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A Mössbauer effect study of the crystal field potential in intermetallic compounds of thulium

Dennis Joseph Genin
Iowa State University

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A MÖSSBAUER EFFECT STUDY OF THE CRYSTAL FIELD POTENTIAL IN INTERMETALLIC COMPOUNDS OF THULIUM

by

Dennis Joseph Genin

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of

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I. INTRODUCTION

A. Background

Atoms of the various transition series are characterized by having incompletely filled inner electron shells. For a given atom, the electrons within the unfilled shell can exist in a variety of energy states corresponding to different relative arrangements of their orbital and spin angular momenta. Most of these atoms are ionized when they enter a solid and the electronic energy states are shifted and split by interactions of the electrons with the electrostatic crystal field setup by the surrounding ions. The extent to which this crystal field interaction shifts the energy levels of the ion is dependent upon the relative magnitude of this external interaction compared with those interactions which are internal to the ion.

The magnitude of the crystal field interaction varies considerably from one series of ions to another. For the 3d-transition metals the splittings produced by the crystal field typically amount to tens of thousands of wave numbers. Since this interaction is large relative to certain of the interactions in the free ion, it cannot be introduced as a perturbation on the free ion states. Instead, the problem is usually solved using the strong field approximation with the internal spin-orbit interaction then being introduced as a perturbation. On the other hand, for the rare-earth ions,
with the well-shielded, partially filled 4f-shell, the crystal
field splittings are small, being at most on the order of
hundreds of wave numbers. Hence the crystal field interaction
can be introduced as a perturbation of the free ion problem.
Since the crystal field interaction modifies electronic orbits,
it has an important influence on magnetic properties. In
solids, forces are present which directly couple the 4f-
electrons of different ions. These may take various forms but
the most important are of the exchange type, giving rise to
cooperative magnetic properties.

The 4f-electrons are responsible for the magnetic prop-
erties of the rare-earth ions. The Coulomb interaction be-
tween f-electrons is stronger than the spin-orbit interaction,
corresponding to the case of fairly good Russell-Saunders
coupling. It splits the configuration up into terms, each
characterized by L and S, the total orbital and total spin
angular momentum, respectively. The vectors of these quanti-
ties are coupled by the spin-orbit interaction to give levels
of different J, the total angular momentum. These levels are
often separated by energies of several thousand wave numbers,
and each J level possesses a \(2J + 1\)-fold degeneracy. The
crystal field, either partially or completely, removes this
degeneracy, depending on its symmetry: if the configuration
of the 4f-shell consists of an odd number of electrons, then
a residual two-fold degeneracy in the energy levels can never be removed by the crystal field.

B. Ionic Energy Levels

Calculations of energy levels of rare-earth ions in crystals are complex due to the large number of interactions involved as well as to inadequate knowledge of the electronic wave functions. The usual assumptions which are made in calculating the crystal field effects are: a) the surrounding lattice consists of point charges situated at the lattice sites and b) there is no overlap between the charge distributions of different ions. This latter assumption is certainly a better approximation to make for rare-earth series ions than for iron series ions. In this model, the crystal field Hamiltonian is written as an expansion in terms of Legendre polynomials and crystal field parameters. These parameters are used to characterize the crystal field potential at the ion site.

The energy levels of an ion in a solid may be investigated using any of several techniques. Two of the more important of these are optical absorption spectroscopy and electron paramagnetic resonance (epr).

Optical absorption spectroscopy is a technique which can only be applied to salts and other transparent materials and hence is not applicable to a study of metals. The rare-earth optical spectra are composed of closely spaced groups of sharp
lines. Each group corresponds to a particular J. The splittings within the groups are crystal field splittings. A major task in this type of experiment is the delineation of the energy level scheme from these data which, of course, are the result of transitions between levels. Optical spectroscopy is the most widely used method of studying ionic energy levels.

Electron paramagnetic resonance is more precise but its applications are limited. For nondilute materials, it can only be applied at low temperatures where $T_1$, the spin-lattice relaxation time, is long compared to $1/\nu$, where $\nu$ is the Larmor precession frequency. At these low temperatures, only the lowest ionic energy level is populated and either a Kramers degeneracy or an accidental degeneracy of this level is required in order to observe the resonance. This degeneracy is removed by the application of an external magnetic field and transitions between these levels are then observed. Single crystals are normally used and the two measured quantities are $g_\parallel$ and $g_\perp$, the electronic g-factor with the principal crystal axis parallel to and perpendicular to the external magnetic field direction, respectively. In cases of low crystal symmetry, these two quantities are not sufficient to determine all of the necessary crystal field parameters.
C. Observation of Crystal Field Effects

Crystal field effects in the rare-earths have been studied mainly by anisotropy of the magnetic susceptibility in single crystals. This anisotropy arises as follows. In a free ion the motion of the electrons in their orbits sets up a magnetic field which interacts with the spin moments, and an external magnetic field orients both the spins and the orbits. In the crystal field the orbits may be greatly distorted and the associated magnetic field, which is proportional to the resultant orbital moment, will have directional properties determined by the crystal field. It may thus happen that the orbital moment is much reduced and also will not be oriented so readily by an external magnetic field. The spin moment sets itself along the resultant of the two fields and anisotropy results. When the orbital moment is very small, the internal field is small, and spin-only paramagnetism results, with small anisotropy. When the orbital motion is only partially quenched, as in the rare-earth series ions, there is some orbital moment remaining, the internal field is appreciable and is to some extent tied to the crystal field and there is large magnetic anisotropy (2).

