discussed. This is then extended to scattering from a continuous charge distribution, and from a continuous, periodic distribution. The key concepts are the form factor and structure factor, which characterize the intensity of the diffracted beam, and the Laue or Bragg conditions, which define the direction of the beam. After deriving the necessary equations, their physical meaning will be discussed. Temperature dependent effects are covered in the following section in a similar format.

It is well known that an accelerated, charged particle will emit electromagnetic radiation. Fig. 5 shows the various points and vectors describing the situation. P is
Fig. 5. The situation for scattering from a point charge. The charge is at the point $P$, and $O$ is the observation point. In x-ray scattering, $r'<\ll R(r')$
the position of a point charge \( dQ \) having a mass \( dm \), \( O \) is the point of observation, and \( n \) is the unit vector in the direction \( PO \). The radiated electric field is given by (see, for example, Jackson\(^1\))

\[
\frac{dE}{c} = \frac{dQ}{c} \left[ \frac{nx(nx\dot{\beta})}{R(r')} \right]_{\text{retarded}}
\]

where \( c \) is the speed of light and \( \dot{\beta} = d/dt(v/c) \). The charge is accelerated by an incident electromagnetic wave (an x-ray in this case) \( E_0 \exp[i(k_0 \cdot r' - \omega t)] \). The magnitude of the incident wavevector is \( k_0 = 2\pi/\lambda \), where \( \lambda \) is the x-ray wavelength.

Thus,

\[
\dot{\beta} = E_0 \cdot \frac{1}{c} \frac{dQ}{dm} \exp[i(k_0 \cdot r' - \omega t)].
\]

Since x-rays scatter from the electrons in a solid, the charge to mass ratio, \( dQ/dm \), can be replaced by \(-e/m_o \) where \(-e \) and \( m_o \) are the electron charge and mass, respectively.

Inserting equation 4 into equation 3 results in the field scattered by the point charge,

\[
dE = -dQ \left( \frac{e}{m_o c^2} \right) \left[ \frac{nx(nxE_0)}{R(r')} \right] \exp[i(k_0 \cdot r' - \omega(t-R(r')/c))] \]

where the retarded time is \( t_{\text{ret}} = t - R(r')/c \).

Now let \( \rho \) be the number density of electrons (number of electrons/cm\(^{-3}\)) in some region. The charge in a small volume
The electric field radiated by this extended charge becomes

\[ E = \left( \frac{e^2}{m_e c^2} \right) [n_x(n_xE_0)] \int \frac{\rho(r')}{R(r')} \exp\left[ i(k_o \cdot r' - \omega(t - \frac{R(r')}{c}) \right] d^3r'. \tag{6} \]

The integration is over the entire charge distribution. Since \( r' \) is on the order of one Ångstrom, \( r' \ll R(r') \). \( R \) in the denominator can then be approximated by \( R_o \), and in the exponent by \( R_o - n \cdot r' \). Therefore, if \( \rho \) represents the charge density around an atom, the electric field scattered by the atom is

\[ E = \left( \frac{e^2}{m_e c^2} \right) \frac{[n_x(n_xE_0)]}{R_o} f_o(q) \exp\left[ i(k \cdot R_o - \omega t) \right] \tag{7} \]

where \( k = n \omega / c \), \( q = k - k_o \) is the scattering, or momentum transfer vector \( (q=4\pi \sin \theta / \lambda) \), and

\[ f_o(q) = \int \rho(r') \exp[-iq \cdot r'] d^3r' \tag{8} \]

is the Fourier transform of the charge density. \( f_o \) is called the atomic form factor. Form factors have been calculated and tabulated for every element.\(^2\)

A periodic charge density can be written as a Fourier series,

\[ \rho(r) = \frac{1}{V} \sum_{H} F(H) \exp[iH \cdot r'] \tag{9} \]
The Fourier transform of $\rho$ in one unit cell is

$$\int_{V} \rho(r') \exp[-i q \cdot r'] d^3 r' = \sum_{H} F(H) \delta_{H, q} = F(q) . \quad [10]$$

$F(q)$ is called the structure factor. Therefore, the expression for the electric field of the wave scattered by one unit cell is the same as equation 7, with $f_0(q)$ replaced by $F(q)$:

$$E_1 = \left( \frac{e^2}{m_0 c^2} \right) \frac{[n \times (n \times E_0)]}{R_0} F(q) \exp[i(k \cdot R_0 - \omega t)] . \quad [11]$$

Since the electron charge is most heavily concentrated near the atomic positions $r_j$, the charge density in the unit cell can be written, to a very good approximation,

$$\rho(r') = \sum_{j} \rho_j(r' - r_j) \quad [12]$$

where $-e \rho_j$ is the electron charge density of the $j^{th}$ atom. The sum is over all the atoms in one unit cell. If this is substituted into equation 10, the structure factor becomes

$$F(q) = \sum_{j} \exp[-i q \cdot r_j] \int_{V} \rho_j(r') \exp[-i q \cdot r'] d^3 r'$$

$$= \sum_{j} f_{0j}(q) \exp[-i q \cdot r_j] . \quad [13]$$

It is this expression for $F$ which is usually seen in the literature.
A second, very important result arises from the Kronecker delta $\delta_{H,q}$ in equation 10. The Fourier transform, and therefore the scattered electric field, is zero unless $q=H$; that is, the scattering vector is equal to a reciprocal lattice vector. The three equations, representing the three components of these vectors, are called the Laue conditions:

$$q_x = k_x - k_{ox} = \frac{2\pi}{a} h$$  \hspace{1cm} [14a]$$
$$q_y = k_y - k_{oy} = \frac{2\pi}{a} k$$  \hspace{1cm} [14b]$$
$$q_z = k_z - k_{oz} = \frac{2\pi}{a} l$$  \hspace{1cm} [14c]$$

If only the vector magnitudes are considered, then $H=q$, yielding the familiar Bragg equation, $2d_{hkl}\sin\theta=\lambda$, where $d_{hkl}$ is the spacing of the $(h,k,l)$ planes. For a cubic crystal, Bragg's law is

$$\sin\theta = \frac{\lambda}{2a}(h^2 + k^2 + l^2)^{1/2}.$$  \hspace{1cm} [15]$$

Returning to the field, $E_1$, scattered by a unit cell, an identical cell at $R_n$ will yield a scattered wave that differs only by a phase: $E = E_1 \exp(-iq \cdot R_n)$. The wave scattered by the entire crystal is the sum of the fields from all unit cells in the crystal. The lattice vectors $R_n$ are given by equation 1, and $N_x$, $N_y$, and $N_z$ are assumed to be small enough that the
entire crystal is bathed in the incident x-ray beam. The result, aside from an unimportant phase factor, is

$$E = \frac{E_1 \sin(aN_x q_x/2) \sin(aN_y q_y/2) \sin(aN_z q_z/2)}{\sin(aq_x/2) \sin(aq_y/2) \sin(aq_z/2)}.$$  \[16\]

This is the standard interference function, which has maxima $E_{\text{max}} = E_1 N$, when the Laue conditions are satisfied. For all other $q$, the amplitude is negligible.

The electric field amplitude is not experimentally observable. However, the intensity (energy/unit area/unit time) can be measured. The intensity, $J$, is related to the amplitude by $J = c|E|^2/8\pi$. Thus, if $I_0 = c|E_0|^2/8\pi$ is the intensity of the incident beam, the diffracted intensity is

$$J = \frac{I_0}{R_0^2} \left( \frac{e^2}{m_c q^2} \right) P |F(H)|^2 \times \frac{\sin^2(aN_x q_x/2)}{\sin^2(aq_x/2)} \frac{\sin^2(aN_y q_y/2)}{\sin^2(aq_y/2)} \frac{\sin^2(aN_z q_z/2)}{\sin^2(aq_z/2)}. \[17\]$$

$P$ is a factor which accounts for the polarization of the incident x-ray beam. $P$ has its origin in the cross product $n \times (n \times E_0)$. If the incident beam is such that the polarization vector is in the scattering plane (the plane containing the vectors $k_0$ and $k$), then $P = \cos^2 \theta$. If, on the other hand, the polarization is perpendicular to the scattering plane, then $P = 1$. The sum of the intensities for these two cases gives the total intensity. Therefore, $P = (1 + \cos^2 \theta)/2$ for an
unpolarized incident beam. Excitation lines in an x-ray spectrum are unpolarized, but the continuous radiation is polarized. Also, reflection from the crystals in a monochromator polarize the beam. The polarization of an x-ray beam can be measured experimentally using the Borrmann effect. Details of the polarization measurements on the instrument used below can be found in reference 74.

In a real experiment, the intensity J is not a good quantity to measure. Equation 17 was derived assuming a perfectly collimated incident x-ray beam. Every real beam, of course, has a nonzero divergence. In addition, the misorientation of the mosaic blocks (the mosaic spread) will have a similar effect even if the beam could be perfectly collimated. This means there is a small range of angles in which diffraction will occur. J is a function of the beam divergence, the intensity profile of the incident beam, and the mosaic spread. A quantity that is independent of the divergence and the beam profile (and also the mosaic spread if extinction, which will be discussed below, can be neglected) is obtained by measuring all of the energy diffracted by the crystal as it is rotated through the angular range. This is called the integrated intensity I. It is found by integrating equation 17 over area and time as the crystal is rotated, with a constant angular velocity \( \omega \), through the Bragg angle. The integration is straightforward, but tedious, and will not be done here (the details can be
found in Warren, pp. 42-45). The final result is

\[ I = \frac{I_0}{\omega} \left( \frac{e^2}{m_0 c^2} \right)^2 \left( \frac{v}{v^2} \right) \lambda^3 L P |F(H)|^2. \]  

[18]

L=1/sin2θ is the Lorentz factor, and v is the volume of the crystal: v=NV. When the crystal is larger than the incident beam, then v is the volume irradiated by the beam. This is the case, for example, in the large, flat-plate crystals used here.

Finally, all crystals absorb x-rays to some extent. μ, the linear absorption coefficient, is a function of the energy of the x-rays. If μ is large enough that the primary beam is entirely absorbed in the crystal, then the integrated intensity is independent of v, becoming

\[ I = \frac{I_0}{\omega} \left( \frac{e^2}{m_0 c^2} \right)^2 \frac{\lambda^3 L P}{2 \mu v^2} |F(H)|^2. \]  

[19]

To summarize the above derivations, the scattering of x-rays from a periodic array of atoms takes place only if the Laue conditions, equations 14a-c, are satisfied. The intensity of the diffracted beam is proportional to the square of the absolute value of the structure factor. These are conclusions of the "kinematical" theory of x-ray diffraction. The interaction between the photon and the crystal takes place only in a small spatial region. This region is large enough that the Laue conditions define the
scattering direction, but the region is small enough to be contained in only one mosaic block. After leaving this mosaic block, the photon does not interact with any other blocks (or very few of them), since the other mosaic blocks are at slightly different orientations. If another mosaic block is almost exactly aligned with the first one, or if the mosaic blocks are very large, the scattered wave can be rediffracted back into the direction of the incident beam. It has been assumed in deriving the above equations, that this does not happen. Therefore the kinematical theory is valid for ideally mosaic crystals.

In a very perfect crystal, multiple scattering does occur. The theory of diffraction in perfect crystals is called the dynamical theory of diffraction. Excellent reviews of the dynamical theory have been given by James,68,75 and by Batterman and Cole.76 Dynamical theory amounts to solving Maxwell's equations in the periodic crystal. The dynamical theory is much more complicated, and is not necessary for the majority of the analysis below. The needed results will simply be stated. Equations 1 through 15 are still valid since they deal only with small units of charge. The dynamical theory deviates from the kinematical theory when the individual fields are added together to find the total scattered amplitude and intensity. This is not done as simply as in the kinematical case because multiple scattering must be included. For a perfect crystal with no
absorption ($\mu=0$), the integrated intensity becomes

$$I = I_0 \frac{8}{3\pi} \left( \frac{e^2}{m_e c^2} \right) \frac{\lambda^2 LP}{V} |F(H)|,$$  \hspace{1cm} [20]

where $P=(1+|\cos 2\theta|)/2$ for an unpolarized incident beam. When $\mu\neq0$, the integration must be done numerically.

Equations 18, 19, and 20 can be written in the more general form

$$I = C(n) \lambda^{n+1} LP(n) |F(H)|^n,$$  \hspace{1cm} [21]

where $C(n)$ is the appropriate constant,

$$P(n) = \frac{1 + |\cos 2\theta|^n}{2}.$$  \hspace{1cm} [22]

$n=1$ for a perfect crystal, and $n=2$ for an ideally mosaic crystal. Most real crystals fall somewhere between the two extremes, usually nearer to the mosaic case. It is important to know where a crystal fits in these categories. Often, single crystals are subjected to rough treatment, such as grinding or rapid thermal cycling to produce defects, ensuring that the kinematical theory is valid. This can, of course, affect other physical properties of the crystal, and is not desirable.

One test of crystal perfection is a dynamical phenomenon called the Borrmann effect, or anomalous transmission. Fig. 6 shows the geometry of the Borrmann effect. An x-ray
Fig. 6. The geometry of the Borrmann effect. $k_0$ is the wavevector of the incident beam and $k$ is the diffracted beam wavevector. The resultant standing waves have a net energy flow parallel to the atomic planes. The wave with maxima on the planes is anomalously absorbed, and the wave with maxima between the planes is anomalously transmitted.
beam is incident on a perfect crystal with wavevector $k_0$. The crystal has a set of lattice planes perpendicular to its surface, and the beam is incident at the Bragg angle for these planes. The primary beam is diffracted into a beam with wavevector $k$. The dynamical interaction of these two electromagnetic waves produces a standing wave parallel to the crystal surface, having an energy flow perpendicular to the surface. Actually, two standing waves are set up: one with nodes at the positions of the planes, and the other with nodes midway between the planes. Since normal photoelectric absorption takes place in regions of high electron density, the standing wave with nodes between the planes (i.e., with its maxima at the atomic planes) will be strongly absorbed. The other wave, however, has its maxima between the planes, in regions of low electron density. Therefore, absorption is greatly diminished. Even for a very thick crystal, with $\mu T_0=50$ or more, a beam can be anomalously transmitted. The Borrmann effect can be observed in crystals with defect densities of about $10^5$ cm$^{-2}$ or less. Failure to observe an anomalously transmitted beam does not indicate where a crystal falls between the perfect and mosaic extremes. If the effect is seen, however, the crystal must be highly perfect.

Before going on to the theory of thermal vibrations, the physical content of the above equations must be discussed. Consider first the form factors $f_0(q)$. These are Fourier
transforms of the electron charge density of free (unbound) atoms, and are strongly dependent on \( q \). When these quantities are calculated, the charge density is assumed to be spherically symmetric. Therefore, the calculated form factor is a function only of the magnitude \( q = 4\pi \sin \theta / \lambda \). When \( q = 0 \), then \( f_0 = Z \), where \( Z \) is the atomic number. Fig. 7 shows the form factors for Ga, As, Cd, and Te\(^{72} \) plotted as a function of \( \sin \theta / \lambda \). Form factors can be approximated by the analytic function

\[
f_0(\sin \theta / \lambda) = \sum_{i=1}^{4} a_i \exp(-b_i \sin^2 \theta / \lambda^2) + c . \tag{23}
\]

Table 2 lists the \( a_i, b_i, \) and \( c \) for these four atoms. Also shown in Fig. 7 are the contributions of the core electrons alone for Ga, As, and Cd (similar calculations have not been done for Te). The difference between the solid and dashed lines is the valence electron contribution to the form factors. It is evident that scattering at large \( \sin \theta / \lambda \) is virtually all due to the atomic cores, while at small \( \sin \theta / \lambda \), there is also scattering from the valence electrons. This is important to keep in mind when studying thermal vibrations. The core electrons are tightly bound to the atomic nuclei. Therefore, the thermal vibrations of the cores can be assumed to be identical to the vibrations of the nuclei. Valence electrons, on the other hand, are much more free in a crystal. While their behavior sometimes does mimic that of
Fig. 7. The atomic form factors, $f_0(q)$, for gallium, arsenic, cadmium, and tellurium. The calculations of $f_0$ assume a spherical charge density about the atom, and therefore the form factors are functions only of $|q|=4\pi\sin\theta/\lambda$. 

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**Atomic Form Factor**

**for Gallium**

---

**Atomic Form Factor**

**for Arsenic**

---

**Atomic Form Factor**

**for Cadmium**

---

**Atomic Form Factor**

**for Tellurium**
Table 2. Coefficients for the analytic approximation of the form factors of Ga, As, Cd, and Te

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<tr>
<td>$b_3$</td>
<td>10.7805</td>
<td>12.9479</td>
<td>24.7008</td>
<td>28.5284</td>
</tr>
<tr>
<td>$a_4$</td>
<td>2.96230</td>
<td>4.27790</td>
<td>1.60290</td>
<td>2.52390</td>
</tr>
<tr>
<td>$b_4$</td>
<td>61.4135</td>
<td>47.7972</td>
<td>87.4825</td>
<td>70.8403</td>
</tr>
<tr>
<td>$c$</td>
<td>1.71890</td>
<td>2.53100</td>
<td>5.06940</td>
<td>4.35200</td>
</tr>
</tbody>
</table>
the nuclei, it cannot be assumed that this is always true.