Recently, Barnes et al. applied Mössbauer effect techniques to the study of the crystal field interaction in thulium salts (3). This technique measures the splitting of nuclear energy levels. In a paramagnetic solid, this
splitting is caused by the interaction of the nuclear quadrupole moment with an electric field gradient at the nucleus. The field gradient at the nucleus is the result of a lattice contribution and, in the case of rare-earth ions, a 4f-electron contribution which is strongly dependent upon the electronic state of the ion. Since the electronic state of the ion depends upon the crystal field interaction with the 4f-electrons, the measurement of the temperature dependence of the nuclear quadrupole interaction can be used to determine the crystal field parameters. Crystal field parameters determined by this technique for Tm-ethylsulfate agreed, within experimental error, with those determined by optical methods (3).

D. The Mössbauer Effect

The Mössbauer effect is the recoilless resonant emission and/or absorption of gamma rays by nuclei. A nucleus in excited state A decays to ground state B with the emission of a gamma ray of energy $E_0$. Resonance occurs when this gamma ray then excites an identical nucleus from state B to state A.

When a free nucleus decays, it must recoil in order to conserve momentum. The gamma ray then has an energy which differs from $E_0$ (the energy of the excited state) by an amount equal to the recoil energy $R$. The absorbing nucleus must also recoil with an energy $R$ to conserve momentum in the absorption process. Thus, in order to meet the resonance
condition, an additional energy of $2R$ must be given to the gamma ray.

Mössbauer discovered that under certain conditions, when an atom is bound tightly in a solid, the whole lattice recoils to conserve momentum $^4$. The energy $R$ may be written

$$R = \frac{P_Y^2}{2M_n} = \frac{E_Y^2}{2M_n c^2}$$

(1)

where $P_Y$ and $E_Y$ are the momentum and energy of the emitted gamma ray, respectively and $M_n$ is the mass of the recoiling nucleus. If the entire lattice recoils, the mass $M_n$ is replaced by the mass of the entire lattice. This makes the energy, $R$, vanishingly small. The gamma ray is thereby emitted with the entire transition energy $E_o$ and can be resonantly absorbed by a similar nucleus.

Interactions of the nucleus with its environment (hyperfine interactions), split the nuclear energy levels. The splittings are on the order of several times $10^{-6}$ eV. Typical gamma ray energies used in Mössbauer effect investigations lie in the range 1 to 100 keV. Thus, effects of one part in $10^9$ to one part in $10^{11}$ must be observed. The lifetime of the excited nuclear state, $T$, is related to the linewidth of the gamma ray energy distribution, $\Gamma$, through the Heisenberg uncertainty principle

$$T \Gamma = \frac{\hbar}{4},$$

(2)
Since the ground state has an infinite lifetime, it contributes nothing to the linewidth. Mössbauer effect linewidths lie in the range $10^{-5}$ to $10^{-9}$ eV. These linewidths are narrow enough to permit measurements of the hyperfine interactions to be made. The sharpness of the gamma ray energy is the property that makes the Mössbauer effect so useful.

The Mössbauer effect resonance is normally observed by destroying the resonance condition. This is accomplished by changing the energy of the emitted gamma ray slightly by moving the radioactive source nucleus during the decay process, giving the gamma ray an extra Doppler energy given by

$$\Delta E = \left(\frac{v}{c}\right)E_0$$  \hspace{1cm} (3)

where $v$ is the velocity of the nucleus at the moment it decays and $c$ is the velocity of light. Since the gamma ray has a narrow linewidth, a velocity of only a few mm/sec is usually sufficient to destroy the resonance.

E. Intent of Present Investigation

The importance of crystal field effects in ferromagnetic, antiferromagnetic, and ferrimagnetic materials has long been recognized. In metals, the exchange interaction usually dominates the crystal field interaction and the principal effect of the latter is to set up an anisotropy energy as mentioned earlier. The rare-earth salts, however, lie at the opposite extreme where the exchange interaction is very small compared with the crystal field effects. We report here an instance
where the latter is also the case for some intermetallic compounds. The experiments to be described were conducted at temperatures above those at which the exchange interaction is important.

Investigations of the magnetic properties of several RNi$_2$ and RCo$_2$ (R is a rare-earth element) intermetallic compounds showed, in all cases, a saturation magnetic moment which was reduced from the free ion value (5). This reduced moment was attributed to partial quenching of the orbital angular momentum by the crystalline field (6, 7). Bleaney has predicted that in intermetallic compounds such as RM$_2$ and RM$_5$ the exchange interaction and the crystal field effects would be comparable. He considered the specific example of the cubic RNi$_2$ compounds and concluded that crystal field splittings are considerably larger than the exchange interaction (7). More recent experimental work by Farrell and Wallace (5) indicates that the crystal field interaction in this series is weaker than anticipated by Bleaney. The crystal field effects are so small as not to be observable in the low temperature paramagnetic region where one expects deviations from Curie-Weiss behavior.

Neutron diffraction work by Felcher et al. showed a saturation magnetic moment on the Tm ion in TmMn$_2$ of 5.28$\pm$0.15 $\mu_B$ (8) which is considerably smaller than the free ion value of 7.0 $\mu_B$. Thus, large crystal field effects are
The present investigation is aimed at a study of the crystal field effects in intermetallic compounds of thulium using the Mössbauer effect. Most of the heavy rare-earths form intermetallic compounds of composition RM$_2$ with the transition elements of groups VIIB and VIII. Many of these compounds form in the cubic Laves phase structure with the Tm$^{3+}$ ion located in a site of cubic symmetry. The Mössbauer effect at the Tm site then shows no quadrupole splitting in the paramagnetic region. In some cases, however, the compounds form in one of the hexagonal Laves phases in which the Tm$^{3+}$ ion occupies a site of trigonal symmetry ($C_{3v}$). The Mössbauer effect at the Tm site in these compounds exhibits a quadrupole interaction. The compounds investigated in this study are of the latter type.