Form factors are calculated under the assumption that the atoms are in their ground states. For a quantum mechanical system under the influence of an electromagnetic wave, this is not valid. In a more complete formalism the form factor is rewritten

$$f(q) = f_0(q) + f'(\lambda) + if''(\lambda). \quad [24]$$

$f'$ is related to the index of refraction of the crystal, taking into account phase changes when the x-rays scatter from an atom. $f''$, the imaginary dispersion term, is due to photoelectric absorption. $f'$ and $f''$ are roughly independent of the scattering angle $\theta$, but they do depend on the wavelength, or energy, of the x-rays. Calculation of these corrections has been carried out by Cromer. Experimental measurements have shown reasonable agreement with the calculations, provided the wavelength is not near an absorption edge of the atom. In the vicinity of the edges, the dispersion corrections also depend on the atomic arrangement; extended x-ray absorption fine structure (EXFAS) measurements, for example, make use of this property. Fig. 8 shows the calculated anomalous dispersion terms for Ga, As, Cd, and Te in the range $0.5 \AA \leq \lambda \leq 2.0 \AA$. The K absorption edges of Ga and As fall in this region, resulting in the discontinuities. Table 3 lists the values of $f'$ and $f''$ for the wavelengths used in the present experiments.
Fig. 8. The anomalous dispersion corrections, $f'$ and $f''$, for gallium, arsenic, cadmium, and tellurium. $f'$ and $f''$ are roughly independent of angle, but are dependent on the x-ray energy.
Table 3. Anomalous dispersion corrections for the wavelengths used

<table>
<thead>
<tr>
<th>λ (Å)</th>
<th>Ga</th>
<th>As</th>
<th>Cd</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f'</td>
<td>f''</td>
<td>f'</td>
<td>f''</td>
</tr>
<tr>
<td>0.546</td>
<td>-1.79</td>
<td>0.75</td>
<td>-1.32</td>
<td>1.05</td>
</tr>
<tr>
<td>0.637</td>
<td>-1.27</td>
<td>0.99</td>
<td>-0.99</td>
<td>1.38</td>
</tr>
<tr>
<td>0.709300</td>
<td>0.14</td>
<td>1.61</td>
<td>-0.05</td>
<td>2.01</td>
</tr>
<tr>
<td>1.28181</td>
<td>-2.41</td>
<td>0.56</td>
<td>-1.52</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>-0.16</td>
<td>3.40</td>
<td>-0.19</td>
<td>4.65</td>
</tr>
</tbody>
</table>
The form factors are also calculated assuming the atoms are free. This is not true in a crystal. The distortion of the charge density that takes place is primarily in the valence region. Thus the calculated form factors may be inaccurate at low \(\sin \theta/\lambda\). In addition, when the calculated structure factor is considered to be a sum of form factors multiplied by phase factors, as in equation 13, the valence electron distortions are ignored. The classic example of this is the \((2,2,2)\) reflection in the diamond structure (e.g., diamond, silicon, or germanium). If equation 13 is used, then \(F(2,2,2) = 0\). However a nonzero \((2,2,2)\) intensity is routinely observed.\(^{81}\) The covalent bond in these crystals causes a buildup of charge midway between nearest neighbor atoms. This charge is not accounted for when using form factors, but it is precisely this charge that produces most of the intensity of the \((2,2,2)\) reflection (about 1% of the intensity is due to anharmonicity). Valence electron scattering is small for larger \(\sin \theta/\lambda\), that is, higher indices \(h, k,\) and \(l\), so equation 13 is accurate for high index reflections. Equation 13 is also fairly good for low index reflections with large structure factors.

The structure factor can be calculated, using equation 13, for a compound \(AB\) with the zincblende structure. The indices \(h, k,\) and \(l\) must all be even or all be odd in order to get a nonzero structure factor. The reciprocal lattice points corresponding to the \((h,k,l)\) with \(F \neq 0\) form a bcc
lattice with lattice parameter $4\pi/a$ as discussed above. The structure factors fall into one of three categories, depending on the sum $h+k+l$:

$$|F(H)| = \begin{cases} 
4|f_A(H) + f_B(H)| & h+k+l=4n \\
4|f_A(H) - f_B(H)| & h+k+l=4n+2 \\
4|f_A(H) \pm if_B(H)| & h+k+l=4n+1 
\end{cases} \tag{25}$$

When $h+k+l=4n$ ($n$ an integer), the scattering from all atoms interferes constructively, resulting in a strong reflection. If $h+k+l=4n+2$, the A and B atoms scatter $180^\circ$ out of phase, and the interference is destructive. Since the form factors are not equal, the structure factor is weak, but not completely zero. In the diamond structure, where A and B are the same, the structure factor is zero. The (2,2,2) reflection is in this category (if the bonding charge is ignored). Lastly, if $h+k+l=4n+1$, the scattering from the A atoms is $90^\circ$ out of phase with that of the B atoms, resulting in a moderately strong reflection. It should be remembered that the intensity depends on the absolute value of $F$, so an imaginary structure factor is not unphysical.

Finally, the problem of extinction must be addressed. Three different types of extinction, systematic, primary, and secondary, occur. Systematic extinction is the disappearance of certain reflections due to the symmetry of the crystal. These extinctions are explained by the
structure factor. As used in the rest of this dissertation, the word extinction will always refer to primary or secondary extinction. As the name implies, extinction is a reduction in the intensity of a diffracted beam. As the incident beam penetrates into a crystal, its intensity is diminished. When the beam is not near a Bragg angle, this reduction is due to normal absorption processes. At the Bragg angle, however, the beam is attenuated even more because some of the incident radiation is reflected away. In a perfect crystal, the reflected waves are in phase over a very large distance, and the reflected wave amplitude builds up rapidly. The incident beam decays just as quickly. This is called primary extinction. Formally, the primary beam intensity is reduced by a factor exp(-2ξ) upon passing through one layer of unit cells, where

$$2\xi = \frac{n}{\nu} \left( \frac{e^2}{m_e c^2} \right) \frac{\lambda^2}{4\sin^2 \theta} |F(H)| . \quad [26]$$

In a mosaic crystal, not all of the mosaic blocks are at the proper angle to deflect the incident beam away from the lower blocks. The extinction is caused by a number of independent blocks rather than one coherent block. Thus, the amplitudes of the reflected waves cannot be added together as was done before. Instead, the intensities must be added. The effect is similar to primary extinction, and is called secondary extinction. Secondary extinction can be accounted
for by introducing an effective absorption coefficient

\[ \mu_e = \mu + g \frac{I}{I_0} \frac{\omega}{\nu}, \]  

[27]

where \( I \) is the integrated intensity given by equation 18. \( g \) is a function of the Bragg angle, the average mosaic block size, and the extent of misorientation between blocks. Since the extinction correction is proportional to the structure factor or its square, the reflections with the largest structure factors will be affected the most. The largest structure factors correspond to the strong reflections with low crystallographic indices (small \( \sin \theta / \lambda \)). Note that primary extinction occurs in perfect crystals, and secondary extinction in ideally mosaic crystals. A crystal between these two extremes will suffer from both types of extinction.

The penetration depth \( D \) is the depth at which the incident intensity has been reduced to \( I_0 e^{-1} \). For strong reflections, the diminution of the incident beam due to diffraction is much greater than that due to absorption. On the other hand, absorption is the dominant mechanism in weak reflections. For these extremes, the penetration depth is

\[
D = \begin{cases} 
\frac{a}{2 \xi} & \text{strong reflections} \\
\frac{\sin \theta}{2 \mu} & \text{weak reflections} 
\end{cases} 
\]  

[28]
The penetration depth at a strong reflection of a mosaic crystal cannot be calculated without knowing the mosaic spread. This depth will always be larger than the penetration depth in a perfect crystal, so $D$ in equation 28 can be used as a lower bound. For weak reflections, the absorption penetration depth is the same whether the crystal is perfect or mosaic. The actual penetration depth will always be somewhere between these two extremes. Note that the penetration depth for the strong reflections is independent of the wavelength, because

$$\sin \theta / \lambda = (h^2 + k^2 + l^2)^{1/2} / 2a$$

is independent of the wavelength. The bottom expression is roughly proportional to $\lambda^{-3}$.

The combination of effects described above — valence electron vibrations, bonding charges and other valence electron distortions, and extinction — show that caution must be exercised when interpreting low index reflections.

### D. Thermal Vibrations in Diffraction Theory

The theory of thermal vibration effects in x-ray diffraction is covered, at some level, in most books on diffraction. Willis and Pryor have published a book entirely devoted to this subject.

The structure factor, given by equation 13, is a sum of terms of the form $f_j(H)\exp(-iH \cdot r_j)$, where $r_j$ is the crystallographic position of the jth atom. The vibration of the atom about this position is represented by the vector $u_j$. 
so that the instantaneous position of the atom is \( r_j + u_j \). The absolute value of the structure factor is obtained by multiplying \( F \) by its complex conjugate \( F^* \). In addition, the time average \( \langle |F(H)|^2 \rangle \), must be taken:

\[
\langle |F(H)|^2 \rangle = \langle F(H)^* F(H) \rangle
\]

\[
= \sum_{j,j'} f_j^*(H) f_{j'}(H) \exp[iH \cdot (r_j - r_{j'})] \exp[iH \cdot (u_j^* - u_{j'})].
\]

The vectors \( u_j \) will be written in complex notation for mathematical convenience. In a purely harmonic crystal, the second exponential in equation 29 can be rewritten\(^\text{33}\) and expanded:

\[
\exp[iH \cdot (u_j^* - u_{j'})] = \exp(- \frac{1}{2} \langle |H \cdot (u_j^* - u_{j'})|^2 \rangle)
\]

\[
= \exp(- \frac{1}{2} \langle |H \cdot u_j^*|^2 \rangle) \cdot \exp(- \frac{1}{2} \langle |H \cdot u_{j'}|^2 \rangle) \cdot \exp(- \frac{1}{2} \langle (H \cdot u_j^*) (H \cdot u_{j'}) \rangle + \cdots )
\]

Substitution back into equation 29 yields

\[
\langle |F(H)|^2 \rangle = \left| \sum_{j} f_j(H) \exp(-H \cdot r_j) \right|^2
\]

\[
- \left| \sum_{j} f_j(H) (H \cdot u_j) \exp(- \frac{1}{2} (H \cdot u_j)^2 \exp(-iH \cdot r_j)) \right|^2
\]

\[+ \cdots \]

Each of these terms will be considered in turn.
The first term in equation 31 is the same as the usual structure factor equation except that the form factors have been multiplied by a Debye-Waller, factor \( \exp(-M_j) \), where

\[
M_j = \frac{1}{2} \langle |H \cdot u_j|^2 \rangle = 8\pi^2 \langle u_{H_j}^2 \rangle \sin^2 \theta / \lambda^2.
\]  

\( u_{H_j} \) is the projection of \( u_j \) onto the direction of \( H \). The structure factor for the zincblende structure, as given by equation 25, must now be modified: each form factor, \( f_j \), must be replaced by \( f_j \exp(-M_j) \). To proceed further requires a physical model for \( u_{H_j} \), and three such models will be described.

1. The Debye Model

The first model was proposed by Debye in 1913 and improved by him in 1914. It is a purely harmonic theory, based on his theory of the specific heat of a solid.

A well known result of lattice dynamics (see, for example, Ashcroft and Mermin, Chap. 22 and 23) is that a crystal with \( N \) unit cells and \( p \) atoms per unit cell has \( 3pN \) normal modes (eigenfrequencies) of vibration. These normal modes form \( 3p \) branches in the dispersion relations with \( N \) allowed wavevectors in each branch. Each mode can be represented by a wavevector \( \kappa \), an index, \( s \), labelling the branch, a frequency \( \omega_s(\kappa) \), an amplitude \( A_s(\kappa) \), and a normalized, \( 3p \)-dimensional eigenvector \( \epsilon_s(\kappa) \). The
eigenvectors can be written

\[
\begin{pmatrix}
\epsilon_s(1,K) \\
\vdots \\
\epsilon_s(p,K)
\end{pmatrix}
\]

Each \( \epsilon_s(j,K) \) is a 3-dimensional vector representing the direction of displacement of the \( j \)th atom from its crystallographic position. The normalization condition on the eigenvector is

\[
\epsilon_s(K) \cdot \epsilon_s'(K) = \sum_{j=1}^{P} \epsilon_s(j,K) \cdot \epsilon_s'(j,K) = \delta_{s,s}'.
\]

The familiar Born-von Karman boundary conditions\(^87\) give the values of the wavevectors as

\[
\mathbf{K} = \frac{2\pi}{a} \left( \frac{n_x}{N_x} + \frac{n_y}{N_y} + \frac{n_z}{N_z} \right).
\]

\( N_x, N_y, \) and \( N_z \) have been defined earlier, and the \( n_i \) are restricted to \(-N_i/2 \leq n_i \leq N_i/2\). At a particular instant, the position of the \( j \)th atom in the unit cell is the sum of the contributions from each normal mode

\[
u_j(t) = \frac{1}{\sqrt{m_j}} \sum_{s=1}^{3P} \sum_{K} \epsilon_s(j,K) A_s(K) \exp\{-i(K \cdot r_j - \omega_s(K)t)\}.
\]
The mass-normalized amplitudes $A_s(\kappa)$ are complex. They contain phase factors that change randomly with time, corresponding to the creation and annihilation of phonons. The desired quantity is the time average of $|H \cdot u_j|^2$, where the average is over a time which is long compared to the period of vibration. Thus,

$$<|H \cdot u_j|^2> = \frac{1}{m_j} \sum_{s,s',K,K'} [H \cdot \epsilon_s(j,K)][H \cdot \epsilon_s(j,K')]A_s^*(K)A_s(K') \times \exp[i(\omega_s(K)-\omega_s(K'))t] \exp[-i(K-K') \cdot r_j]$$

For a given term in the sum of equation 37, the time average of $<A_s^*(K)A_s(K')\exp[i(\omega_s(K)-\omega_s(K'))t]>$ is zero if $\omega_s(K) \neq \omega_s(K')$. However, if $K \neq K'$ and $s \neq s'$, the random, time dependent phases in the amplitudes cause the average to be zero even when $\omega_s(K) = \omega_s(K')$. This leaves

$$<|H \cdot u_j|^2> = \frac{1}{m_j} \sum_{s,K} (H \cdot \epsilon_s(j,K))^2 |A_s(K)|^2$$

Since this is a harmonic oscillator, the total energy $E$ in the crystal is twice the kinetic energy:

$$E = \sum_{j=1}^{P} \sum_{n=1}^{N} m_j |\dot{u}_j|^2$$

By differentiating equation 36 to find $\dot{u}_j$, taking a time average, and using the orthonormality condition, equation 34,
an expression is found relating the energy per normal mode $E_S(K)$, to the amplitudes:

$$E = \sum_{S,K} E_S(K) = \sum_{S,K} N\omega_S^2(K)|A_S(K)|^2$$ \[40\]

Therefore,

$$M_j = \frac{1}{2Nn_j} \sum_{S,K} (H\cdot\epsilon_S(j,K))^2 \left( \frac{E_S(K)}{\omega_S(K)^2} \right)$$ \[41\]

The normal modes are solutions of the Schrödinger equation for a particle in a harmonic potential well. Thus, the energy eigenvalues are\(^88\)

$$E_S(K) = \tilde{\omega}_S(K)[\eta_S(K) + 1/2]$$ \[42\]

where the occupation numbers are\(^89\)

$$\eta_S(K) = \left[ \exp(\tilde{\omega}_S(K)/k_BT) - 1 \right]^{-1}.$$ \[43\]

Debye's assumption was that all waves travelled with the same speed $v$. The dispersion relation is then $\omega_S(K)=KV$ when $\omega_S(K)$ is less than some maximum frequency $\omega_M$, and zero for larger frequencies. The allowed wavevectors are so closely spaced that the sum over $K$ in equation 41 can be replaced by an integral: \(\frac{1}{N} \sum_K \rightarrow \frac{a}{2\pi}^3 \int d^3 K\). $\epsilon_S$ is a function only of the direction of $K$, and $\omega_S$ and $E_S$ are functions of the magnitude of $K$. Thus the angular part of the integral is simple. For
the radial part, a characteristic Debye temperature $\Theta_M$ is defined by $k_B \Theta_M = \hbar \omega_M = \hbar \nu / k_M$. Only three branches ($s=1,2,3$) are assumed to exist. Thus, $k_M$ is the radius of a sphere in reciprocal space containing $pN$ wavevectors ($3pN$ normal modes), each wavevector occupying a volume $(2\pi/a)^3/N$. This results in

$$M_j = \frac{3\hbar^2 |\mathcal{H}|^2}{2m_j k_B \Theta_M^2} \sum_s |\epsilon_s(j)|^2 \left[ \frac{\phi(x)}{x} + \frac{1}{4} \right]$$  \[44\]

where $x=\Theta_M/T$ and the Debye integral function is

$$\phi(x) = \frac{1}{x} \int_0^x \frac{V}{e^y - 1} \, dy.$$  \[45\]

A graph of $\phi(x)/x$ is shown in Fig. 9. The Debye function is independent of $s$ and can be taken out of the summation. Note that the Debye temperature is the same for all atoms. The only dependence on $j$ is in the atomic mass $m_j$, and in the sum over the eigenvectors. Using the orthonormality condition and replacing $|\mathcal{H}|$ by $4\pi \sin \theta / \lambda$, one can write

$$\sum_{j=1}^p m_j M_j = \frac{6 \hbar^2}{k_B \Theta_M} \left[ \frac{\phi(x)}{x} + \frac{1}{4} \right] \frac{\sin^2 \theta}{\lambda^2}.$$  \[46\]

For a monatomic solid, $p=1$, and equation 46 reduces to

$$M = \frac{6 \hbar^2}{mk_B \Theta_M} \left[ \frac{\phi(x)}{x} + \frac{1}{4} \right] \frac{\sin^2 \theta}{\lambda^2}.$$  \[47\]
Fig. 9. The Debye integral function $\Phi(x)/x$

\[
\Phi(x) = \frac{1}{x} \int_0^x \frac{y \ dy}{e^{y-1}}
\]
The mean square displacement of the atom along the direction of \( H \) is

\[
\langle u_H^2 \rangle = \frac{3h^2}{4\pi^2 mk_B \Theta_M} \left\{ \frac{\phi(x)}{x} + \frac{1}{4} \right\}. \tag{48}
\]

For diatomic solids like GaAs and CdTe, the Debye theory gives

\[
m_A m_A + m_B m_B = \frac{12h^2}{k_B \Theta_M} \left\{ \frac{\phi(x)}{x} + \frac{1}{4} \right\} \frac{\sin^2 \frac{\Theta}{\lambda^2}}{\lambda^2}. \tag{49}
\]

If \( m \) is the average atomic mass and \( M \) is the average thermal parameter, then to a good approximation, the left hand side of equation 49 is equal to \( 2mM \). Equation 49 then reduces down to the monatomic expression, equation 47. A further deviation from the Debye theory is often taken. The thermal parameter \( M_j \) for each atom is assumed to be given by equation 47, where \( m \) is the mass of the particular atom, and each atom has its own "Debye temperature." While these "Debye temperatures" no longer have the same physical meaning as the real Debye temperature, they are still good measures of the mean square atomic displacement.

Since the Debye theory is most commonly used in the measurement of the specific heat, it is important to point out the relationship between the results of the two methods. Zener and Bilinsky\textsuperscript{90} pointed out in 1936 that the Debye temperatures extracted from the two methods were not the same.
for monatomic solids. The difference is associated with the way the velocities of the transverse and longitudinal modes are averaged. In theory, $\Theta_M$ and $\Theta_D$ (the Debye temperature from specific heat measurements) should be different by only a few percent. This is found to be the case in most elements, although a number of important discrepancies have been found.\(^{91}\)

The difference between $\Theta_M$ and $\Theta_D$ is more fundamental in polyatomic solids. When $m$ and $M$ are taken as the average atomic mass and thermal parameter, respectively, the left hand side of equation 46 becomes $pmM$. This $p$ cancels the $p$ on the right hand side resulting in an expression, valid for any $p$, identical to the monatomic equation. On the other hand, the specific heat is the temperature derivative of the total energy (equation 39):

$$c_v = \frac{\partial}{\partial T} \sum_{n=1}^{N} \sum_{j=1}^{D} m_j |\dot{u}_j|^2 = \frac{12}{5}\pi^4 N p k_B \left(\frac{T}{\Theta_D}\right)^3. \quad [50]$$

In contrast to the x-ray case, the $p$ on the right hand side of equation 50 is not cancelled by a $p$ on the left hand side. $\Theta_M$ and $\Theta_D$ are therefore significantly different. The root cause is that the thermal parameter $M_j$ accounts for the motion of only one atom, while the specific heat reflects the collective motion of all atoms. In the classical limit, $T/\Theta_M$, $\psi(x)/x+1/4$ reduces to $T/\Theta_M$. Therefore
If this were to be treated like the specific heat case, the result would be

\[ M = \frac{6h^2T \sin^2\theta}{m k_B \Theta_M^2} \]  \hspace*{1cm} \text{[51]} \]

These two expressions would be fit to the same data, and must therefore be equal. They yield the relation

\[ \Theta_N' = \sqrt{\frac{p}{m}} \Theta_M \]  \hspace*{1cm} \text{[53]} \]

Thus, rather than comparing \( \Theta_D \) to \( \Theta_M \) for GaAs and CdTe, \( \Theta_D \) should be compared with \( \sqrt{\frac{p}{m}} \Theta_M \).

2. The Debye-Einstein Model

In the Debye model, the optic branches of the phonon dispersion curves are represented by the high \( \kappa \) values of the linear expression used to describe the acoustic branches. An alternate, and probably more realistic approach, would be to represent only three branches (\( s=1,2,3 \)) by the linear Debye model. The remaining \( 3(p-1) \) branches are accounted for using the Einstein approximation\(^9\) in which the frequency is a constant, \( \omega_E \). An Einstein temperature is defined by \( k_B \Theta_E = h \omega_E \). Fig. 10 illustrates the comparison between the
Fig. 10. Comparison of the Debye and Debye-Einstein models for a diatomic solid. The Debye model has a linear dispersion relation and is integrated in a sphere having a volume equal to the volume of the first two Brillouin zones. The Debye-Einstein model uses a linear dispersion relation for the acoustic modes, a constant for the optic modes, and is integrated only in the first Brillouin zone.
Debye and the Debye-Einstein models as applied to a diatomic crystal.

The development of the Debye-Einstein approach parallels the Debye theory up to the point where the dispersion relation is applied. The Debye approximation is now made only for \( s=1, 2, \) and 3, and \( \kappa_M \) is the radius of a sphere containing only \( N \) wavevectors. The dispersion relation for the remaining branches is simply \( \omega_s(\kappa)=\omega_E \). The integration for these branches is carried out in a sphere containing \((p-1)N\) wavevectors. The final result is

\[
\sum_{j=1}^{D} m_j^N j = \frac{6h^2}{k_B \Theta_M} \left( \frac{\phi(x)}{x} + \frac{1}{4} \right) \frac{\sin^2 \theta}{\lambda^2} + \frac{2(p-1)h^2}{k_B \Theta_E} \left( \frac{1}{\exp(x_E) - 1} + \frac{1}{2} \right) \frac{\sin^2 \theta}{\lambda^2} \tag{54}
\]

where \( x_E = \theta_E / T \). The left hand side of equation 54 can be written \( pM \) in analogy to the Debye case. Thus, the average thermal parameter is

\[
M = \frac{6h^2}{pmk_B \Theta_M} \left( \frac{\phi(x)}{x} + \frac{1}{4} \right) \frac{\sin^2 \theta}{\lambda^2} + \frac{2(p-1)h^2}{pmk_B \Theta_E} \left( \frac{1}{\exp(x_E) - 1} + \frac{1}{2} \right) \frac{\sin^2 \theta}{\lambda^2} \tag{55}
\]

In the classical limit, the Debye and Einstein parts of this expression have the same temperature dependence.
least squares fit will be unable to distinguish between the two terms. However, the optic modes contribute less to the mean square displacement, especially at low temperatures. Therefore a reasonable solution to the fitting problem is to extract an Einstein temperature from the measured phonon density of states (when available) and fit the data by varying θ_M only. It should be emphasized that the Debye temperature in this model is again different from θ_M in the pure Debye model and from θ_D. For a diatomic crystal, the Debye temperature in this model should be √2 smaller than θ_M in the Debye model, and a factor of √2 smaller than θ_D.

3. The One-Particle Potential Model

The third model of thermal vibrations that will be used is the one-particle potential (OPP) model. In this approach, each atom is assumed to vibrate independently in a potential well of the form (appropriate for 43m point group symmetry)

\[ V = V_0 + \frac{1}{2} \alpha u^2 + \beta u_1 u_2 u_3 + \gamma u^4 + \delta(u_1^4 + u_2^4 + u_3^4 - \frac{3}{5} u^4) \]  

[56]

\( u_1, u_2, \) and \( u_3 \) are the Cartesian components of the deviation of the atom from its crystallographic position, and \( u^2 = u_1^2 + u_2^2 + u_3^2 \). The key assumption is that the atoms vibrate independently of each other which is, of course, not true. It can easily be shown, however, that the first term in equation 31 (the structure factor including vibration
effects) has the same mathematical form whether the atoms interact or not. The atomic interactions are buried in the value of $\langle u_H^2 \rangle$. The Debye theory accounts for this in a crude way, while the OPP model does not. The obvious advantage of the OPP model is that anharmonic ($\beta$, $\gamma$, and $\delta$) and anisotropic ($\beta$ and $\delta$) effects can be studied.

The Debye-Waller factor corresponding to the OPP potential was first derived by Willis. The time average $\langle \exp(-iH \cdot u) \rangle$ must be done directly, since the replacement of $\langle \exp(-iH \cdot u) \rangle$ by $\exp(-|H \cdot u|^2/2)$ in equation 30 is valid only for a harmonic potential. The averaging is accomplished by taking the thermodynamic average

$$
\langle \exp(-iH \cdot u) \rangle = \frac{\int \exp(-iH \cdot u) \exp(-V/k_BT) \, d^3u}{\int \exp(-V/k_BT) \, d^3u} \tag{57}
$$

with $V$ given by equation 56. The anharmonic terms in $V$ are small compared to the harmonic term. Therefore, Willis expanded, and kept only first order terms in $\beta$, $\gamma$, and $\delta$. Later, Mair et al. showed that second order terms in $\beta$ should also be included since they can sometimes be of the same order of magnitude as first order terms in $\gamma$ and $\delta$. The integrations are straightforward, with the final result for the Debye-Waller factor being
\[
\langle \exp(-i\mathbf{H} \cdot \mathbf{u}) \rangle = C \exp(-|\mathbf{H}|^2 k_B T/2\alpha) \left( 1 - k_B T \left( \frac{15\gamma}{\alpha^2} - \frac{\beta^2}{2\alpha^3} \right) \right)
\]

\[
+ (k_B T)^2 \left( \frac{2\pi}{\alpha} \right)^2 \left( \frac{10\gamma}{\alpha^3} - \frac{\beta^2}{2\alpha^4} \right) (h^2 + k^2 + l^2)
\]

\[
+ i(k_B T)^2 \left( \frac{2\pi}{\alpha} \right)^3 \left( \frac{\beta}{\alpha^3} \right) hkl
\]

\[
- (k_B T)^3 \left( \frac{2\pi}{\alpha} \right)^4 \left( \frac{\gamma}{\alpha^4} \right) (h^2 + k^2 + l^2)^2
\]

\[
- (k_B T)^3 \left( \frac{2\pi}{\alpha} \right)^4 \left( \frac{\delta}{\alpha^4} \right) [h^4 + k^4 + l^4 - \frac{3}{5}(h^2 + k^2 + l^2)^2]
\]

\[
+ (k_B T)^3 \left( \frac{2\pi}{\alpha} \right)^4 \left( \frac{\beta^2}{2\alpha^5} \right) (h^2 k^2 + k^2 l^2 + l^2 h^2)
\]

where \( C = \left[ 1 - k_B T \left( \frac{15\gamma}{\alpha^2} - \frac{\beta^2}{2\alpha^3} \right) \right]^{-1} \).

The mean square displacement in the harmonic limit is

\[
\langle v_H^2 \rangle = \frac{k_B T}{\alpha}.
\]

4. Relationship to Experimental Data

Two different approaches can be taken for extracting the parameters \( \theta_H, \alpha, \beta, \gamma, \) and \( \delta \) from diffraction data. The most commonly used method is to measure the structure factors of a large number of reflections at one temperature, usually room temperature. Equation 47 (Debye model), equation 55
(Debye-Einstein model), or equation 58 (OPP model) can be fit to the variation of the measured structure factors with h, k, and l. This is illustrated by Vaipolin's work on CdTe at room temperature. Since the measurements are done at a single temperature, no knowledge can be gotten on the changes of the vibrational properties with temperature. The method used below was to measure a few structure factors at many temperatures. The fit is then done as a function of the temperature as well as h, k, and l, allowing comparison with room temperature results as well as with physical models. This technique has been used on CdTe powder samples by Walford and Schoeffel. Obviously, the more reflections measured, the better the results will be.

Because the three models above are only approximations to a true solid, the equations do not describe experimental data exactly. The models work best in the classical limit; in fact, the OPP model is valid only in this regime. It has become customary to depict the deviations from the models by plotting the Debye temperature or $\alpha$ as a function of temperature. A temperature range in the classical region should exist where $\Theta_M$ and $\alpha$ are nearly constant. If the temperature falls below this region, quantum effects will cause the values to deviate from the constant. If the temperature is too high, anharmonicity will become significant and again cause a deviation.

Given the experimentally measured structure factors as a
function of temperature, the data can be fit in the temperature range (this will be called the reference range) where \( \Theta_M \) and \( \alpha \) are constant. Equations 47, 55, and 58 are valid in this case. With \( \Theta_M \) and \( \alpha \) known at one temperature \( T_0 \), \( \Theta_M \) and \( \alpha \) at any other temperature can be found using the relation

\[
\ln \left( \frac{|F(T)|^2}{|F(T_0)|^2} \right) = -2[M(T) - M(T_0)] .
\]

where the thermal parameter \( M \) is given by the appropriate model. Each temperature in the reference range can be used as \( T_0 \) in equation 60. There will then be a \( \Theta_M(T_1) \) or \( \alpha(T_1) \) for each \( T_0 \). The final \( \Theta_M(T_1) \) and \( \alpha(T_1) \) can be taken as the average of these values. It must be noted that if \( \Theta_M(T) \) and \( \alpha(T) \) are not constant in the reference range, then a new range must be chosen and the procedure repeated.

D. Thermal Diffuse Scattering

The first term in equation 31, which was discussed in the previous sections, represents elastic scattering of the x-rays. The change in momentum of the diffracted x-rays is \( hq \) where \( q = H \), a reciprocal lattice vector. The second term represents inelastic scattering. The momentum change is \( h(H+g) \) where \( g \) is the momentum of a phonon in the crystal. The third, and higher order terms represent inelastic
scattering involving two or more phonons. These terms give rise to diffuse background scattering which is largest near the Bragg peaks. It is called thermal diffuse scattering, or TDS. TDS is the same as one-phonon, two-phonon, etc., inelastic scattering of thermal neutrons. The difference is that x-ray energies are orders of magnitude larger than phonon energies, while thermal neutrons and phonons have comparable energies. Thus, TDS is an almost continuous background, while the neutron diffraction pattern shows individual phonon peaks. TDS can be used to measure phonon dispersion curves, but it is much more difficult.97

Figure 11 shows a typical peak, composed of elastic scattering and TDS. The energy resolution of x-ray detectors is not good enough to separate the elastic and inelastic scattered photons. Therefore, the measured integrated intensity includes the TDS. This must be accounted for before analyzing the elastic part. A relatively new technique called quasi-elastic gamma ray scattering98 uses the Mössbauer effect to separate the elastically and inelastically scattered photons. The energy resolution of this method is on the order of $10^{-6}$ eV, making direct measurement of the TDS possible. This would clearly be the best method of correction.

The TDS correction has been the subject of a large number of articles. The method used here is due to Cooper and Rouse,99 with a modification by Walker and Chipman,100 and
Fig. 11. A typical diffraction peak showing the elastic scattering and inelastic scattering (TDS)
corrects for one-phonon TDS only. Briefly, the integrated intensity of the thermal diffuse scattering alone is $\psi I$, where $I$ is the Bragg reflected intensity. $\psi$ is a function of the temperature and the elastic constants of the crystal, which are themselves temperature dependent. If only one-phonon TDS is considered, then

$$\psi = \frac{2k_B T}{3\pi} V_r f(C_{\text{elastic}})$$ \hspace{1cm} [61]$$

where $V_r$ is the volume of reciprocal space swept out during the scan, and $f(C_{\text{elastic}})$ is a function of the elastic constants. The elastically scattered intensity is then given by the corrected formula

$$I = \frac{I_{\text{measured}}}{1 + \psi}. \hspace{1cm} [62]$$
III. X-RAY DIFFRACTION: EXPERIMENTAL

This section describes the experimental equipment and techniques that were used. Two major techniques will be discussed: a qualitative, photographic method using the Buerger precession camera, and precise quantitative measurements on a diffractometer.

A. Precession Photography

Before a crystal can be studied by x-ray diffraction, it must be oriented so that it satisfies the Laue conditions. Epitaxial layers are usually grown with their surfaces parallel to some crystallographic plane. Therefore, the orientation can be partially found by scanning reflections which have their scattering vectors perpendicular to the surface. Nothing can be learned from these reflections, however, about the orientation of the epilayer in the plane of the surface. A technique such as grazing incidence diffraction\textsuperscript{65} can provide information about this orientation. These scans sample only a very small region of reciprocal space. A view of a large region of reciprocal space would be advantageous because it would determine all orientations at once. More importantly, additional structure in the diffraction pattern - such as diffuse scattering, or reflections from a second phase - would be overlooked if only a small part of reciprocal space was scanned.
To see a large region of reciprocal space, crystallographers collect information photographically. A particularly elegant technique is precession photography. A precession photograph is an undistorted, magnified image of a plane in the reciprocal space of a crystal. All other photographic methods produce distorted images of reciprocal space. The samples used on a precession camera are usually small single crystals with dimensions on the order of 0.1 mm. In contrast, thin films are grown on large flat plates with dimensions of several millimeters or more. Despite this, high quality precession photographs can be taken of thin film systems. This method is not limited to single crystal films; it works just as well with polycrystalline films. No modifications to the precession instrument are needed. The principles of precession photography will be outlined first. The method of mounting and photographing composite systems will then be explained. Two precession photographs will be shown to illustrate the method; a wider variety of thin films have been studied with this technique, and described in references 103-105. Finally, the precession method will be compared with other characterization techniques, pointing out the advantages and disadvantages of the method.

A detailed explanation of the theory and operation of the Buerger precession camera can be found in Buerger’s work. Fig. 12 shows the arrangement. A crystal is oriented so that one of its crystallographic axes, hereafter
Fig. 12. Diagram of a precession camera. O is the origin of reciprocal space and \( O' \) is the center of the photographic plate. \( S \) is the center of the Ewald sphere. If the film and level are kept parallel, the image on the film will be an undistorted replica of the reciprocal space level.
called the precession axis, is parallel to a monochromatic beam of x-rays (i.e., a plane, or "level", in reciprocal space is perpendicular to the beam). The crystal is then tilted so that the precession axis makes an angle $\mu$ (the precession angle) with the x-ray beam, and this axis is subsequently precessed about the beam. A photographic plate is mounted a distance $F$ from the crystal. The plate is coupled to the crystal so that the level is always parallel to the photographic film. By comparing the similar triangles $SOP$ and $SO'P'$ in Fig. 12, it follows that the resulting photograph is an undistorted image of the reciprocal space level. The amount of reciprocal space recorded on the photograph increases with increasing precession angle.