Since the hexagonal RM$_2$ compounds can be expected to exhibit crystal field effects via the quadrupole interaction at temperatures above those at which the exchange interaction becomes important, the inherent problem of separating the two interactions is resolved. The Curie temperatures of the compounds studied in this investigation lie below 15$^\circ$K. Thus, crystal field effects can be studied over a large temperature range from 15-300$^\circ$K.
II. THEORY

In this section we will consider the theoretical derivations necessary to interpret the Mössbauer effect data. This section is conveniently divided into three subsections, one involving the interaction of the crystal field with the 4f-electrons, the second concerned with the interaction of the electric field gradient with the nuclear quadrupole moment, and the third concerned with other hyperfine interactions.

A. Crystal Field Interaction

A paramagnetic ion in a solid can be assumed to be surrounded by a more or less continuous distribution of charges due to the other ions in the lattice. These charges overlap the electronic distribution of the paramagnetic ion to some extent. Attempts to calculate the resultant charge distribution and its effect on the ionic energy levels have been largely unsuccessful (9, 10).

The simplifying concept was introduced with the assumption of the static "crystal field" or "ligand field". Kramers (11) and later in more detail, Van Vleck (12), and Penney and Schlapp (13, 14) made the assumption that one should regard the surrounding ions as point charges or point dipoles placed at the lattice points and should neglect the overlap of charges between ions. The effect of the ligands is to set up a static electric field which acts on the paramagnetic ion.
The problem then reduces to one of determining the energy levels in a Stark field of a given magnitude and symmetry determined by the static charges. This is the origin of the crystal field model.

The mathematical problems of representing the crystal field in this approximation and the calculation of the matrix elements are not very difficult (15). Surrounding ions are considered as point charges and the potential arising from them is calculated at the ion site. Since no overlap is assumed, the potential must obey Laplace's equation, \( \nabla^2 V = 0 \). The solutions of this equation are the generalized Legendre polynomials. We can thus expand the potential in terms of these polynomials, that is

\[
V = \sum_{n,m} V_n^m = \sum_{n,k} \sum_{m=-n}^{n} A_n^m r_k^n y_n^m (\theta_k, \phi_k). \tag{4}
\]

The lattice sums \( A_n^m \) are defined as

\[
A_n^m = \sum_i \left[ V_i^m (\theta_i, \phi_i) / P_i^{n+1} \right] J_i \tag{5}
\]

and the normalized harmonics \( Y_n^m \) are defined as

\[
Y_n^m (\theta_k, \phi_k) = (-1)^n \left[ \frac{(2n+1)(n-|m|)!}{4\pi (n+|m|)!} \right]^{1/2} P_n^m (\cos \theta_k) e^{i m \phi_k}. \tag{6}
\]

The sum in the equation for \( A_n^m \) is over all charges, \( j_i \), in the lattice. The summation over \( k \) in the equation for \( V \) is over all 4f-electrons.

All terms in \( V \) for which \( n > 6 \) will have zero matrix elements and can be omitted. The reason is that in evaluating
a matrix element such as $<X|\mathcal{V}_n^m|\psi>$, where $X$ and $\psi$ denote $f$-electron wave functions, the density $X^*\psi$ can also be expanded in spherical harmonics and does not contain harmonics for which $n>6$. Hence, by the orthogonality properties of the spherical harmonics, if $\mathcal{V}_n^m$ is a spherical harmonic with $n>6$, the matrix element will be zero. By a similar argument, all terms for which $n$ is odd have zero elements because the product $X^*\psi$ is unchanged by the substitution $x,y,z \rightarrow -x,-y,-z$, whereas $\mathcal{V}_n^m$ reverses sign. This means the matrix element does not have inversion symmetry and must be zero. The relevant values of $n$ and $m$ for various crystal symmetries are given in a compilation by Prather (16). The symmetry of the site determines the crystal field terms necessary to describe the potential and the form of the radial part of $\mathcal{V}$ is important only for the magnitude (17).

In the case of $C_{3v}$ symmetry the six terms that remain in the potential are $A_2^0$, $A_4^0$, $A_4^3$, $A_6^0$, $A_6^3$ and $A_6^6$. These lattice sums can be written explicitly as follows

$$A_2^0 = -\frac{\varepsilon^2}{4} \sum_i \frac{Z_i}{r_i^3} (3\cos^2 \theta_i - 1)$$

$$A_4^0 = -\frac{\varepsilon^2}{64} \sum_i \frac{Z_i}{r_i^5} (35\cos^4 \theta_i - 30\cos^2 \theta_i + 3)$$

$$A_4^3 = -\frac{35}{8} \varepsilon^2 \sum_i \frac{Z_i}{r_i^5} (\sin^3 \theta_i \cos \theta_i \cos 3\phi_i)$$
The form of the potential in this symmetry in terms of Cartesian coordinates is given by (15)

\[ V_{3v} = A_2^0(x^2 + y^2 - 2z^2) + A_4^0(35z^4 - 30r^2z^2 + 3r^4) + A_6^0(231z^6 - 315r^2z^4 + 105r^4z^2 - 5r^6) + A_6^0(x^6 - 15x^4y^2 + 15x^2y^4 - y^6) + 2A_4^3(x^3 - 3xy^2) + A_6^3(11z^3 - 3zr^2)(x^3 - 3xy^2). \]  

The Hamiltonian which describes the interaction of this crystal field with the 4f-electrons can be written as

\[ H_{CF}^{(4f)} = \Sigma_{k,n} \Sigma_{m=-n}^n A_m^r c_{k}^m \gamma_{n}^{m}(\theta_k, \phi_k) \]  

where the shielding by the outer 5s^2p^6 electrons is indicated by the prime. The summation \( k \) is over all electrons in the 4f-shell. The shielding arises from the polarization of the outer shells by the crystal field. This polarization changes the magnitude of the crystal field as seen by the 4f-electrons.

Calculations of the amount of shielding of the crystal field by the outer electrons is presently a subject of much
controversy. In the 3d-series ions the paramagnetic electrons are exposed directly to the crystal field. In these ions the crystal field interaction is large compared with the spin-orbit coupling. In the 4f-series the paramagnetic electrons are buried in the ion below the closed $5s^2p^6$ electron shell. In this series the crystal field interaction is smaller than the spin-orbit coupling. Lenander and Wong (18), Ray (19) and Watson and Freeman (20) conclude that the difference in the relative magnitudes of the crystal field interaction in these two series is due to the shielding of the outer electrons. Burns (17, 21) contends that though the outer electrons do partially shield the 4f-electrons in the rare-earth series the major difference is not due to this shielding. The relative size of the crystal field interaction is smaller in the rare-earths than in the iron series ions because the rare-earths are larger ions. Thus, the neighbors which produce the crystal field in the rare-earths are farther away and the crystal field potential is then reduced. Also, since the 4f-electrons of the rare-earths have a smaller radial extent than the 3d-electrons of the iron series ions, the 4f-electrons will interact with the crystal field less than the 3d-electrons. Since the 4f-electrons have a smaller radial extent and a higher effective nuclear charge than the 3d-electrons the spin-orbit coupling of the 4f-electrons will be larger. This will change
the relative magnitudes of the crystal field and spin-orbit interactions in the rare-earths (17).

The interaction described by the Hamiltonian in Eq. 9 splits the electronic ground state of the free ion, characterized by a particular value of \( J \), into a number of crystal field levels. In calculating these crystal field levels we will assume the electronic wave functions can be factored into an angular and a radial part and that higher terms with different \( J \) values can be neglected (3). Under these assumptions we are dealing with a manifold of states belonging to the same value of \( J \). The most convenient way to calculate the matrix elements of this Hamiltonian is by the use of operator equivalents (22, 23). In this method one replaces operators in the potential function by similar operators, that is each \( x, y, z \) is replaced by \( J_x, J_y, J_z \) respectively, which are the angular momentum operators for manifolds of constant \( J \). Proper regard for the commutation rules of the angular momentum operators must be observed in this conversion. The appropriate proportionality constants as well as the matrix elements themselves are available in the literature (15, 22, 23). The relevant matrix elements for this investigation are of the form

\[
H_{m_J, m_J'} = \sum_{n, m} A_n \langle r^n \rangle_{4f} \langle J || \theta_n || J > < J, m_J || O_n^m (J_x, J_y, J_z) || J, m_J' >
\]

where

\[
\langle r^n \rangle_{4f} = \langle U_{4f} || r^n || U_{4f} >
\]
and

$$
\theta_n = \alpha, \beta, \gamma \quad \text{for} \quad n = 2, 4, 6.
$$

In these expressions $U_{4f}$ is the radial part of the 4f-electronic wave function. The functions $\mathcal{C}_n^m(J_x, J_y, J_z)$ are the operator equivalents and may be found in the literature \((3, 15)\). The expressions $\langle J | \theta_n^m | J \rangle$ are reduced matrix elements \((24)\) which, for the more general case of intermediate coupling, may be found in the literature also \((25, 26)\).

In principle it is possible to calculate the unshielded lattice sums, $A_n^m$, but difficult in practice. The major source of uncertainty comes from insufficient knowledge of ionic positions and their temperature dependence. Another difficulty arises in attempting to estimate overlap of electronic wave functions between ions. In addition, the uncertainty in the shielding makes the conversion from $A_n^m$ to $A_n^{m'}$ equally difficult. The usual crystal field parameters and the ones to be determined in this investigation reflect the inability to calculate these terms. The crystal field parameters are defined as

$$
\mathcal{C}_n^{m'} = \langle r_n \rangle_{4f} A_n^{m'}.
$$

The wave functions for the ionic energy levels will be assumed to be linear combinations of eigenvectors of $J$. This assumption is consistent with the above assumption that the terms with different $J$ values are to be neglected. The wave functions then have the form
The eigenvalues of the Hamiltonian given by Eq. 9 are the ionic energy levels. These may be determined by diagonalizing the matrix given by Eq. 10. At the same time, the expansion coefficients, $a_{\nu}^{(m_J)}$, for the ionic wave functions may be determined.

B. Nuclear Quadrupole Interaction

The first evidence that many nuclei possess magnetic moments came from a study of hyperfine structure of atomic spectra (27). The interaction of the nuclear magnetic moment with the magnetic field set up by the atomic electrons gives rise to a relatively simple hyperfine spectrum which is characterized by the well-known "interval rule". Schöller and Schmidt (28) first showed the existence of nuclear quadrupole moments in explaining deviations from this interval rule.

The discovery of the nuclear quadrupole moment, $Q$, was important since it meant that a nucleus could interact not only with a magnetic field but also with an electric field gradient. The moment reflects the deviation of the nucleus from spherical symmetry. An oblate (flattened) nucleus has a negative quadrupole moment and a prolate (elongated) nucleus has a positive quadrupole moment. The moments of a given nucleus (both magnetic and quadrupole) are parameters which are characteristic of that nucleus and cannot be changed by

$$\psi_{\nu} = U(r) \sum_{m_J} a_{\nu}^{(m_J)} \psi_{m_J}^{J}$$ (12)
external means (27). Nuclei with spin 0 or 1/2 are spherically symmetric and have no quadrupole moment. The ground state of Tm$^{169}$ with spin, I, equal to 1/2 is such a case.

The nuclear quadrupole moment cannot be measured directly. This is a consequence of the fact that, unlike the magnetic case, external field gradients are not large enough to affect the nuclear energy levels. In measurements of the quadrupole interaction the quantity which is measured is a product of the internal field gradient and the nuclear quadrupole moment. Since accurate calculations of the field gradient at the nucleus are not presently possible, the two factors cannot be separated.