The magnitudes of the lattice parameters are directly related to the separation of the spots on the photograph. This information is lost in any type of Laue photograph. Let $d_f$ be the distance from the center of the photograph to one of the diffraction spots. This distance is related to the crystallographic indices and the lattice parameters by the relation $d_f = F\lambda/d_{hkl}$, which, for a cubic crystal is

$$d_f = \frac{F\lambda}{a} (h^2 + k^2 + l^2)^{1/2}.$$  \[63\]

There are many levels which are perpendicular to the precession axis. The level which contains the origin of reciprocal space is called the zero level, and the others are labelled 1, 2, \ldots. All of these levels diffract x-rays onto
the photographic film. A layer line screen, a metal plate with an annular opening, is placed between the crystal and the film to isolate the diffraction pattern of a single level.

Fig. 13 shows how a substrate/epilayer system is mounted on a precession camera. The precession axis is in the surface of the crystal. When $\mu=0^\circ$, the normal to the surface of the sample is perpendicular to the x-ray beam, and the crystal cuts the beam in half. This part of the centering procedure can be accomplished very easily if the precession camera is equipped with an autocollimator. If not, however, the conventional methods for orienting single crystals can be used (see, for example, Chapter 8 in ref. 102). The spindle axis of the precession camera is also parallel to the sample surface when $\mu=0^\circ$. Best results are obtained when the spindle axis is less than about 1 mm from the edge of the sample closest to the photographic plate. There are two reasons for this. First, since the crystal is large, the spots on the film will be large. The arrangement described above decreases the amount of crystal in the x-ray beam, which reduces the spot size slightly. A narrow, well collimated beam also helps in this regard. Second, a shadow will be cast on the lower half of the photographic plate, and part of the upper half, due to absorption of the beams that diffract through the substrate. This shadow makes pattern recognition more difficult. When the spindle axis is near the edge of the crystal, this absorption is diminished. This
Fig. 13. Mounting a substrate/thin film on the precession camera when $\mu=0^\circ$. The surface of the crystal is parallel to the plane defined by the x-ray beam and the spindle axis. The axis of rotation is also called the spindle axis.
shadow can be seen in all the precession photographs presented here. Most precession cameras can be set to precess through only part of the full 360°. When only the upper 180° is used, the exposure time is cut in half.

Since two or more "crystals" are present in a composite system, the zero level photograph will show both the substrate and the epilayer. When an upper level photograph is taken, and if the two materials have sufficiently different lattice spacings, the diffraction from only one of the components will be recorded.

The example shown here is a (1,1,1) CdTe epilayer on a (0,0,1) GaAs substrate. All precession photographs in this dissertation were made on a Huber Model 200 precession camera with a crystal to film distance of F=60 mm. The x-ray source was a standard molybdenum x-ray tube (λ=0.7093 Å for the Kα excitation line). A Zr filter was used to remove the Mo Kβ radiation.

1. (1,1,1) CdTe on (0,0,1) GaAs: Twinning

A number of (1,1,1) CdTe epitaxial layers were grown on (0,0,1) GaAs substrates by MBE (obtained from J. P. Faurie), and studied by precession photography. Fig. 14 shows two precession photographs of this system. The upper photograph was made with the the [1,1,0] of GaAs as the precession axis. The lower photograph had the GaAs [1,1,0] as the precession axis (90° from the top photograph). Fig.'s 15 and 16 are diagrams showing the crystallographic indices
Fig. 14a. Precession photograph of a (1,1,1) CdTe epilayer on (0,0,1) GaAs

Fig. 14b. Precession photograph of the same system rotated 90° about the surface normal. Twinning of the CdTe epilayer can be seen in this photograph.
Fig. 15. Indexing of the precession photograph in Fig. 14a. Open circles represent reflections from the GaAs substrate and solid dots represent CdTe reflections. The vector diagram shows two GaAs (solid lines) and two CdTe (dashed lines) reciprocal lattice vectors. All spots can be indexed simply by adding vectors. The center of the photograph, which corresponds to the origin of reciprocal space, is marked by a +. Twinning cannot be seen in this orientation because both the substrate and epilayer have two-fold symmetry about the vertical axis.
Fig. 16. Indexing of the bottom photograph in Fig. 14. The top diagram labels the GaAs substrate and one of the CdTe twin domains and the bottom diagram labels the substrate and the other domain. The precession photograph is the sum of these two diagrams.
of the various spots on the photographs. Open circles represent reflections from the GaAs substrate and solid dots represent epilayer reflections. The orientation of epilayer to substrate can immediately be given as \((1,1,1)\parallel (0,0,1)\) with \([1,1,0]\parallel [1,1,0]\), which is the same as \([1,1,2]\parallel [1,1,0]\). For reference, the \((1,1,1)\) and \((0,0,1)\) stereographic projections are shown in Fig. 17.

The photograph in Fig. 14a was taken with the precession axis being the \([1,1,0]\) of GaAs and the \([1,1,2]\) of the CdTe epilayer. The reflections in a precession photograph all fall along the line, in the stereographic projection, perpendicular to the precession axis in the stereographic projection, and passing through the center of the projection. Note that for both materials, there is two-fold symmetry along this line. When Fig. 14b is indexed, one finds that there are actually three diffraction patterns present. One is due to the GaAs substrate. The other two are from the epilayer and are mirror images of each other; the CdTe contains twin faults. The reflections from the two domains have roughly the same intensity and are therefore present in equal amounts. Twinning in bulk crystals was described as a rotation of \(180^\circ\) about the \((1,1,1)\) axis. This is a rotation in the plane of the epilayer surface. The stereographic projections show why twin faults can be seen in Fig. 14b. The precession axis is now the \([1,1,0]\) of GaAs and the \([1,1,0]\) of CdTe. Again, the diffracted spots are found along the lines, on the stereographic projections, perpendicular to
Fig. 17. Stereographic projections for (0,0,1) and (1,1,1) oriented crystals.
the precession axes. There is two-fold symmetry on the 
(0,0,1) projection, but not on the (1,1,1) projection. Thus 
if the (1,1,1) oriented crystal is twinned, spots will appear 
from both crystal orientations. It should be noted that the 
CdTe reflections in Fig. 14a are also reflections from both 
domains. However, because of the two-fold symmetry about the 
vertical axis, the spots from one domain are superimposed on 
the spots of the twin. Fig. 18 is a sketch of the atomic 
structure in the two orientations. Atoms not in the plane of 
the left side of the figure have not been shown for clarity. 
The twin faults can be seen easily on the left hand side. 
The right side of Fig. 18 shows the same "chains" of atoms 
viewed 90° from the left hand side. Although the twin faults 
are present, they cannot be seen. Ponce et al.\textsuperscript{49} have 
recently published TEM photographs that look very similar to 
Fig. 18. The twin faults are easily visible, with the domain 
thickness increasing as the distance from the interface 
increases. 

The precession method was also applied to (1,1,1) CdTe 
epilayers on (1,1,1) GaAs substrates, and to (1,1,1) 
Hg\textsubscript{1-x}Cd\textsubscript{x}Te/CdTe and (1,1,1) Hg\textsubscript{1-x}Mn\textsubscript{x}Te/CdTe superlattices on 
(0,0,1) GaAs, (1,1,1) CdTe, and (1,1,1) Cd\textsubscript{1-x}Zn\textsubscript{x}Te 
substrates. Some of these were grown by MBE and others by 
MOCVD. Twinning was observed in all cases. Several (1,1,1) 
Hg\textsubscript{1-x}Cd\textsubscript{x}Te epilayers grown on (1,1,1) CdTe substrates by 
Liquid Phase Epitaxy (LPE) were also photographed and these 
did not show twinning. There is often a mechanical force in
Fig. 18. The right hand side of this figure is a view of the substrate and epilayer as seen in Fig. 14a. The precession axis is normal to the page. The left hand side is the same view rotated 90°. When the precession axis is normal to this side of the figure, twinning can be observed. The central column shows the stacking sequence of the layers.
one direction parallel to the surface in the LPE process, and this has apparently inhibited the tendency to twin. It is likely that any device containing twin faults will suffer a reduction in the electronic mobility. As a final note, this type of stacking disorder was also seen in (1,1,1) oriented Ni/Cu superlattices grown by sputtering. It is apparent that this fcc twin fault, which is characteristic of bulk growth methods, is also inherent in the large scale surface deposition techniques unless something is present to uniquely define a direction in the surface.

2. Conclusions

The precession method allows a rapid visual inspection of a large region of reciprocal space. It is easy to interpret the information contained in a precession photograph since it is an exact replica of a plane in reciprocal space. On the other hand, electronic detectors are much more sensitive and accurate than photographic film. Precession photography is a complement to diffractometer measurements and should be used as a guide for such work.

Electron diffraction methods are also visual and/or photographic. However, there are a number of advantages that the precession method has over electron diffraction: i. since x-rays are much more penetrating than electrons, both the substrate and thin film can be seen at the same time; ii. precession photography can cover a larger area of reciprocal space, and is not limited to the zeroth level; iii. x-ray
equipment is less expensive, easier to operate and easier to maintain than electron diffraction equipment; iv. no high vacuum equipment is needed for the precession method; and v. the long exposure times possible with the precession method give increased sensitivity.\textsuperscript{104} Electron diffraction is a more valuable tool for studying very thin layers. An epilayer less than a few tenths of a micron thick will be almost invisible to x-rays. An x-ray beam is large (~1 mm in diameter) so the information in a precession photograph is indicative of the overall crystal quality. Electron beams are small, and are more important for studying defects and the distribution of defects.

Compared to other photographic x-ray techniques, the precession method has the advantages of preserving the lattice parameters and of yielding undistorted views of reciprocal space. The sensitivity of this method is also greater in some cases. For example, the x-ray beam passes through the photographic film in the back-reflection Laue method, causing exposure times to be relatively short. The Weissenberg method offers the same sensitivity as the precession method.

B. Diffractometer Measurements

1. The Equipment

Before discussing the measurements themselves, the equipment will be described. Fig. 19 shows the main features
Fig. 19. Sketch of the monochromator and diffractometer. The refrigerator was mounted directly on the diffractometer
of the setup. X-rays were produced by an Elliot GX21 rotating anode generator. The anode material could be either tungsten or molybdenum. Continuous power of up to 10 kW could be achieved with both anodes.

The radiation exited the source through a beryllium window, into a double monochromator enclosed in a He atmosphere. Helium, rather than air, was used because it greatly reduced the attenuation of the beam as it traversed the monochromator. The monochromator crystals were ZYB grade highly-oriented pyrolytic graphite. The (0,0,2) planes were usually used to monochromate the beam, and the (0,0,4) planes were used occasionally. The first monochromator crystal was actually a bank of five crystals, mounted on a flexible frame. The frame could be bent to allow focussing of the x-rays and an accompanying increase in the flux. Both monochromator crystals were mounted on rotating tables, and the table of the first monochromator could be translated toward or away from the source. Thus any x-ray wavelength, whether an excitation line or in the bremsstrahlung, could be chosen between about 0.5 Å and 1.8 Å. Three adjustable slits were present in the system. One horizontal slit was positioned 15 cm after the second monochromator crystal. A second horizontal slit and a vertical slit were placed 25 cm beyond this point (nearer the sample). A thin piece of plastic was placed behind the final slit, and the scattering from the plastic was recorded by a scintillation detector. This served as a monitor of fluctuations in the incident
beam. Finally, the beam was collimated by a choice of circular, tapered collimators with diameters ranging from 0.5 mm to 3.5 mm.

The samples were placed 40 cm from the final slit in the monochromator. They were mounted on a Huber four-circle diffractometer with a full Eulerian cradle. The diffracted x-rays were detected by an EG&G ORTEC Si(Li) energy sensitive detector. Circular collimators, with diameters from 1 mm to 8 mm, were screwed onto the detector. The detector output was amplified and fed through a single-channel analyzer (SCA) to remove contamination from background noise and from the harmonic wavelengths ($\lambda/2$, $\lambda/3$, etc.). The output of the SCA went to a counter and was then recorded by a computer. The driving of all angles and translations in the monochromator and diffractometer, as well as the counting operations, could be controlled manually or by computer. The data were stored on 8" diskettes. Fig. 20 is a block diagram of the control and counting chain.

For the low temperature measurements, one end of the crystal was wrapped in indium foil for mechanical padding and thermal contact. This was then mounted in a copper clamp which was fixed onto a copper block tightly screwed onto the cold finger of a CTI-Cryogenics closed cycle refrigerator. Two Si diode thermometers, calibrated by Lake Shore Cryotronics, were placed at two different levels on the copper block: one near the cold finger and the other as close as possible to the sample. With one Be vacuum outershroud
Fig. 20. A block diagram of the motor control and counting chain
and two Be radiation shields, the refrigerator could operate between 8 K and 380 K. The temperature was monitored and stabilized by a DRC-81C Lake Shore temperature controller.

2. The Measurements

Figure 21 is a diagram of the four-circle diffractometer. The principal angles are $\theta$, $\phi$, $\chi$, and $\omega$. $2\theta$ is the angle between the incident and diffracted beam. $\omega$ is the same as $\theta$; the notation $\omega$ is used rather than $\theta$ since this angle can be rotated independently, and is therefore not always half of the angle $2\theta$. When desired, $\omega$ can be coupled to $2\theta$, driving half as fast. $\chi$ and $\phi$ allow the specimen to be placed in any orientation. For a given family of reflections, $\chi$ and $\phi$ are the same; only $\omega$ and $2\theta$ change.

Two different types of scans are usually done during data collection: an $\omega-2\theta$ scan and an $\omega$ scan. In the $\omega-2\theta$ scan, $\omega$ and $2\theta$ are coupled together. Therefore, the crystal is rotated through the Bragg angle and the detector through twice the Bragg angle with twice the angular velocity. The geometry of an $\omega-2\theta$ scan is shown in Fig. 22a. For convenience, the crystal is shown as being fixed in place while the incident and diffracted beam moves (in an experiment, the incident beam is fixed while the crystal and diffracted beam moves). At the Bragg angle, the scattering vector $q$ is equal to a reciprocal lattice vector. During a small rotation $\Delta\omega$, the diffraction vector changes by $\Delta q$ which is radially outward from the reciprocal space origin.
Fig. 21. Definition of the angles on a diffractometer. The \( \omega \) circle is in the same plane as the \( 2\theta \) circle, and the detector is mounted on the \( 2\theta \) arm.
Fig. 22a. $\omega-2\theta$ scan. The change in the scattering vector, $\Delta q$, is radially outward from the origin of reciprocal space.

Fig. 22b. $\omega$ scan. The magnitude of $q$ is constant and $\Delta q$ represents only a change in direction. $\Delta q$ is perpendicular to the $\Delta q$ in the $\omega-2\theta$ scan.
Therefore the magnitude of \( q \) changes but its direction is constant. Fig. 22b is the situation for an \( \omega \) scan, again shown in the reference frame in which the crystal is motionless. In a real \( \omega \) scan the incident beam and detector are fixed. Only the crystal is rotated. The figure shows that the magnitude of \( q \) is constant but its direction changes. The path in reciprocal space scanned by an \( \omega \) scan is perpendicular to the path scanned by an \( \omega-2\theta \) scan. The third orthogonal direction would be scanned by leaving the incident and diffracted beams fixed, and rotating \( \chi \).

This leads, in a very natural way, to the procedure used to center and orient the crystals. When a crystal is first mounted, it is generally off-center, and the proper \( \chi \) and \( \phi \) are not known. The crystals were flat plates with their surfaces parallel to either the \((0,0,1)\) or the \((1,1,1)\) lattice planes. Therefore a \((0,0,1)\) or \((h,h,h)\) reflection could be found with only a small amount of searching. Three scans were then done in succession: a \( \phi \) scan (nearly equivalent to an \( \omega \) scan), a \( \chi \) scan, and an \( \omega-2\theta \) scan. During each scan, the centroid of the peak was computed, and the angle was rotated back to this position before continuing on. The crystal was then translated in the diffractometer and set at the position giving the largest count rate. This process was repeated until no further increase in the count rate could be obtained. Narrow collimators, usually with diameters of 1 mm, were used on the incident beam and the detector during this procedure to determine the orientation
as accurately as possible.

For the data collection, the detector collimator was fully opened to 8 mm, resulting in an angular beam divergence of about 0.75°. An ω-2θ scan was done for each reflection, followed immediately by an ω scan, with the detector set at the centroid of the ω-2θ scan. These resulted in profiles of the number of counts as a function of angle. The background was considered to be the average of the count numbers at the edges of the scan. The peak limits for integration were the angles at which the count numbers were one standard deviation above the background, and the count numbers between these limits were summed. This sum, minus the average background at each point between the limits, yielded the integrated intensity. The quantity of physical interest was the structure factor rather than the integrated intensity. This was extracted using equation 21. The Lorentz and polarization factors are usually applied simply by using the angle of the peak centroid. However, this can lead to errors at low angles. Therefore, the Lorentz and polarization factors, and wavelength correction were applied to each point in the scans, and the profiles were integrated again. The other constants, including I₀, were not accounted for. Therefore, the structure factors were only on a relative scale.

The center of a peak measured in an ω-2θ or an ω scan is related to the lattice parameter by Bragg's law, which is rewritten here as
\[ a = \frac{\lambda}{2} \left( \frac{h^2 + k^2 + l^2}{\sin(\Theta - \Theta_0)} \right)^{1/2}. \] [64]

\(\Theta\) is the measured angle and \(\Theta_0\) is a possible constant offset in the measurements. If several reflections, \((h_1, k_1, l_1)\), are measured, then for any two of them, equation 64 yields

\[
\sin(\Theta_1 - \Theta_0)(h_1^2 + k_1^2 + l_1^2)^{1/2} = \sin(\Theta_2 - \Theta_0)(h_2^2 + k_2^2 + l_2^2)^{1/2} \quad [65]
\]

because the lattice parameter is constant. The sines can be expanded, giving an equation for the zero offset

\[
\tan\Theta_0 = \frac{(h_2^2 + k_2^2 + l_2^2)^{1/2}\sin\Theta_1 - (h_1^2 + k_1^2 + l_1^2)^{1/2}\sin\Theta_2}{(h_2^2 + k_2^2 + l_2^2)^{1/2}\cos\Theta_1 - (h_1^2 + k_1^2 + l_1^2)^{1/2}\cos\Theta_2} \quad [66]
\]

A value of \(\Theta_0\) will be found for each pair of reflections. The average \(\Theta_0\) can be put back into equation 64 to find the lattice parameter. A warning must again be made concerning low angle reflections. It can be shown that systematic errors, such as poor centering of the crystal, lead to errors in the measured Bragg angles. These types of errors are greatest at low angles and are negligible at higher angles. Naturally, a larger number of reflections will provide a more accurate lattice parameter.