The atomic beam method provides the most accurate technique for determining both magnetic and quadrupole moments. Magnetic transitions between the hyperfine structure (hfs) levels of an atomic fine structure (fs) state are induced by subjecting an atomic beam to a radio-frequency field. The separation between hfs levels is determined by a very precise frequency measurement. If the hfs splitting is entirely magnetic, caused by an external magnetic field, the magnetic moment can be calculated from an accurate measurement of the applied magnetic field. If the magnetic splitting is perturbed by an electric quadrupole interaction, the determination of the quadrupole moment depends upon a calculation of the electric field gradient at the nucleus. Such calculations
can be made with only limited accuracy because of major uncertainties arising from shielding effects of core electrons. A complete discussion of this technique and its applications is given by Ramsey (29).

The atomic beam technique cannot be applied to Tm\textsuperscript{169}, however, because the nuclear ground state has no quadrupole moment. Mössbauer effect techniques measure the interaction of the quadrupole moment of the first excited state with the electric field gradient. The results of the present study depend only on a measurement of the quadrupole interaction and on the change in this interaction as a function of temperature so that knowledge of the value of Q is not required.

The interaction between the nuclear electric quadrupole moment and the gradient of the electric field is expressed by the Hamiltonian (30)

\[ H_Q = \vec{Q} \cdot \vec{\nabla}E \]

where

\[ Q_{ij} = \int \rho x_i x_j d^3x \]

or

\[ H_Q = \frac{e^2 q_{zz} Q}{4I(2I-1)} \left[ (3I_z^2-I^2) + \frac{\eta}{2} (I_+^2-I_-^2) \right] \quad (13) \]

where \( \eta \) is an asymmetry parameter. In the case of C\textsubscript{3v} symmetry we have an axially symmetric electric field gradient and \( \eta=0 \). We will specialize to this case for the remainder of the derivations.
There are many contributions to the field gradient at the nucleus. Since we cannot hope to distinguish between the direct contributions and those due to shielding effects of core electrons, we shall lump the contributions together and refer only to the principle sources. In the case of the rare-earth salts there are only two sources; the lattice of ion cores and the polarized 4f-electrons. For the intermetallic compounds, now under investigation, an additional contribution due to the conduction electrons must be added. The total electric field gradient at the nucleus may then be written as

\[ e_{ij} = e_{ij}^{(4f)} + e_{ij}^{(lig)} + e_{ij}^{(c)}, \quad i,j = 1,2,3. \quad (14) \]

The primes are again used to indicate shielding effects of the core electrons.

The nuclear Hamiltonian then becomes

\[ H_Q = \frac{e^2 Q}{4I(2I-1)} \left[ q_{zz}^{(4f)} + q_{zz}^{(lig)} + q_{zz}^{(c)} \right] (3I_z^2 - I^2). \quad (15) \]

It should be noted that this Hamiltonian holds only in the principal axis system of the electric field gradient tensor.

The unshielded lattice contribution \( q_{zz}^{(lig)} \) may be related to the \( A_n^m \) of the potential expansion by using the definition

\[ e_{ij} = \frac{d^2(-V/e)}{dx_i dx_j} \text{ where } V \text{ is given by Eq. 4.} \]

We then have that

\[ e^2 q_{zz}^{(lig)} = -4A_2^0. \quad (16) \]
The unshielded 4f-electron contribution $q^{(4f)}_{11}$ is defined by

$$q^{(4f)}_{11} = \frac{d^2(S_k - e/r_k)}{dx_1 dx_1}$$  \hspace{1cm} (17)

where the sum extends over all 4f-electrons in the partially filled shell and $r_k$ represents the radius vector for the various 4f-electrons. We can then calculate the expectation value of $q^{(4f)}_{11}$ for each crystal field level as

$$<v|q^{(4f)}_{zz}|v> = -\sum_k <v|(3z^2 - r^2)/r^5_k|v>$$

$$= -<J||a||J><r^3>_{4f}<v|3J^2_z - J^2 |v>$$  \hspace{1cm} (18)

A similar expression may be obtained for the conduction electron contribution where the integral is taken over all conduction electrons, not just those at the Fermi surface (31). The expression for $q^{(c)}_{zz}$ is given by

$$q^{(c)}_{zz} = Z<\psi|(3z^2 - r^2)/r^5|\psi>$$  \hspace{1cm} (19)

where $Z$ is the number of conduction electrons per ion.

Each of the ionic crystal field levels produces an electric field gradient at the nucleus. At elevated temperatures where the spin-lattice relaxation phenomenon produces rapid transitions between the crystal field levels the electric field gradient at the nucleus is an average over the contributions of all the electronic states weighted according to their population numbers. This averaging process holds only if the significant electron relaxation times are short.
compared to all other relevant times such as nuclear lifetimes and nuclear precession times, a situation prevailing at temperatures above a few degrees Kelvin (3).

Usually one cannot observe the contributions of each crystal field level directly but only an average over all energy levels weighed according to their Boltzmann factors as described above. The usual procedure is to average over the lowest J multiplet. The generalization to include effects of other values of J has been made (3) but since these contributions are only of the order of one percent for Tm$^{169}$, they will be neglected in the present case. For a particular temperature T, this average is given by

$$<q_{11}^{(4f)}>_T = \frac{\sum_{\nu=1}^{2J+1} <\nu|q_{11}^{(4f)}|\nu> e^{-E\nu/kT}}{\sum_{\nu=1}^{2J+1} e^{-E\nu/kT}}.$$  \hspace{1cm} (20)

The total Hamiltonian describing the average quadrupole interaction at the temperature T may now be written as

$$H_Q(T) = \frac{e^2 Q}{4I(I+1)} \left[ <q_{zz}>_T (I_Z^2 - I^2) \right]$$  \hspace{1cm} (21)

where

$$<q_{zz}>_T = q_{zz}'(\text{lig}) + q_{zz}'(\text{c}) + <q_{zz}^{(4f)}>_T.$$  \hspace{1cm} (22)

The temperature dependences of the ligand and of the conduction electron contributions have been neglected.

We must now apply these results to the specific case of Tm$^{169}$. Since the spin of the ground state is 1/2 and it has
no quadrupole moment, its two-fold degeneracy is not removed by the Hamiltonian Eq. 15. The spin of the 8.4 keV excited state is $3/2$; its quadrupole moment interacts with the electric field gradient and its four-fold degeneracy is partially removed. The energy separation of the excited state levels is given by the difference between the eigenvalues of the above Hamiltonian. Since the Hamiltonian is diagonal, in our case, the eigenvalues may be readily evaluated. The splitting is then given by

$$<\Delta E>_T = \frac{e^2 Q}{2} <q_{zz}>_T.$$  

This expression may be written in more detail using Eqs. 11, 16, 18 and 22:

$$<\Delta E>_T = \frac{e^2 Q}{2} \left[ <J||a||J><r^{-3}>_Q <3j^2_z-J^2>_T ight.$$

$$+ \frac{4c_2'(1-\gamma_{\infty})}{e^2<r^2>_E} - q_{zz}^{(c)} \right]$$  

(24)

where $<3j^2_z-J^2>_T$ is a thermal average defined by Eq. 20, while the parameters $<r^{-3}>_Q$ and $<r^2>_E$ are defined by

$$<r^{-3}>_Q = (1-R_Q)<r^{-3}>_{4f}$$  

(25)

$$<r^2>_E = (1-\sigma_2)<r^2>_{4f}.$$  

(26)

The Sternheimer shielding factors $R_Q$ and $\sigma_2$ and the anti-shielding factor $\gamma_{\infty}$ are introduced here and will be discussed
in Section IV. It is the splitting $<\Delta E>_T$ which is measured in Mössbauer effect experiments.

In order to compare experimental results directly within the framework of the crystal field model it is valuable to replace all quantities in the expression for $<\Delta E>_T$ which involve radial integrals. These integrals can only be performed with limited accuracy due to insufficient knowledge of the 4f wave functions. We thus introduce the following dimensionless parameters

$$
\rho_1 = e^2 Q <r^{-3}>_Q <J||a||J>/C_2^0
$$

$$
\rho_2 = \left[ \frac{Q(1-Y_\infty)}{<r^2>_E} - \frac{e^2 q'(c) Q}{4C_2^0} \right]
$$

which will be determined in the experiment. The prime is used on $\rho_2$ to distinguish it from a similar parameter defined by Barnes et al. (3). The conduction electron contribution was absent in their definition of $\rho_2$.

Written in terms of these parameters the quadrupole splitting in Tm$^{169}$ reduces to

$$
<\Delta E>_T = \frac{1}{2} (C_2^0 \rho_1 <3J_z^2-J^2>_T + 4C_2^0 \rho_2')
$$

The thermal average $<3J_z^2-J^2>_T$ within the framework of the crystal field model depends only on the experimentally determined parameters $C_n^m$. 
C. Additional Hyperfine Interactions

Some additional hyperfine interactions which arise in second-order perturbation theory and which affect the quadrupole interaction at the nucleus have been neglected. Contributions from higher terms with different values of \( J \) are considered small because the first excited state \(^3H_5\) of the free ion lies 8500 cm\(^{-1}\) above the ground state \(^2H_6\) in Tm (32). The over-all crystal field splitting in the compounds studied in this investigation will be shown to be less than 100 cm\(^{-1}\).

Another contribution is one which arises directly from the magnetic hyperfine interaction itself and is known as the pseudo-quadrupole coupling. Recently this effect was observed in Mössbauer effect investigations of TmCl\(_3\) · 6H\(_2\)O and Tm\(_2\)(SO\(_4\))\(_3\) · 8H\(_2\)O at temperatures below 4\(^o\)K (33). In non-degenerate electronic states there is no first order magnetic hyperfine interaction since the electronic states are invariant under time reversal. If the energy separation, \( k\theta \), of the two lowest electronic states is quite small, comparable to the magnetic hyperfine energies, a large magnetic hyperfine interaction arises in second order. This pseudo-quadrupole interaction can cause a shift of the center of gravity of the gamma ray spectrum line positions when there is a difference in the thermal populations of the two electronic levels involved. In the compounds investigated (33) the effect was observable at
temperatures between 1 and \(3^0K\) with a splitting between lowest lying states of \(1\text{ cm}^{-1}\). In the present work this effect is considered negligible because all of the investigations were carried out above \(4^0K\) which means the two lowest lying levels, which are split by less than \(1\text{ cm}^{-1}\) in the compounds under investigation, are equally populated.

The effects of a magnetic interaction at the nucleus have been neglected. This interaction arises via an exchange between ionic spins which produces an effective magnetic field at the nucleus. The exchange may be direct between the ionic spins themselves, or indirect via the spins of the conduction electrons. This exchange interaction polarizes the ionic spins. At temperatures well above the magnetic ordering temperature of the compound, however, the spin-lattice relaxation time is short compared to the lifetime of the nuclear excited state and the magnetic hyperfine interaction averages to zero. As the temperature is decreased, the spin-lattice relaxation time increases. When it becomes comparable with the nuclear lifetime, net magnetic effects will be observed. In the paramagnetic region, these exchange effects should manifest themselves as a broadening of the Mössbauer effect resonances. As magnetic ordering occurs, the resonances are split from two, characteristic of the quadrupole spectrum, into six, characteristic of the magnetic spectrum.
III. APPARATUS AND EXPERIMENTAL TECHNIQUE

In Section I we discussed the phenomenon colloquially referred to by physicists as the Mössbauer effect. Now we will discuss the experimental equipment used in the present study and how it is used to measure nuclear hyperfine interactions.