Accurate lattice parameter measurements require an accurate knowledge of the x-ray wavelength. The wavelength of x-rays from an excitation line is typically known to a precision of a few parts per million. X-rays from the
continuous spectrum are less precisely known. To determine these wavelengths, a crystal was used (e.g., Si or Ge) whose lattice parameter was very well known. The wavelength was approximately known from the monochromator settings. The estimated wavelength and the known lattice parameters yielded an estimated Bragg angle. By differentiating Bragg's law, one finds

\[ \Delta \theta = \frac{180}{\pi} \frac{\Delta \lambda}{\lambda} \tan \theta \]  

where \( \Delta \lambda = \lambda - \lambda_{\text{estimated}} \) and \( \Delta \theta = \theta_{\text{measured}} - \theta_{\text{estimated}} \) in degrees. A graph of \( \Delta \theta \) versus \( \tan \theta \) is a straight line with a slope proportional to \( \Delta \lambda \). The wavelength could be measured to about four significant figures this way, which was as good as, or better than the energy resolution of the graphite monochromators. To measure integrated intensities, this precision was acceptable, but to measure accurate lattice parameters, an excitation line had to be used.
IV. THE EXPERIMENTS: SINGLE CRYSTALS

A. GaAs

Very little work was done on GaAs single crystals. The crystal used was rectangular in shape with dimensions of 12x10x0.5 mm, and was cut from a commercial (0,0,1) oriented Cominco Materials, Inc. wafer. The surface was polished as if the wafer was to be used for subsequent CdTe deposition.\(^{55}\)

The $\phi$, $\chi$, and $\omega-2\theta$ scans for optimization and centering were done on the (0,0,4) reflection at each temperature. $\phi$ and $\chi$ were then fixed while $\omega$ and $2\theta$ were varied to record the (0,0,2), (0,0,4), and (0,0,6) Bragg reflections. The Bragg angles of higher order reflections were too large to be reached by the diffractometer.

Fig. 23 is a graph of the measured lattice parameter (LP) of GaAs versus temperature. Standard deviations are 0.0005 Å or less. The LP was measured with an x-ray wavelength of 1.28181 Å ($\text{W L}\beta_1$ excitation line). The room temperature lattice parameter, $a=5.6539\pm.0003$ Å, agrees well with previous measurements.\(^{109}\) No earlier measurements of the lattice parameter as a function of temperature, at low temperature, could be found. The thermal expansion coefficient, however, has been measured by several groups.\(^{110,111,112}\) The solid line in Fig. 23 was obtained as follows: the four lowest temperature LPs were averaged to get a lattice parameter at $T=0$ K; using the thermal expansion
Fig. 23. GaAs lattice parameter as a function of temperature
coefficient from the data of Novikova,\textsuperscript{110} the LP was calculated at $T=5$ K; this new LP was then used to calculate the LP 5 degrees higher, and the procedure was repeated up to 325 K. The measured lattice parameters agree excellently with those calculated from the thermal expansion data. Low temperature thermal expansion measurements by Sparks and Swenson,\textsuperscript{111} and by Smith and White\textsuperscript{112} show that the thermal expansion coefficient is negative between 12 K and 56 K. Our data were not precise enough to observe this small effect.

At room temperature, the $(2,2,0)$ lattice planes were used to check for the Borrmann effect. These planes are perpendicular to the $(0,0,1)$ surface. A large transmitted peak was observed when the crystal was rotated to the $(2,2,0)$ Bragg angle. The absorption coefficient of GaAs is $\mu=328$ cm$^{-1}$ for Mo K\textalpha{} radiation ($\lambda=0.7093$ Å), the wavelength used for this observation. Thus $\mu T_0=16.4$. Under normal conditions, $e^{-16.4}$ of the incident beam (less than one part in $10^7$) would be transmitted due to absorption. Therefore, the peak could unambiguously be identified as a Borrmann transmitted peak. Although the Borrmann effect was not looked for at low temperatures, the GaAs crystal was treated as a perfect crystal throughout the temperature range studied.

Two problems were encountered in the integrated intensity measurements of GaAs. First, since the wavelength was large, primary extinction was large. Both primary and secondary extinction are temperature dependent, because they are
functions of the temperature dependent structure factor. The larger $|F|$ is, the larger the extinction correction will be (see eq. 27). As $|F|$ decreases, the correction decreases. Therefore the measured structure factor will diminish with increasing temperature, but not as much as it would if extinction was not present. The smaller slope means that the Debye temperature will appear to be higher than it really is. The structure factors that were measured from GaAs were from low index reflections and were strongly affected by extinction. Therefore the results were not meaningful.

Secondly, higher order reflections would be affected negligibly by extinction, but because of the long wavelength, these reflections were not observable.

The second harmonic wavelength, $\lambda/2=0.6409$ Å, from the bremsstrahlung, was also present in the incident beam. It was diffracted by the (0,0,4) planes of the graphite monochromators. At this wavelength extinction was reduced significantly for the (0,0,8) reflection [the (0,0,8) reflection at $\lambda=0.6409$ Å was at the same angle as the (0,0,4) of the fundamental wavelength]. Fig. 24 shows the measured (0,0,8) structure factor as a function of temperature at this wavelength. The low incident intensity made the counting statistics quite poor. A fit of equation 47 to these data, taking $m$ as the mean atomic mass of Ga and As, yielded a Debye temperature of $\Theta_D=275\pm50$ K. This agrees, to within the experimental uncertainty, with the results of Arnold and Nereson\textsuperscript{113} who report $\Theta_D=247$ K for GaAs. The
Fig. 24. $(0,0,8)$ structure factor of GaAs measured with the harmonic wavelength of $\lambda = 0.6409 \text{ Å}$
Debye temperature from specific heat measurements is between 350 K and 360 K in the same temperature range. Dividing this by \( \sqrt{2} \) gives \( \Theta_D/\sqrt{2} = 250 \) K, in excellent agreement with Arnold and Nereson, and within one standard deviation of our result.

CdTe

Two CdTe crystals were studied. One crystal had a (0,0,1) orientation and the other had a (1,1,1) orientation. Both were grown by J. L. Schmit using the vertical Bridgman technique, and were prepared as if they were to be used for subsequent vapor phase epitaxial deposition. The (0,0,1) oriented crystal was rectangular in shape with dimensions 3x8x1.5 mm, and the (1,1,1) crystal had dimensions 12x10x0.5 mm.

The lattice parameter as a function of temperature was measured on the (0,0,1) crystal using the W L\( \beta_1 \) excitation line (\( \lambda = 1.28181 \) Å). These results are shown in Fig. 25. The room temperature value of \( a = 6.4820 \pm 0.0003 \) Å matches previously reported measurements. No earlier lattice parameter measurements as a function of temperature could be found for comparison, but thermal expansion data were available. The solid line in Fig. 25 was calculated from these data using the same procedure that was used for GaAs above. The agreement between the measured lattice parameters and the solid line is again excellent. As in GaAs and other tetrahedrally bonded solids, there is a low
**CdTe**  
\[ \lambda = 1.28181 \, \text{Å} \]  
[1,0,0] orientation  

From thermal expansion data  

**Fig. 25.** CdTe lattice parameter as a function of temperature
temperature region in which the thermal expansion coefficient of CdTe is negative. The effect is much more pronounced in CdTe than in GaAs, and is easily visible in our data. To understand this, consider the simple model of a linear chain of three atoms. Kittel\textsuperscript{118} has shown how anharmonic terms in the potential of each pair of adjacent atoms produce a positive thermal expansion coefficient. However, only longitudinal vibrations were considered in this calculation. A transverse vibration of the center atom in the chain increases the separation between the atom and each of the adjacent atoms. These forces on the adjacent atoms reduce their separation.\textsuperscript{12} Thus, transverse modes can result in a negative thermal expansion coefficient, while longitudinal modes yield a positive coefficient. An overall negative coefficient of thermal expansion results from a higher weighting (population) of the transverse modes.

The Borrmann effect could not be seen in the CdTe crystals, indicating that they were mosaic. This was not surprising in light of the inherent dislocations and impurities present in bulk grown CdTe. The integrated intensities were therefore analyzed as if the crystals were ideally mosaic.

Integrated intensities of the (0,0,1) Bragg reflections were measured\textsuperscript{119} using the x-ray wavelength $\lambda=0.546\pm0.001$ Å, in the bremsstrahlung of the tungsten anode. The short wavelength was chosen to minimize the effects of secondary extinction, and to probe reflections with large scattering
vectors. The \((0,0,8)\) and \((0,0,12)\) were used for optimization and centering at each temperature. Although the incident beam fluctuations were less than 1\%, they have been accounted for in the analysis. The measured structure factors were corrected for TDS as outlined above. The elastic constants used in the TDS correction were obtained as follows: elastic constants at room temperature and 77 K were taken from the literature,\(^{12}\) and are listed in Table 4; linear interpolation was used to obtain elastic constants between these temperatures; elastic constants below 77 K were set equal to the 77 K values. The TDS correction was done independently on the \(\omega-\varphi\) and the \(\omega\) scans. The two corrected structure factors at each temperature were then averaged and this average was used in the subsequent analysis. The \((0,0,1)\) reflections fall into two of the three categories: strong if \(l=4n\), and weak if \(l=4n+2\). The measured structure factors as a function of temperature are shown in Fig. 26 (strong) and Fig. 27 (weak). The structure factors are plotted in the form \(\ln|F|^2\) so that they can all be shown on the same scale.

The \((h,h,h)\) Bragg reflections were measured from the \((1,1,1)\) oriented crystal at \(\lambda=0.637\pm.001\) Å from the white radiation of the tungsten anode. Optimization and centering was done on the \((4,4,4)\) and \((5,5,5)\) reflections. The structure factors were treated the same as the \((0,0,1)\) reflections. Fig. 28 shows the measured \((h,h,h)\) structure factors as a function of temperature. All three categories—strong, moderate, and weak—are seen in this series.
Table 4. Elastic constants for CdTe

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$C_{11}$ ($N/m^2$)</th>
<th>$C_{44}$ ($N/m^2$)</th>
<th>$C_{12}$ ($N/m^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>$5.78 \times 10^{10}$</td>
<td>$2.04 \times 10^{10}$</td>
<td>$4.02 \times 10^{10}$</td>
</tr>
<tr>
<td>300</td>
<td>$5.35 \times 10^{10}$</td>
<td>$2.02 \times 10^{10}$</td>
<td>$3.69 \times 10^{10}$</td>
</tr>
</tbody>
</table>
Fig. 26. Strong (0,0,l) CdTe structure factors as a function of temperature. Strong reflections have l=4n
Fig. 27. Weak \((0,0,1)\) CdTe structure factors as a function of temperature. Weak reflections have \(l=4n+2\)
Fig. 28. (h,h,h) CdTe structure factors as a function of temperature. Circles represent strong reflections, squares represent moderate reflection, and triangles represent weak reflections.
Since Cd and Te have nearly the same mass, the strong and moderate intensity reflections can be analyzed assuming both atoms have the same thermal parameter. The resulting Debye-Waller factor is a weighted average of the Debye-Waller factors of the individual atoms:

\[
e^{-2M} = \begin{cases} 
\frac{|f_{Cd} \exp(-M_{Cd}) + f_{Te} \exp(-M_{Te})|^2}{|f_{Cd} + f_{Te}|^2} & \text{h+k+l=4n} \\
\frac{|f_{Cd} \exp(-M_{Cd})|^2 + |f_{Te} \exp(-M_{Te})|^2}{|f_{Cd}|^2 + |f_{Te}|^2} & \text{h+k+l=4n+1}
\end{cases}
\]  

[68]

Table 5 lists the Debye temperatures and harmonic coefficients for all of the strong and moderate reflections. Through trial and error, it was found that \(\Theta_M\) and \(\alpha\) were constant for temperatures above about 75 K (and below the highest temperature of 360 K). The (0,0,1) reflections were fit in this entire range. The temperature range for the (0,0,4) had to be reduced to \(T>135\) K because \(\Theta_M(T)\) was not constant below that temperature. The range, \(130\leq T\leq 260\) K, was used for the (h,h,h) reflections because anharmonicity was expected to be more pronounced in that direction. The intensities over the smaller temperature range would be less affected by the anharmonicity.

It will be noticed that \(\Theta_M(0,0,4)\) is lower than the other Debye temperatures. This cannot be attributed to secondary extinction since that would cause the Debye temperature to be
Table 5. Average Debye temperatures and harmonic OPP coefficients for the strong and moderate reflections. $\Theta_B=210$ K was used in the Debye-Einstein model

<table>
<thead>
<tr>
<th>h,k,l</th>
<th>Debye $\Theta_D$ (K)</th>
<th>Debye-Einstein $\Theta_D$ (K)</th>
<th>OPP $\alpha$ (eV/Å^2)</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,0,4</td>
<td>105±4</td>
<td>76±4</td>
<td>1.05±.04</td>
<td>135 - 360</td>
</tr>
<tr>
<td>0,0,8</td>
<td>139±4</td>
<td>100±4</td>
<td>1.36±.04</td>
<td>70 - 360</td>
</tr>
<tr>
<td>0,0,12</td>
<td>137±4</td>
<td>100±4</td>
<td>1.35±.04</td>
<td>70 - 360</td>
</tr>
<tr>
<td>0,0,16</td>
<td>140±4</td>
<td>103±4</td>
<td>1.41±.04</td>
<td>70 - 360</td>
</tr>
<tr>
<td>0,0,20</td>
<td>142±7</td>
<td>105±4</td>
<td>1.49±.08</td>
<td>70 - 215</td>
</tr>
<tr>
<td>3,3,3</td>
<td>164±5</td>
<td>123±4</td>
<td>1.96±.05</td>
<td>130 - 260</td>
</tr>
<tr>
<td>4,4,4</td>
<td>154±4</td>
<td>114±4</td>
<td>1.71±.04</td>
<td>130 - 260</td>
</tr>
<tr>
<td>5,5,5</td>
<td>141±4</td>
<td>103±4</td>
<td>1.43±.04</td>
<td>130 - 260</td>
</tr>
<tr>
<td>7,7,7</td>
<td>142±4</td>
<td>105±4</td>
<td>1.46±.04</td>
<td>130 - 260</td>
</tr>
<tr>
<td>8,8,8</td>
<td>143±4</td>
<td>105±4</td>
<td>1.48±.04</td>
<td>130 - 260</td>
</tr>
<tr>
<td>9,9,9</td>
<td>132±5</td>
<td>97±5</td>
<td>1.25±.04</td>
<td>130 - 260</td>
</tr>
</tbody>
</table>

Averages: 140±14 103±11 1.45±23

Averages excluding (0,0,4), (3,3,3), (4,4,4), and (9,9,9): 141±2 103±2 1.43±.06

Averages excluding (0,0,4), (3,3,3), and (4,4,4): 140±4 102±3 1.40±.08
higher than normal. It can be postulated that the small $\theta_M$ is due to a "softness" in the vibration of the valence electrons. That is, the valence electrons are loosely bound to the atomic nuclei with correspondingly larger mean square displacements. An argument against this interpretation is that secondary extinction must be present to some extent in this low order reflection, meaning the actual Debye temperature would be even lower than the apparent value of 105 K. Thus, the explanation of the low Debye temperature for this reflection is not clear. The slope of the (1,1,1) reflection was too small to fit accurately, indicating a very large apparent Debye temperature. The (3,3,3) and (4,4,4) reflections also had higher Debye temperatures than the others. This is clearly due to secondary extinction since it occurs in the low order reflections. The fact that the deviation from the average decreases with increasing $(h,k,l)$ is also characteristic of extinction. Finally, the (9,9,9) reflection yielded a lower $\theta_M$ than normal. It is not clear why this is. Two possible factors could be anharmonicity and the neglect of two-phonon and higher order thermal diffuse scattering in the TDS correction. The agreement between the results of the remaining reflections was taken as an indication that secondary extinction was negligible in those cases.

The averages, $\theta_M=141\pm2$ K and $\alpha=1.43\pm.06$ eV/Å$^2$, agree excellently with earlier results. Walford and Schoeffel arrived at a Debye temperature of $\theta_M=141\pm5$ K using a method
similar to the one used here on powder samples of CdTe. They measured four reflections between 96 K and 296 K. Zubik and Valvoda\textsuperscript{120} used the same procedure between 281 K and 608 K and arrived at $\Theta_M = 140 \pm 3$ K from a powder sample and $\Theta_M = 145 \pm 8$ K from a single crystal. The strong and moderate reflections could, in principle, have different Debye temperatures (see equation 68). Our results and those of Walford and Schoeffel, and Zubik and Valvoda, show that the difference is minor, indicating that $M_{\text{Cd}} = M_{\text{Te}}$ to within the experimental uncertainty. This will be discussed further when the weak reflections are included. A fit using the data that had not been corrected for TDS gave a Debye temperature 3 K higher: $\Theta_M = 144$ K.

Fig. 29 shows the procedure for finding the x-ray Debye temperature as a function of temperature, using the (0,0,12) reflection. $\Theta_{M}(T)$ computed from other reflections looks identical to this plot. The Debye temperature from specific heat measurements must be compared with $\sqrt{2}\Theta_{M} = 199$ K. Fig. 30 shows the specific heat Debye temperature as a function of temperature.\textsuperscript{121,122} $\Theta_D = 200$ K between 50 K and 175 K, in agreement with our results, but decreases at higher temperatures. It is immediately obvious that $\Theta_M(T)$ is constant over a wider range than $\Theta_D(T)$. Herbstein\textsuperscript{123} and Hunt and Ishida\textsuperscript{124} state that this is generally the case when comparing x-ray and specific heat Debye temperatures. The low frequency modes are weighted more heavily in the x-ray case, so $\Theta_M$ is less affected by the high frequency acoustic
Fig. 29. The procedure for determining the Debye temperature as a function of temperature. The top graph is the raw data. The middle graph shows the data plotted versus $\phi(x)/x+1/4$. In the classical regime, this should be, and is, a straight line with a slope inversely proportional to $\Theta^2$. This Debye temperature is used as a reference value to calculate the Debye temperature at all other temperatures.
Fig. 30. The specific heat Debye temperature as a function of temperature.

Fig. 31. The OPP harmonic coefficient, $\alpha$, as a function of temperature. This is determined in the same way as $\Theta_M(T)$. 

CdTe (8,8,8)
modes and the optic modes. Fig. 31 shows an analogous plot of $\alpha(T)$ computed from the CdTe (8,8,8) data.

Based on the above averages, the mean square atomic displacement of the average atom can be calculated using equations 48 and 59. These results are given in Table 6. The Debye and OPP models give displacements which agree to well within one standard deviation for all but the lowest temperature. This, of course, is due to the neglect of quantum statistics in deriving the OPP temperature factor. Quantum effects become noticeable below the Debye temperature, and 75 K is $-\theta_M/2$.

Three different corrections were done to account for the effects of thermal expansion, which could bias the results. All three were based on the fact that the Bragg angle changed slightly as the lattice parameter changed. The first correction was the so-called quasiharmonic approximation, which reflects the change in the phonon frequencies, and thus $\theta_M$, due to thermal expansion. The second was the change in the value of $(\sin \theta / \lambda)^2$ in the exponent of equations 47 and 58. Finally, the atomic form factors changed slightly since they are functions of $(\sin \theta / \lambda)^2$. The first two corrections are largest for high order reflections and the third is more significant for low orders. A fit based on these corrections found that the change in $\theta_M$ was, at most, 0.2 K. This was much less than the uncertainty in $\theta_M$, and therefore not significant.

Table 5 also lists the Debye temperatures obtained from a
Table 6. Root mean square atomic displacement versus temperature. $\langle u^2 \rangle^{1/2}$ was computed using equations 48 and 59. The Debye temperature used was 141 K and the harmonic OPP coefficient was 1.43 eV/Å$^2$. Standard deviations are 0.003 Å.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\langle u^2 \rangle^{1/2}$ (Å)</th>
<th>Debye</th>
<th>OPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>0.071</td>
<td>0.067</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.080</td>
<td>0.078</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.097</td>
<td>0.095</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.111</td>
<td>0.110</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>0.124</td>
<td>0.123</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.136</td>
<td>0.135</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>0.146</td>
<td>0.145</td>
<td></td>
</tr>
</tbody>
</table>
fit to the Debye-Einstein model. Fig. 32 shows the phonon dispersion curves and the phonon density of states for CdTe, measured by inelastic neutron scattering.\textsuperscript{125} The region between 3.7 THz and 5 THz represents the optic branches. The centroid of $g(v)$ in this region is $v=4.4$ THz, which corresponds to an Einstein temperature of $\Theta_E=210$ K. This was fixed in the fit and $\Theta_M$ was varied, giving the tabulated values.

The treatment above could not be applied to the weak reflections ($h+k+l=4n+2$). Their structure factors are a difference between the form factors of Cd and Te. The reflections were therefore very sensitive to differences in the thermal parameters, $M_{\text{Cd}}$ and $M_{\text{Te}}$, of the two atoms. The temperature dependence of the weak reflections in Fig. 27 and Fig. 28 illustrates this point dramatically. Intensities usually decrease as the temperature is raised but the opposite effect is seen here. Anomalous behavior of this sort has been observed in several other compounds having the zincblende structure, namely InSb,\textsuperscript{126} CuI,\textsuperscript{127,128} CuBr,\textsuperscript{128,129} and CuCl.\textsuperscript{130}

The (0,0,2) and (2,2,2) were influenced by valence effects, so they were not used in the analysis. The kink in the (0,0,6) data at about 270 K is not understood. Less pronounced kinks are seen in the (0,0,10), (6,6,6), (0,0,14), and (0,0,18) data at ~250 K, 200 K, 100 K, and 75 K, respectively. For $T>70$ K ($\Theta_M/2$) these last features can be explained by the following calculation.
Fig. 32. The phonon dispersion curves and density of states as measured by inelastic neutron scattering. The region between $\nu=3.7$ THz and 5 THz in the density of states corresponds to the optic branches.
\[ M = |H|^2 \langle u^2 \rangle / 2 = U T |H|^2 / 2 \]  \[69\]

where \( U \) is independent of temperature. Thus,

\[ |F| = |f_{Cd} \exp(-U_{Cd} T |H|^2 / 2) - f_{Te} \exp(-U_{Te} T |H|^2 / 2)| \]

A positive slope in the temperature dependence, \((d|F|/dT)>0\), imposes the condition

\[ \frac{U_{Cd}}{U_{Te}} > \frac{f_{Te}}{f_{Cd}} \exp\left[-\left(U_{Te} - U_{Cd}\right) T |H|^2 / 2\right] \]  \[70\]

Using equation 70, the temperature at which the slope goes to zero can be estimated. Taking \( U_{Cd}=7.94 \times 10^{-5} \text{ Å}^2/\text{K} \) and \( U_{Te}=5.79 \times 10^{-5} \text{ Å}^2/\text{K} \) from the room temperature data of Vaipolin,95 and the form factors from references 72 and 79, the temperatures \( T_k \) at which the kinks are expected are listed in Table 7, along with the observed temperatures. The agreement is acceptable for all but the \((0,0,6)\). Data above the kink in the \((0,0,6)\) were not used, and to be consistent, points on the \((0,0,10)\) and \((0,0,14)\) graphs were also not used above that temperature.

The Debye temperatures of the individual atoms were found by fitting two or more reflections together. Because of the large correlation between \( \theta_{M-Cd} \) and \( \theta_{M-Te} \) in any fit, at least one of the reflections had to be strong or moderate and at least one reflection had to be weak. The reflections used in the fits were the \((0,0,1)\) reflections with \( l=6, 8, 10, 12, \ldots \)
Table 7. $T_k$, the temperature at which the weak structure factors, as a function of temperature, have zero slope

<table>
<thead>
<tr>
<th>$h,k,l$</th>
<th>$T_k$ (K)</th>
<th>Calculated</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,0,6</td>
<td>580</td>
<td></td>
<td>270</td>
</tr>
<tr>
<td>0,0,10</td>
<td>240</td>
<td></td>
<td>250</td>
</tr>
<tr>
<td>0,0,14</td>
<td>110</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>0,0,18</td>
<td>55</td>
<td></td>
<td>75</td>
</tr>
<tr>
<td>6,6,6</td>
<td>220</td>
<td></td>
<td>~200</td>
</tr>
</tbody>
</table>
14, and 16, and the \((h,h,h)\) reflections with \(h=5, 6, 7,\) and 8. The other reflections, except the \((0,0,18)\) and \((0,0,20)\), were excluded for the reasons given above. The \((0,0,18)\) and \((0,0,20)\) were not used because they had poor statistics, and had only been corrected for one-phonon TDS. In addition, the \((0,0,20)\) could only be seen below 215 K. The results were \(\Theta_{\text{M-Cd}}=134\pm3\) K and \(\Theta_{\text{M-Te}}=146\pm3\) K in the temperature range \(130\leq T \leq 260\) K. These results are in exact agreement with Vaipolin,\(^95\) who took the complementary approach of measuring a large number of reflections at room temperature and fitting against \(h, k,\) and \(l.\) The corrections based on thermal expansion were again checked and found to be negligible.

Equation 48 was used to calculate the root mean square displacements, \(\langle u_{\text{Cd}}^2 \rangle^{1/2}\) and \(\langle u_{\text{Te}}^2 \rangle^{1/2}\), which are plotted in Fig. 33. When an Einstein temperature of \(\Theta_{\text{E}}=210\) K was included in the model, the Debye temperatures changed to \(\Theta_{\text{M-Cd}}=98\pm3\) K and \(\Theta_{\text{M-Te}}=108\pm3\) K. The harmonic OPP model in this temperature range gave \(\alpha_{\text{Cd}}=1.24\pm.03\) eV/Å\(^2\) and \(\alpha_{\text{Te}}=1.63\pm.03\) eV/Å\(^2\). Fig. 34 is a plot of the potential wells of the Cd and Te atoms. The smaller harmonic coefficient for cadmium means this atom is in a broader well, with correspondingly larger mean square displacements. The r.m.s. displacements according to equation 59, are plotted in Fig. 33 as dotted lines.

Fitting of the anharmonic parameters \(\beta, \gamma,\) and \(\delta\) was attempted in the larger temperature range \(70 \leq T \leq 360\) K. The larger temperature range, and especially the higher
Fig. 33. The mean square atomic displacements for Cd and Te, using both the Debye and OPP models.
Fig. 34. The potential wells of Cd and Te in the OPP model, using $\alpha_{\text{Cd}}=1.24 \text{ eV/Å}^2$ and $\alpha_{\text{Te}}=1.63 \text{ eV/Å}^2$.
temperatures, should make anharmonic effects more noticeable. It would be expected that the cubic anharmonic term (β) would be dominant. X-ray and neutron diffraction studies on other crystals with the zincblende structure have usually found this to be the case.\textsuperscript{130,131,132,133}

Fits were done on the (0,0,1) data alone, the (h,h,h) data alone, and all data together. Table 8 lists the results. \( \chi \) is the square root of the standard goodness-of-fit parameter, \( \chi^2 \), which was minimized in the least squares fit. \( R \) is the crystallographic \( R \) factor

\[
R = \frac{\sum w_i |F_i|^2 - |F_{calc}|^2}{\sum w_i |F_i|^2},
\]

where the \( F_i \) are the measured structure factors, \( F_{calc} \) are the calculated structure factors, and the weighting factor is \( w_i = 1/\sigma_i^2 \), \( \sigma_i \) being the standard deviation of the structure factor. Due to their similarities, when \( \chi \) is minimized, \( R \) will also be very near its minimum. The \( R \) factor ratio test\textsuperscript{134} can be used to decide if the improvement in \( R \), when going from the harmonic to the anharmonic function, is statistically significant. In other words, the test is a comparison of the physical significance of two models, based on how well the models fit the data.

One first notices that \( \alpha_{Cd} \) is significantly different in the (0,0,1) and (h,h,h) fits. To verify that this was a general feature of the data the fitting was repeated using
Table 8. Anharmonic OPP fits using the (0,0,1) reflections (1=6, 8, 10, 12, 14, and 16) and the (h,h,h) reflections (h=5, 6, 7, and 8) in the temperature range 70<T<360 K. All fits in which other anharmonic parameters were varied did not result in statistically significant improvements in R

<table>
<thead>
<tr>
<th>h,k,l</th>
<th>$\alpha_{Cd}$ (eV/A²)</th>
<th>$\alpha_{Te}$ (eV/A²)</th>
<th>Anharmonic parameters (eV/A⁴)</th>
<th>R</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>all</td>
<td>1.25±.04</td>
<td>1.62±.04</td>
<td></td>
<td>0.026</td>
<td>3.00</td>
</tr>
<tr>
<td>all</td>
<td>1.60±.05</td>
<td>2.32±.06</td>
<td>$\gamma_{Cd}=-0.8±1$ $\gamma_{Te}=-1.8±1$</td>
<td>0.016</td>
<td>1.87</td>
</tr>
<tr>
<td>all</td>
<td>1.24±.04</td>
<td>1.62±.04</td>
<td>$\delta_{Cd}=0.6±1$ $\delta_{Te}=2.6±1$</td>
<td>0.024</td>
<td>2.74</td>
</tr>
<tr>
<td>(0,0,1)</td>
<td>1.18±.04</td>
<td>1.54±.04</td>
<td></td>
<td>0.034</td>
<td>3.00</td>
</tr>
<tr>
<td>(0,0,1)</td>
<td>1.78±.04</td>
<td>2.57±.04</td>
<td>$\gamma_{Cd}=-1.4±1$ $\gamma_{Te}=-2.7±1$</td>
<td>0.020</td>
<td>1.81</td>
</tr>
<tr>
<td>(0,0,1)</td>
<td>1.23±.04</td>
<td>1.63±.04</td>
<td>$\delta_{Cd}=0.7±1$ $\delta_{Te}=3.7±1$</td>
<td>0.031</td>
<td>2.79</td>
</tr>
<tr>
<td>(h,h,h)</td>
<td>1.38±.04</td>
<td>1.58±.04</td>
<td></td>
<td>0.013</td>
<td>1.97</td>
</tr>
<tr>
<td>(h,h,h)</td>
<td>1.52±.05</td>
<td>1.93±.04</td>
<td>$\gamma_{Cd}=-0.4±1$ $\gamma_{Te}=-0.8±1$</td>
<td>0.0074</td>
<td>1.22</td>
</tr>
<tr>
<td>(h,h,h)</td>
<td>1.37±.04</td>
<td>1.72±.04</td>
<td>$\delta_{Cd}=-1.3±1$ $\delta_{Te}=-8.5±1$</td>
<td>0.010</td>
<td>1.51</td>
</tr>
</tbody>
</table>
two reflections at a time. Table 9 shows the results from all possible pairs of strong (or moderate) and weak reflections. Obviously, the difference in the harmonic coefficients is a general feature; that is, it is not simply due to a spurious reflection. A marked difference between the [0,0,1] and [1,1,1] direction at a site of cubic point group symmetry is unexpected and unexplained. Further measurements are needed to resolve this anomaly.

Referring again to Table 8, the data were very insensitive to variations in $\beta_{\text{Cd}}$ and $\beta_{\text{Te}}$. Therefore fits were done in which $\beta_{\text{Cd}}$ and $\beta_{\text{Te}}$ were held at fixed values, with $\beta_{\text{Cd}}=\beta_{\text{Te}}$, while $\gamma_{\text{Cd}}$ and $\gamma_{\text{Te}}$ were varied. Fig. 35 shows a plot of the R factor versus $\beta_{\text{Cd}}$ for the fit involving all the data. There is a clear minimum at $\beta_{\text{Cd}}=-0.35$ eV/Å$^3$. However, the change in R with $\beta$ is so small that the standard deviation of $\beta$ is very large. Based on the R factor ratio test, the standard deviation would be larger than 1 eV/Å$^3$. The same conclusions were drawn from the (h,h,h) data alone, which should be the most sensitive to $\beta$. Therefore, the cubic anharmonic term is not significant. It is probable that $\beta$ could have been found if there had been more weak reflections. The (6,6,6) was the only one used here.

The improvements in R when $\gamma$ was varied were significant. This could be interpreted as follows. The covalent part of the Cd-Te bond is directional, while the ionic and metallic components are basically nondirectional. The latter components are more significant in CdTe than in almost
Table 9. Harmonic OPP fits using pairs of (0,0,l) reflections (l=6, 8, 10, 12, 14, and 16) or pairs of (h,h,h) reflections (h=5, 6, 7, and 8), in the temperature range 70 ≤ T ≤ 360 K.

<table>
<thead>
<tr>
<th>h,k,l</th>
<th>$\alpha_{\text{Cd}}$ (eV/Å²)</th>
<th>$\alpha_{\text{Te}}$ (eV/Å²)</th>
<th>$R$</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1=6, 8</td>
<td>1.18±.04</td>
<td>1.57±.04</td>
<td>0.017</td>
<td>1.40</td>
</tr>
<tr>
<td>1=6,12</td>
<td>1.16±.04</td>
<td>1.54±.04</td>
<td>0.017</td>
<td>1.26</td>
</tr>
<tr>
<td>1=6,16</td>
<td>1.19±.04</td>
<td>1.58±.04</td>
<td>0.016</td>
<td>1.26</td>
</tr>
<tr>
<td>1=10, 8</td>
<td>1.18±.04</td>
<td>1.57±.04</td>
<td>0.032</td>
<td>1.11</td>
</tr>
<tr>
<td>1=10,12</td>
<td>1.16±.04</td>
<td>1.55±.04</td>
<td>0.043</td>
<td>0.95</td>
</tr>
<tr>
<td>1=10,16</td>
<td>1.19±.04</td>
<td>1.58±.04</td>
<td>0.036</td>
<td>0.91</td>
</tr>
<tr>
<td>1=14, 8</td>
<td>1.22±.04</td>
<td>1.53±.04</td>
<td>0.034</td>
<td>1.11</td>
</tr>
<tr>
<td>1=14,12</td>
<td>1.20±.04</td>
<td>1.51±.04</td>
<td>0.050</td>
<td>0.94</td>
</tr>
<tr>
<td>1=14,16</td>
<td>1.25±.04</td>
<td>1.55±.04</td>
<td>0.040</td>
<td>0.89</td>
</tr>
<tr>
<td>h=6,5</td>
<td>1.37±.04</td>
<td>1.59±.04</td>
<td>0.012</td>
<td>1.99</td>
</tr>
<tr>
<td>h=6,7</td>
<td>1.37±.04</td>
<td>1.58±.04</td>
<td>0.016</td>
<td>1.70</td>
</tr>
<tr>
<td>h=6,8</td>
<td>1.37±.04</td>
<td>1.58±.04</td>
<td>0.022</td>
<td>1.52</td>
</tr>
</tbody>
</table>
Fig. 35. A plot of the R factor as a function of the cubic anharmonic parameter $\beta_{Cd}$, with $\beta_{Te} = -\beta_{Cd}$. Although there is a definite minimum, the change in R is so small that the standard deviation of $\beta$ is greater than 1 eV/Å$^2$. 
all other compounds with the zincblende structure. The strength of the nondirectional part is reflected in the insignificance of the (highly directional) parameter \( \beta \), and the importance of the isotropic parameter \( \gamma \). The signs of the parameters \( \gamma_{\text{Cd}} \) and \( \gamma_{\text{Te}} \) are consistently negative, but their absolute values vary greatly. At best, these coefficients can be set at \( \gamma_{\text{Cd}}=0.8 \pm 0.5 \) eV/Å\(^4\) and \( \gamma_{\text{Te}}=-1.8 \) eV/Å\(^4\). The nonzero \( \gamma \)'s are accompanied by considerable increases in \( \sigma_{\text{Cd}} \) and \( \sigma_{\text{Te}} \). A negative \( \gamma \) corresponds to a "softening" of the potential well at large \( \langle u^2 \rangle \). Until more is done, especially at higher temperatures, these values should be viewed with caution, although they are probably qualitatively correct.