The application of the Mössbauer effect to the present study requires a radioactive source which provides a monoenergetic beam of gamma rays. The material to be studied is used as an absorber; the gamma rays from the source being incident upon it. Those gamma rays which pass through the absorber are detected and counted as a function of source velocity. Resonant gamma rays excite nuclei, in the absorber, from the ground state to the excited state and thereby are removed from the incident beam. When nuclei return to the ground state, the emitted gamma rays have an equal probability of being emitted in any direction. The number of gamma rays detected by the radiation detector is thus reduced at the resonant velocity.

A. Source

A single-line source is to be preferred in most Mössbauer effect investigations. In such a source the nuclear hyperfine interactions average to zero so there is no splitting of the nuclear energy levels. The gamma radiation emitted by the
source is monoenergetic. Any structure revealed in the Mössbauer effect spectrum is due only to interactions in the absorber.

The trivalent state of the rare-earth ions is the one most frequently encountered in ionic compounds. The point-group symmetries associated with rare-earth sites in ionic crystals are usually rather low. The preference for a trivalent ionization state renders it difficult to obtain the rare-earth ion in a surrounding of cubic symmetry, i.e., with a vanishing field gradient and thereby a vanishing quadrupole interaction (32). This difficulty leads to the consequence that it is often almost impossible to find a suitable single-line source.

The cubic Laves phase compound ErAl₂ was considered first to be a possible source material. The symmetry at the Er site is cubic and the isostructural compound HoAl₂ has been successfully used as a single-line source in Mössbauer effect experiments involving Er¹⁶⁶ (34). Tantalum impurities produced an intense background of high energy gamma radiation. Specially selected Ta-free (less than 300 ppm Ta) Er was used in the preparation of additional ErAl₂. The linewidth of the single line observed using this ErAl₂ was almost twice the linewidth reported for an Er₂O₃ source (35). The origin of this broadening could not be determined so we decided against using ErAl₂ as a source.
The ternary oxide LiErO$_2$ was next considered as a possible source material. An ordered NaCl type structure was reported for this type of compound (36). Since the crystal structure of this particular compound is only slightly tetragonal, the possibility existed that the electric field gradient at the Er nucleus might be small or even vanish completely. The compound was prepared following the procedure of Vorres (36). It was then sealed, in air, in a quartz tube for the neutron irradiation. During the irradiation, heating in the reactor initiated a chemical reaction between the lithium in the sample and the quartz tube. This led to a decomposition of the source.

After these unsuccessful attempts to find a better source material, we decided to use Er$_2$O$_3$. This source has been used in other Mössbauer effect studies of Tm$^{169}$ (35, 37, 38, 39) but is far from ideal. The chief disadvantage is that a large nuclear quadrupole interaction exists at room temperature. A single line source may be achieved by heating the Er$_2$O$_3$ to 400°C. At this temperature the nuclear quadrupole interaction reaches a minimum. The single line thus achieved has a linewidth that is 1.79 times as broad as expected theoretically. In transmission type experiments an emission line of width $\Gamma$ is moved over an absorption line also of width $\Gamma$. One then expects a minimum experimental linewidth of $2\Gamma$. In the present case this is (in velocity units)
\[ 2\Gamma c/E_\gamma = 2\hbar c/T E_\gamma = 1.14 \text{ cm/sec} \quad (29) \]

based on the lifetime, \( T = 4.13 \times 10^{-9} \text{ sec} \) and energy \( E_\gamma = 8.42 \text{ keV} \), of the first excited state of \( \text{Tm}^{169} \) (40). However, for an absorber of finite thickness, this width increases by a correction factor which is 1.47 in our case for an absorber with an areal density of 5 mg/cm\(^2\) of thulium and a total internal conversion coefficient of 325 (35). Thus the predicted linewidth is 1.68 cm/sec. The observed linewidth is 3.00 cm/sec which leads to the factor of 1.79. Part of this broadening is due to the residual quadrupole interaction. The situation is also complicated by non-equivalent erbium sites in the oxide (32).

An aluminum source oven was constructed and was attached directly to the transducer (3). An ambient source temperature of 400°C was maintained in the oven. The sources were prepared from \( \text{Er}_2\text{O}_3 \) enriched to 95% in \( \text{Er}^{169} \). Each source consisted of 25 mg of the \( \text{Er}_2\text{O}_3 \) which was irradiated in the MTR at Arco, Idaho for 18 days at a flux of \( 4 \times 10^{13} \text{ n/cm}^2 \text{ sec} \). This produced a useable activity of 700 mC. The radioactive powder was placed in a small aluminum holder and covered by a 0.020" Be disk and retaining ring. This holder effectively contained the radioactive powder and prevented it from sluffing off onto the rest of the equipment. The holder was securely attached to the oven. An integral chromel-alumel
thermocouple provided a constant monitor on the source temperature.

B. Absorber

The absorbers used in this investigation were intermetallic compounds of the hexagonal Laves phase type (41). They were prepared by arc-melting stoichiometric amounts of the constituents. Under an argon atmosphere, the arc was struck to the component which had the lowest melting point. The molten metal was then allowed to flow over the other material. The "button" formed in this manner was turned over and melted several times to homogenize the compound. The final button was checked for weight loss. The absence of impurity phases in amounts in excess of five percent was checked by standard x-ray diffraction and metallographic analysis.