Allowing \( \delta \) to change also led to significant improvements in the R factor. The corresponding changes in the harmonic coefficients were not as drastic as when \( \gamma \) was varied. However the magnitudes of \( \delta_{\text{Cd}} \) and \( \delta_{\text{Te}} \) were quite large. Since the temperature factor was derived assuming they were small, the validity of the equation would be questionable. The signs of the coefficients are not consistent in the fits, casting more suspicion on the results for this parameter.

From the results of the fits using the harmonic models, the OPP, Debye, and Debye-Einstein models can be compared. The R factors for the three models were 0.00844, 0.00825, and 0.00827, respectively. The R factor ratio test shows that these do not represent statistically significant differences. Therefore, the models are equivalent between 130 K and 260 K.
This is not too surprising since this is a temperature range in which the CdTe vibrations are classical oscillators. All three models have the same temperature dependence (linear in $T$) in this limit. The agreement between the r.m.s. atomic displacements, shown in Fig. 33, is another indicator of the equivalence of the models. $<u_{Cd}^2>^{1/2}$ from the OPP model is consistently lower than from the Debye model by about $3\%$. This is still within one standard deviation, however. Aside from that, the lines calculated from the Debye and OPP models are the same for $T>\Theta_M$. At the low temperature end of the curves ($T=\Theta_M/2$) there is some disagreement. This is because the OPP model is valid only in the classical limit; the model ignores zero-point motion. At 70 K, the deviation amounts to about $5\%$, in agreement with the theoretical conclusions of Mair and Wilkins\textsuperscript{135} who used quantum statistics to extend the OPP result to lower temperatures.

The Debye-Einstein model is the most physically realistic of the three because it simulates the phonon dispersion curves (albeit rather crudely). The measured dispersion curves, Fig. 32, show that the optic modes are well occupied at room temperature ($\nu=6.25$ THz). In practice, however, the Debye-Einstein model reveals little that cannot be learned from the Debye model alone. Because the Debye and Einstein parts of equation 55 have the same temperature dependence, $\Theta_M$ and $\Theta_E$ cannot both be extracted from the data. The Einstein temperature must be found by other means. As explained above, $\Theta_M$ in this model is not the same as $\Theta_M$ in the Debye
model, or \( \Theta_D \) from the specific heat. A Debye-Einstein model has been used occasionally with specific heat measurements,\(^{136}\) but this is the first known application to x-ray diffraction. In this regard, there are very few specific heat measurements with which to compare the x-ray results. The Debye theory, on the other hand, is commonly used in both fields, allowing comparison in many cases.

It is apparent that fitting harmonic models to temperature dependent data could be done readily. The extension to anharmonic models did not work as well with this type of data. Anharmonic effects were subtle and difficult to identify. They could be seen easier at higher temperatures. The temperature dependence of the anharmonic terms was different than that of the harmonic terms, but the correlations between the coefficients during the fitting was large. Therefore the parameters could not be found accurately. The best remedy would be to measure a larger number of reflections, to compensate for the increased number of variable parameters in the fit.

The dashed curve in Fig. 32 is the r.m.s. displacement calculated using a modified rigid ion model of the lattice dynamics of CdTe.\(^{137}\) The Cd and Te atoms have the same displacement in this model. The calculation is 12% lower than the experimental result for Te and 24% too low for Cd. Apparently, this model does not give a very good fit to the neutron scattering data either.\(^{12}\) Similar calculations are not available using the rigid ion model, which does fit the
neutron data.

It has been shown that the potential well of the Cd atom is broader than that for Te. In this regard, it would be interesting to do similar studies, or accurate single crystal studies on the isoelectronic series αSn-InSb-CdTe-γAgI. All these materials have the same structure, and the "fractional ionicity" of the bond increases along the series. Obviously, the potential wells are the same for all Sn atoms. As one goes along the isoelectronic series, the potential well of the cation broadens to the extent that the metastable γ phase of AgI undergoes a superionic transition at elevated temperatures;\textsuperscript{138} the iodine atoms rearrange into a bcc lattice while the Ag sublattice "melts" and the atoms are free to move about. Due to the many similarities, the isoelectronic series Ge-GaAs-ZnSe-CuBr would also present an interesting comparison. All these compounds have the zincblende structure, and CuBr also has superionic transition.
V. THE EXPERIMENTS: EPILAYERS

A. (0,0,1) CdTe on (0,0,1) GaAs: Sample #1

The first composite system studied was a 3 μm thick, (0,0,1) oriented CdTe epilayer on a (0,0,1) GaAs substrate. It was grown by J. L. Schmit. The substrate was cut from a commercially obtained wafer from Cominco Materials, Inc. It was prepared prior to deposition using standard polishing techniques, and then loaded directly into an MOCVD system for growth of the CdTe layer. The epilayer was grown in a horizontal laminar flow reaction chamber at a temperature of 410°C. After the growth, Auger spectroscopy on a cross section of the material revealed an extremely sharp interface between the substrate and the epilayer.

Measurements of this system were made three times, using two different X-ray wavelengths: \( \lambda = 1.28181 \text{ Å (W } L_\beta_1) \) and \( \lambda = 1.6782 \text{ Å (W } L_1) \). The first two measurements were made with the sample glued onto a beryllium plate with Duco cement. The beryllium plate was mounted on the cold finger of the refrigerator. It was suspected that the anomalies in the results below may have been caused by this method of mounting the crystal. Therefore a third measurement was done with the sample mounted directly in the copper clamp described earlier. Similar results were obtained on all three occasions, indicating no significant hysteresis. No change in the FWHMs of the Bragg peaks were observed to
within two minutes of arc, the equatorial angular resolution of the beam. Typical FWHMs were $0.14^\circ$ for the GaAs $(0,0,4)$ reflection and $0.18^\circ$ for the CdTe $(0,0,4)$. Unfortunately, the sample was destroyed after the third measurement during other tests.

Because of the stress present at the interface, both the epilayer and the near-surface region of the substrate were expected to deform tetragonally. The lattice parameters perpendicular to the surface, $a_\perp$, were obtained by measurements on the $(0,0,1)$ Bragg reflections, which had scattering vectors perpendicular to the surface. Since these were the only reflections measured on this system, the lattice parameters in the surface plane, $a_\parallel$, were not known. Fig. 36 is a graph of the measured lattice parameters as a function of temperature. The single crystal results are reproduced on the plot for comparison. Above about 200 K, the substrate and epilayer lattice parameters are the same as the bulk values. Below 200 K, however, there is an enormous deviation: the region of negative thermal expansion in the bulk crystals has undergone considerable enhancement. The overall variation in the lattice parameters between 10 K and 200 K was 0.012 Å and 0.024 Å for the substrate and epilayer, respectively. This is compared to 0.003 Å for bulk GaAs and 0.002 Å for bulk CdTe in the same temperature range.

The thermal expansion coefficient of GaAs is slightly larger than the thermal expansion coefficient of CdTe above
Fig. 36. The GaAs substrate and CdTe epilayer lattice parameters, from sample #1, as a function of temperature. The solid lines are the corresponding single crystal lattice parameters.
room temperature. As the sample is cooled to room temperature after growth, the GaAs lattice parameter will shrink more than \( a_{\text{CdTe}} \). Therefore, one would expect the substrate to compress the CdTe lattice parameter in the surface. This would be accompanied by a corresponding increase in \( a_{\perp} \) in the epilayer. The exact opposite would be anticipated for the GaAs lattice parameters: \( a_{\perp} \) should decrease and \( a_{\parallel} \) should be extended. The measured GaAs lattice parameter does have the behavior expected for the substrate. The lattice parameter of the epilayer, however, is the reverse of what is expected. It is conceivable to go a step further and try to quantitatively understand the measured behaviors. If the stress is small enough, the unit cell volume can be assumed to be conserved; in other words, the unit cell volumes of the substrate and epilayer are the same as the volumes in the bulk materials. Therefore

\[
V = a_{\text{bulk}}^3 = a_{\parallel} a_{\perp}^2.
\]

The thermal expansion coefficient, \( \alpha \), obeys the relation

\[
3 \alpha_{\text{bulk}} = \frac{1}{V} \left( \frac{dV}{dT} \right)_P = \frac{2}{a_{\parallel}} \left( \frac{da_{\parallel}}{dT} \right)_P + \frac{1}{a_{\parallel}} \left( \frac{da_{\perp}}{dT} \right)_P = 2 \alpha_{\parallel} + \alpha_{\perp}.
\]

Fig. 37 shows the ratio \( a_{\parallel}/a_{\perp} \) deduced from the assumption that the unit cell volumes are conserved. This ratio is larger than one for both materials. Fig. 38 shows the thermal expansion coefficients extracted from the lattice
Fig. 37. Ratio of the parallel to the perpendicular lattice parameters, assuming the unit cell volume is conserved.

Fig. 38. Thermal expansion coefficients for sample #1, assuming that the unit cell volume is conserved.
parameters. The thermal expansion coefficients of the substrate and epilayer are more than an order of magnitude larger than they are in the bulk materials. Given the large strain present in $a_\perp$, the assumptions made above are questionable. Measurements of the lattice parameters parallel to the surface are needed to resolve this problem.

The penetration depth, $D$, can be estimated from equation 28. Table 10 shows the results for GaAs and CdTe reflections. For each reflection, the "best value" of $D$ is the smaller of the two limits, $D_\xi$ and $D_\mu$. The measured lattice parameters are averages of the lattice parameters over a depth equal to the average $D$. Since the $(0,0,4)$, $(0,0,6)$, and $(0,0,8)$ reflections were used to find the lattice parameter, the average penetration depth was $\approx 13 \, \mu m$ for GaAs, and $\approx 3.4 \, \mu m$ for CdTe. The measured lattice parameter for the CdTe epilayer is therefore an average over the entire layer, and the GaAs lattice parameter is an average over the top 13 $\mu m$ of the substrate.

The Borrmann effect was not looked for in this sample. The measured FWHM of the $(0,0,4)$ GaAs reflection was more than twice as large as the FWHM from a single crystal sample. Therefore it is suspected that no Borrmann transmitted peak would have been seen. Also, the severe strain below 200 K would have destroyed the effect at low temperatures.

Fig. 39 shows the measured $(0,0,4)$ structure factor for the GaAs substrate. Data taken with the fundamental wavelength of $\lambda=1.6782 \, \text{Å}$, and with the second harmonic,
Table 10. Upper and lower limits on the penetration depth in GaAs and CdTe. \( D_\xi \) is calculated assuming negligible absorption in a perfect crystal. \( D_\mu \) is the penetration depth due to ordinary absorption.

<table>
<thead>
<tr>
<th>( h,k,l )</th>
<th>( D_\xi (\mu m) )</th>
<th>( D_\mu (\mu m) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GaAs</td>
<td>CdTe</td>
</tr>
<tr>
<td></td>
<td>( \lambda=0.7093 , \text{Å} )</td>
<td>( \lambda=1.28181 , \text{Å} )</td>
</tr>
<tr>
<td>0,0,2</td>
<td>26.</td>
<td>16.</td>
</tr>
<tr>
<td>0,0,4</td>
<td>1.3</td>
<td>2.8</td>
</tr>
<tr>
<td>0,0,6</td>
<td>210.</td>
<td>160.</td>
</tr>
<tr>
<td>0,0,8</td>
<td>25.</td>
<td>18.</td>
</tr>
<tr>
<td>0,0,10</td>
<td>850.</td>
<td>1000.</td>
</tr>
<tr>
<td>0,0,12</td>
<td>89.</td>
<td>55.</td>
</tr>
<tr>
<td>1,1,1</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>2,2,2</td>
<td>52.</td>
<td>87.</td>
</tr>
<tr>
<td>3,3,3</td>
<td>7.5</td>
<td>9.9</td>
</tr>
<tr>
<td>4,4,4</td>
<td>16.</td>
<td>12.</td>
</tr>
<tr>
<td>5,5,5</td>
<td>46.</td>
<td>31.</td>
</tr>
</tbody>
</table>
Fig. 39. The (0,0,4) structure factors for the GaAs substrate, using the fundamental and second harmonic wavelengths. \( I_{hkl} \) is the ratio of the structure factor at temperature \( T \) to the maximum value.

Fig. 40. The (0,0,4) structure factors for the CdTe epilayer using the fundamental and second harmonic wavelengths.
\( \lambda = 0.8391 \, \text{Å} \), are both shown. Least squares fits found Debye temperatures of \( \Theta_M = 222 \pm 4 \, \text{K} \) and \( \Theta_M = 269 \pm 7 \, \text{K} \) for the fundamental and harmonic data, respectively. Despite the fact that extinction was expected to be a problem with this reflection, these results are within the experimental uncertainty of the measurements made on the single crystal of GaAs. Both numbers are about 10\% different than the more accurate result of Arnold and Nereson\textsuperscript{113} on bulk GaAs: \( \Theta_M = 247 \, \text{K} \).

Fig. 40 is an analogous plot of the \((0,0,4)\) structure factor of the CdTe epilayer. These data yield \( \Theta_M = 144 \pm 5 \, \text{K} \) using \( \lambda = 1.6782 \, \text{Å} \), and \( \Theta_N = 134 \pm 6 \, \text{K} \) from the harmonic wavelength. Again, extinction would be expected to be a problem here, but the Debye temperatures agree with the Debye temperature of bulk CdTe to within the experimental error.

More trustworthy values can be obtained from the \((0,0,8)\) reflections of the second harmonic wavelength, \( \lambda = 0.8391 \, \text{Å} \), shown in Fig. 41. These data yield a CdTe Debye temperature of \( \Theta_M = 145 \pm 5 \, \text{K} \), which is within the experimental error of the bulk CdTe value. If the GaAs substrate is treated as a perfect crystal, the Debye temperature is \( \Theta_M = 250 \pm 20 \, \text{K} \), again, the same as in the bulk. If the substrate is analyzed as a mosaic crystal, however, then \( \Theta_M = 350 \pm 25 \, \text{K} \). It is probable that above \( \sim 150 \, \text{K} \), the substrate diffracts nearly as a perfect crystal.

This sample was the first to be studied using the refrigerator. Therefore, a number of obstacles were encountered in the analysis. The wavelengths used in the
Fig. 41. (0,0,8) structure factors collected with the second harmonic wavelength.
integrated intensity measurements were large. Therefore, the effect of extinction in most of the reflections could not be adequately assessed. Without this knowledge, the interpretation of the (0,0,4) Debye temperatures is unclear. The state of perfection of the GaAs substrate was also not known, so the GaAs Debye temperature was in question for this reason as well. The (0,0,8) Debye temperatures yield more easily to interpretation. They are both the same as those of the bulk crystals, provided the GaAs substrate is a perfect enough crystal to be diffracting dynamically. Thus the overall vibration spectra of the two materials has not been altered considerably. The one sure result is the anomalous behavior of the lattice parameter perpendicular to the surface. At the present time, no mechanism has been found to explain the large dips, especially in the CdTe epilayer. Since the lattice parameters were not measured parallel to the surface, an explanation cannot be given with certainty. It is clear that this system cannot be viewed simply as two crystals "glued" together, more-or-less conserving their respective physical properties.

B. (0,0,1) CdTe on (0,0,1) GaAs: Sample #2

Epilayer #2 was grown by MOCVD in a vertical flow chamber on a (0,0,1) GaAs substrate at a temperature of 380°C. The substrate was cut 2° off the [0,0,1] direction toward the [1,1,0]. The final thickness of the epilayer was 2.8 μm. Initial characterization was done by
photoluminescence, double-crystal x-ray diffraction, and x-ray precession photography. Fig. 42 is a precession photograph of this sample. The precession axis for this photograph was the \([\bar{1},1,0]\) axis of the GaAs substrate. Indexing (Fig. 43) reveals the orientation of epilayer to substrate to be \((0,0,1) \parallel (0,0,1)\), with \([1,0,0] \parallel [1,0,0]\) in the plane.

Using an x-ray wavelength of 0.7093 Å (Mo Ka) the \((0,0,1)\) and \((h,h,h)\) Bragg reflections were measured between 10 K and 360 K. The short wavelength was chosen to lessen the effects of extinction, and to make more reflections available. The \((h,h,h)\) reflections, which were off of the growth axis, were measured to determine the lattice parameter in the surface plane. \(\phi\), \(\chi\), and \(\omega-2\theta\) scans were done on the \((0,0,8)\) and \((5,5,5)\) reflections at each temperature for centering and orientation. The optimum \(\phi\) and \(\chi\) for the substrate and epilayer were slightly different, indicating that the orientation of the CdTe was 0.10\(\pm\)0.02° from the orientation of the substrate. The \((0,0,4)\) reflections had FWHMs of 0.07° and 0.20° for the substrate and epilayer, respectively. This epilayer FWHM was about the same as that of sample #1, but the substrate FWHM was half of the substrate FWHM in sample #1. This shows that the substrate in sample #2 was under less stress. The FWHMs did not change with temperature.

Figure 44 shows the lattice parameters of the substrate and epilayer as a function of temperature. \(a_\perp\) was obtained
Fig. 42. A precession photograph of sample #2. The reflections are always paired, meaning the substrate and epilayer have the same orientation. The inner spot of each pair is a CdTe reflection and the outer spot is due to GaAs.
Fig. 43. A diagram of the precession photograph in Fig. 42, with the crystallographic indices labelled. Open circles correspond to GaAs reflections and solid dots represent CdTe reflections.
Fig. 44. Lattice parameters as a function of temperature for sample #2
from the $(0,0,1)$ reflections. $a_m$ was found using $a_\perp$ and the measured angles of the $(h,h,h)$ reflections. For comparison, the lattice parameters of bulk GaAs and CdTe are shown as solid lines. It is immediately seen that there was little or no tetragonal distortion of the GaAs lattice above 100 K. Below 100 K, the unit cell was strained such that $a_\perp < a_m$.

This is consistent with the earlier expectations since the GaAs lattice parameter in the plane of the surface is being stretched by the larger CdTe lattice. It is also seen from Fig. 44 that there was a tetragonal distortion in the CdTe epilayer, with $a_\perp < a_m$ over most of the temperature range. This is again what one would predict as the result of stress exerted by the smaller GaAs unit cell. The average ratio was $a_\perp/a_m = 1.0012$, about four times smaller than the corresponding value in the anomalous region of sample #1.

Above room temperature, both lattice parameters were larger than the bulk lattice parameter. This has been seen in many samples from the same source. The volume ratio was $V_{\text{epilayer}}/V_{\text{bulk}} = 0.9998 \pm 0.0004$ throughout the rest of the temperature range studied. It therefore can be concluded that the volume was conserved to within the standard deviation. The lattice parameters were found using the $(0,0,6)$, $(0,0,8)$, $(0,0,10)$, and $(0,0,12)$ reflections, and represent the average lattice parameter in a depth of 8.9 $\mu$m of GaAs (using equation 28 and Table 10). In the epilayer, $D = 12 \mu$m is larger than the 2.8 $\mu$m epilayer thickness, so the CdTe lattice parameters are averages over the entire layer.
The Borrmann effect was observed at room temperature in the GaAs substrate. Since this can only be explained by the dynamical theory of diffraction, the substrate cannot be significantly different from the original GaAs wafer. No attempts were made to see the Borrmann effect at lower temperatures, but the substrate was treated as if it was a perfect crystal at all temperatures. It is likely that the anomalous transmission would have been destroyed by strain below about 100 K.

Figures 45 and 46 show the GaAs structure factors, in the form $\ln|F_{hkl}|^2$, as a function of temperature. The TDS correction was not done. Table 11 summarizes the results of the least squares fits. The GaAs (0,0,8) and (0,0,12) Debye temperatures are in fair agreement with the bulk GaAs value of 247 K. The (0,0,8) Debye temperature is probably high due to primary extinction.

Individual thermal parameters were extracted using the (0,0,6), (0,0,8), (0,0,10), and (0,0,12) structure factors. The GaAs reflections, in the temperature range $T > 120$ K, yielded $\theta_{M-Ga}=219 \pm 5$ K and $\theta_{M-As}=254 \pm 5$ K, or $\alpha_{Ga}=2.20 \pm 0.04$ eV/Å$^2$ and $\alpha_{As}=3.20 \pm 0.04$ eV/Å$^2$. Corresponding values from bulk GaAs were measured by Bilderback: $\alpha_{Ga}=2.80$ eV/Å$^2$ and $\alpha_{As}=3.35$ eV/Å$^2$. The parameters for both atoms in the substrate of sample #2 are lower than in bulk GaAs. Since the measured values may be a bit high due to extinction in the (0,0,8) reflection, the (0,0,8) reflection was discarded. The fitted parameters then became
Fig. 45. Measured structure factors for the (0,0,1) reflections of the GaAs substrate
Fig. 46. Measured structure factors for the \((h,h,h)\) reflections of the GaAs substrate
Table 11. Debye temperatures for the strong and moderate reflections of the GaAs substrate and the CdTe epilayer in sample #2

<table>
<thead>
<tr>
<th>h,k,l</th>
<th>$\theta_N$ (K)</th>
<th>$\alpha$ (eV/Å$^2$)</th>
<th>Temperature Range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0,0,8</td>
<td>280±5</td>
<td>3.28±0.03</td>
<td>100-360</td>
</tr>
<tr>
<td>0,0,12</td>
<td>232±5</td>
<td>2.39±0.03</td>
<td>100-360</td>
</tr>
<tr>
<td>3,3,3</td>
<td>251±5</td>
<td>5.19±0.03</td>
<td>150-360</td>
</tr>
<tr>
<td>4,4,4</td>
<td>189±4</td>
<td>1.53±0.03</td>
<td>100-360</td>
</tr>
<tr>
<td>5,5,5</td>
<td>182±4</td>
<td>1.21±0.03</td>
<td>100-360</td>
</tr>
<tr>
<td>CdTe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0,0,4</td>
<td>200±6</td>
<td>2.87±0.05</td>
<td>120-360</td>
</tr>
<tr>
<td>0,0,8</td>
<td>142±3</td>
<td>1.46±0.03</td>
<td>75-360</td>
</tr>
<tr>
<td>0,0,12</td>
<td>142±4</td>
<td>1.44±0.03</td>
<td>100-360</td>
</tr>
<tr>
<td>3,3,3</td>
<td>169±6</td>
<td>1.77±0.06</td>
<td>150-360</td>
</tr>
<tr>
<td>4,4,4</td>
<td>123±5</td>
<td>1.10±0.05</td>
<td>75-360</td>
</tr>
<tr>
<td>5,5,5</td>
<td>103±4</td>
<td>0.75±0.04</td>
<td>75-360</td>
</tr>
</tbody>
</table>
\[ \Theta_{\text{M-Ga}} = 213 \pm 5 \text{ K} \] and \[ \Theta_{\text{M-As}} = 250 \pm 5 \text{ K} \], which are not significantly different.

The \((0,0,1)\) and \((h,h,h)\) structure factors for the CdTe epilayer are shown in Fig. 47 and Fig. 48. The TDS correction was not applied since it was not known how the elastic constants might be affected by strain. Table 11 also lists the results of these fits. The \((0,0,4)\) structure factor was clearly affected by secondary extinction. For comparison, the Debye temperature of bulk CdTe was 141 K when the TDS correction had been done, and 144 K without the correction. Thus the \((0,0,8)\) and \((0,0,12)\) have Debye temperatures which are the same as in the bulks. The thermal parameters of the individual atoms, taken from the \((0,0,6)\), \((0,0,8)\), \((0,0,10)\), and \((0,0,12)\), were \(\Theta_{\text{M-Cd}} = 130 \pm 5 \text{ K} \) and \(\Theta_{\text{M-Te}} = 150 \pm 5 \text{ K} \), or \(\alpha_{\text{Cd}} = 1.14 \pm 0.04 \text{ eV/Å}^2 \) and \(\alpha_{\text{Te}} = 1.72 \text{ eV/Å}^2 \). The corresponding bulk values were 134 K and 146 K \((1.24 \text{ eV/Å}^2 \) and \(1.63 \text{ eV/Å}^2 \)) for Cd and Te, respectively. Thus the epilayer result is about 8% lower than the bulk for Cd and about 6% higher for Te.

Table 11 further shows the results of fits to the \((h,h,h)\) reflections. These planes are not parallel to the surface of the crystal or the CdTe/GaAs interface. Only an average Debye temperature (or \(\alpha\)) could be found for this direction, because no high order weak reflections could be measured; the \((6,6,6)\) was at too high of an angle. The results are anomalously low for both the substrate and the epilayer. The decrease of \(\Theta_{\text{M}}\) and \(\alpha\) with increasing \((h,k,l)\) is
Fig. 47. Measured structure factors for the (0,0,1) reflections of the CdTe epilayer
Fig. 48. Measured structure factors for the (h,h,h) reflections of the CdTe epilayer.
characteristic of extinction, but even the highest values are lower than the corresponding results from the bulk materials.

An interesting observation can be made on the GaAs reflections. It seems reasonable that extinction is nearly absent from the (4,4,4) and (5,5,5) data, so analysis of these reflections should give meaningful results. If these data are analyzed as a mosaic crystal, the Debye temperatures become 267 K and 257 K, respectively. These numbers are very close to the results using the (0,0,1) reflections. This suggests that the type of defect present in the near surface region of the substrate is such that perfect crystal behavior still exists parallel to the surface, but is destroyed in other directions. In other words, the (0,0,1) planes are highly parallel and evenly spaced, while a slight mosaic spread can be found along other axes. The lattice parameters and the Borrmann effect are evidence that the substrate is in nearly the same condition as when it was cut from the wafer. Therefore it is highly unlikely that the thermal properties could be so different in the [0,0,1] and [1,1,1] directions. In fact, since the GaAs remained cubic, there should be no difference at all between these directions. The explanation above is therefore more plausible. This could be checked by making the same type of measurement on a GaAs single crystal (which had, perhaps, undergone the same heat treatment), to see if the (0,0,1) and (h,h,h) reflections showed similar features. If they do, then the explanation is probably correct for the GaAs substrate. A second test would be the
use of grazing incidence diffraction$^6$ to try to directly measure a mosaic spread in the surface plane.

Since the CdTe was already mosaic, the explanation above will not work for the epilayer. Secondary extinction was apparently present in the (3,3,3) and (4,4,4) reflections, as was the case in bulk CdTe (this is because the extinction penetration depth, $D_x$, is comparable to the absorption penetration depth, $D_\mu$, as can be seen in Table 10). However, the (5,5,5) is free from those effects. It is reasonable to assume that the vibrational properties have been altered by the tetragonal distortion. Since the total unit cell volume was conserved, however, it would be surprising if the effect was that large. In analogy with the substrate, it is most likely that there is some temperature dependent effect which is destroying the coherence of the (h,h,h) planes. A probable candidate would be a small static displacement of the atoms from their crystallographic positions. At higher temperatures, this displacement is large enough to cause a change in the unit cell volume as observed. Cowley$^{140}$ has shown that static displacements cause a decrease in the intensities of Bragg reflections. This decrease has the same form as the Debye-Waller factor. The static Debye-Waller factor is independent of temperature provided that the static displacement is temperature independent. This is typically the case in the event of static displacements caused by relaxation around impurities. However, a temperature dependent displacement due to an overall stress field is not
unlikely. According to Cowley, the effect of both the static and dynamic displacements is to modify the form factors as

\[ f_j(q) = f_j(q) \exp\left\langle -\frac{H^2 u_j^2}{2} \right\rangle \exp\left\langle -\frac{H^2 \Delta^2}{2} \right\rangle, \tag{74} \]

where \( \Delta \) is the static displacement and \( \Delta_H \) is the projection of \( \Delta \) on \( H \). The average in the second exponent is not an average over time, as in the first exponent, but over all atoms in the crystal. If \( \Delta \) has a temperature dependence of the form \( \Delta_H = \Delta_0 + \delta T \), then \( \Delta^2_H = \Delta_0^2 + 2 \delta \Delta_0 T \). The decay of the strong and moderate Bragg reflections would therefore be larger than the decay due to the normal Debye-Waller effect. In the classical temperature range, the slope \( \frac{d(\ln|F|^2)}{dT} \) becomes

\[ \frac{d(\ln|F|^2)}{dT} = -\left( \frac{12h^2}{mk_B \Theta_M^2} + 32\pi^2 \Delta_0 \delta \right) \frac{\sin^2 \theta}{\lambda^2} \tag{75} \]

If the Debye temperature from the \((0,0,1)\) reflections, \( \Theta_D = 142 \text{ K} \), is used, we find the product \( \Delta_0 \delta = 2.71 \times 10^{-5} \text{Å}^2/\text{K} \). Fig. 49 is a graph of \( \delta \) versus \( \Delta_0 \). The magnitude of the effect says that \( \Delta_0 \) should be observable in a careful determination of the crystal structure of the epilayer. A similar study well above room temperature would also be valuable. This result represents a static displacement along the \([1,1,1]\) direction. Apparently there is no displacement in the \([0,0,1]\) direction.
Fig. 49. A graph of $\delta$ versus $\Delta_o$. If $\delta \ll \Delta_o$, as would seem reasonable, then $\Delta_o$ could be greater than 0.01 Å.
C. (1,1,1) CdTe on (1,1,1) GaAs

The (1,1,1) CdTe on (1,1,1) GaAs epilayer was obtained from the same source as the (0,0,1) epilayers, and was grown under the same conditions as sample #1: the substrate temperature during deposition was 410° C, and the MOCVD reactor was a horizontal flow chamber. The final epilayer thickness was 2.85 μm.

Fig. 50a is a precession photograph of this system taken with the GaAs [1,1,2] being the precession axis. Fig. 50b shows the same sample rotated 90°, with the GaAs [1,1,0] as the precession axis. The indices of a standard (1,1,1) crystal with the orientation of Fig. 50a are shown in Fig. 51. Spots on the photograph always occur in pairs, the inner spot coming from the CdTe epilayer and the outer one from the substrate. The substrate and epilayer have the same orientation. Fig. 52 shows a similar diagram of the indices of Fig. 50b. This photograph shows twinning as described earlier. One set of reflections corresponds to the GaAs substrate, and there are two CdTe patterns. One of the CdTe diffraction patterns has the same form as the GaAs pattern, and the other is the mirror image of the first.

The Borrmann effect was seen in the GaAs substrate at room temperature. No attempts to see this effect were made at lower temperatures.

The measurements on this sample were cut short because a bearing in the refrigerator was ruined. Data were collected at room temperature, and between 10 K and 125 K. This is too
Fig. 50a. Precession photograph of the (1,1,1) CdTe epilayer on (1,1,1) GaAs. No twinning can be seen in this orientation. Spots are always paired, with the inner spot from the epilayer and the outer spot from the substrate.

Fig. 50b. Precession photograph of the same system rotated 90° from the above orientation. Twinning of the CdTe epilayer can be seen in this photograph.
Fig. 51. A diagram showing the indices of the precession photograph in Fig. 50a
Fig. 52. A diagram showing the indices for a precession photograph with the orientation of Fig. 50b.
small of a temperature range to extract useful information from the intensities.

The widths of the CdTe peaks were so large that lattice parameters for the epilayer could not be measured to better than 0.001 Å. The GaAs lattice parameters were measured in the [1,1,1] and [0,0,1] directions. These are shown in Fig. 53 along with the corresponding single crystal lattice parameter. a\textsubscript{111} is the lattice parameter perpendicular to the surface. a\textsubscript{001} is not the same as a\textsubscript{m}, however. The lattice parameter parallel to the surface will be slightly smaller than a\textsubscript{001}. There is a distortion such that both the parallel and perpendicular lattice parameters are smaller than the bulk value. This system apparently has some anomalies similar to, but smaller than those seen in sample #1. Clearly, the measurements must be continued on this sample.
Fig. 53. Lattice parameters from the (h,h,h) and (0,0,1) reflections of the (1,1,1) oriented GaAs substrate. The corresponding single crystal lattice parameter is shown as a solid line.
VI. CONCLUSIONS

It has been demonstrated that measuring Bragg reflections as a function of temperature is a valid way to study single crystals and epitaxial systems. Compared to the alternative method, measuring many reflections at a single temperature, there are several advantages and several disadvantages. Among the advantages are the following: i. some of the behavior seen above could not have been observed at a single temperature; ii. since the slope of $|F|^2$ is the quantity of interest, there is no need to normalize to the incident beam intensity, or to make the correction for absorption (which is difficult on reflections not perpendicular to the surface); iii. the data can be compared to various physical models of lattice dynamics; and iv. deviations from these physical models (e.g., at low or high temperatures) can be detected. The difficulty of doing a single temperature measurement on a composite system is compounded by the unusual behavior seen in sample #2, especially if the substrate is a "perfect" crystal. Therefore, comparison of temperature dependent measurements between composite systems and bulk crystals is easier, and provides additional insight. On the other hand, it was difficult to get accurate anharmonic parameters from the data. Measurements at a single temperature have had more success in extracting those parameters. The results of the two methods using harmonic models are identical.
A comparison of the Debye, Debye-Einstein, and OPP models was made using the CdTe data. In the classical temperature regime, all three models were identical, as expected. Below the Debye temperature, the Debye and OPP models were seen to diverge, because the OPP model is purely classical. The Debye-Einstein model is a physically better model, but its use is limited by the inability to extract both $\Theta_M$ and $\Theta_E$ from the data at the same time. The Debye and Einstein parts of the Debye-Waller factor have the same temperature dependence in the classical limit. At low temperatures, these two models should also diverge. However, since the optic modes do not contribute significantly to the atomic mean square displacements at low temperatures, the difference would not be very large.

A variety of novel effects were seen in the composite systems. Continued work is needed to verify the hypothesis of a static displacements in the CdTe epilayer. If this is found to be true, it could have a significant effect on the understanding of the large strain seen in sample #1. The most significant difference between the two (0,0,1)||(0,0,1) epilayers was in the growth temperature. There was a great deal more strain in the sample deposited at the higher temperature (#1). This means that the density of defects at the interface is small in sample #1 and large in sample #2. The large defect density reduces the interaction between the substrate and epilayer, reducing the strain. For the success of the future applications of this composite substrate, the
low strain sample is probably better suited for making good quality devices, especially if the device is operated at low temperatures.

Finally, although it is not related to the temperature dependent effects, the method of precession photography has been shown to be an excellent technique for characterizing epitaxial, and other thin film systems. The fact that precession photography gives an undistorted view of reciprocal space is a tremendous advantage in interpreting unusual structure.
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