Since these compounds, TmRu₂ and TmMn₂, are very brittle, the buttons were crushed in a diamond mortar and pestle and sieved to 325 mesh. A quantity of powder sufficient to produce an areal density of 5 mg/cm² of thulium was weighed out. This powder was then settled out of acetone onto a 0.020" Be disk providing a uniform deposition. The resulting layer was covered with a thin layer of a spray lacquer. This provided a simple bond between the sample and the Be disk which was maintained even at low temperatures.
C. Spectrometer

A block diagram of the Mössbauer effect spectrometer used in this investigation is shown in Fig. 1. The source "shaker" is a velocity scanning transducer which was operated in the constant acceleration mode. In this mode, the shaker velocity is a linear function of time. The design of Kankeleit (42) was used for this transducer. It was driven by a constant-acceleration feedback amplifier modeled after the one developed by Cohen et al. (43). The integral push-pull power amplifier was replaced by a Ling model TP100 to provide the power level necessary to drive the shaker at high velocities with the source oven attached. The drive system was operated at a frequency of 12 cps with the reference signal for the feedback amplifier provided by a Hewlett-Packard 202A function generator. Velocities up to ±16 cm/sec could be achieved using this system. The error signal, i.e., the difference between the reference voltage and the pickup voltage, was less than 0.5% over 90% of the cycle.

A homemade proportional counter (44) filled with a mixture of 90% argon and 10% methane was used to detect the 8.42 keV radiation. A 0.020" thick Be entrance window allowed this low energy radiation to enter the counter. In the energy range below 20 keV, the resolution of the proportional counter is considerably better than the resolution of the standard sodium iodide scintillation crystal and photomultiplier assembly.
Fig. 1. Block diagram of the Mössbauer effect spectrometer. The source oven was located on the end of the shaker nearest the cryostat. The absorber was located in the tail of the cryostat.
An RIDL preamp and DD2 linear amplifier converted the pulses from the proportional counter to a shape and size acceptable to the RIDL 34-12B 400 channel analyzer. The single channel analyzer selected the proper portion of the energy spectrum. A time-base generator (crystal-controlled oscillator), triggered by the function generator, advanced the address of the analyzer at a constant rate. The function generator was adjusted so that its period corresponded to the time required to scan through the entire 400 channels once. The analyzer, operated in the multiscalar mode, was then "synched" to the velocity drive so that each channel corresponded to a unique velocity. As the analyzer was scanned, each channel was opened, for a set time, to the incoming counts detected by the proportional counter. At the end of each run the analyzer contained a profile of the number of counts which were transmitted through the absorber as a function of the source velocity. Typical Mössbauer effect spectra are shown in Fig. 2.

D. Calibration

Calibration of the drive was performed using the Mössbauer effect spectrum for Armco iron. The internal magnetic field and the magnetic moments of both the ground and excited states are well known (45). There are six resonance lines in this spectrum corresponding to the six allowed M1 (dipole) nuclear transitions in ferromagnetic iron. The
Fig. 2. The upper spectrum is that of TmRu₂ at room temperature. The solid line is a best fit of a single Lorentzian lineshape to the data. The lower spectrum shows TmRu₂ at 35⁰K. In this case two Lorentzian lineshapes were fit to the data. The source was Er₂O₃ at 400⁰C in both cases. Broadening of the lines in the low temperature spectrum are evident even though the velocity scales are not the same. Note the asymmetry in the intensities of the two lines in the lower spectrum.
splittings between these resonances are measured, in channel numbers, and divided by the known separation, in velocity units. This provides individual calibrations over selected portions of the spectrum. These calibrations are then averaged together to determine the over-all calibration (mm/sec/channel) for the entire spectrum. The only problem in calibrating in this manner is that involved in extrapolating from the small velocities required for the iron calibration (+0.5 cm/sec) to the large velocities required in this investigation (+16 cm/sec). The reference signal for the feedback amplifier, which determines the velocity of the shaker, is varied by a ten-turn helipot which is linear to ±0.25%. The calibration was performed with the helipot set at 50. The actual work was done using settings up to 1000 which means that the calibration had to be multiplied by factors up to 20. Based on the repeatability of the results and comparison of data taken using different calibrations, it is felt that this extrapolation is good to at least two percent.

E. Cryostat

The heat-leak cryostat used throughout this study is shown in Fig. 3. The helium can has a capacity of 1.5 liters and, with the sample at 4.2°K, hold times of 30-36 hours were achieved on one fill. The nitrogen can has a capacity of 3 liters. An automatic level control refilled the nitrogen can every 4 hours, 24 hours a day. Using a variety of cryogenic
Fig. 3. Details of heat-leak cryostat used throughout this investigation. The diameter of the outside can is six inches and the over-all length is about thirty inches. The absorber was placed in the slot in the tail of the cryostat where temperatures between $4.2^\circ K$ and $300^\circ K$ could be maintained for extended periods of time.
liquids in the helium can, sample temperatures between $4.2^\circ K$ and $300^\circ K$ could be reached. A temperature control designed and built by coworkers maintained temperatures within $0.2^\circ K$, indefinitely, across the entire temperature range.

The sample chamber was accessible from the top of the cryostat to permit exchange of absorbers while the cryostat was cold. The absorber, attached to a copper holder, could be lowered into or fished out of the sample chamber by means of a threaded thin stainless steel rod. The flat absorbers were automatically aligned perpendicular to the gamma ray beam by a slot in the sample chamber. Four 0.020" Be and two 0.001" mylar windows in the path of the gamma radiation resulted in a net transmission of the cryostat for the 8.42 keV radiation of only about 10%.
IV. EXPERIMENTAL RESULTS AND DATA ANALYSIS

A. Introduction

Mössbauer effect data are accumulated in a multichannel analyzer. The x-axis of the analyzer is calibrated in velocity units with the number of counts at each velocity given by the y-coordinate. The transmission geometry employed in this study produces a background counting rate that yields a flat baseline of as many as a million counts per channel. Superimposed on this baseline are the Mössbauer effect resonances and a parabolic curvature which is due to a geometric effect. The geometric effect manifests itself when the displacement of the shaker becomes an appreciable fraction of the separation between the source and the detector. The change in solid-angle intercepted by the detector is large enough to produce a detectable change in the background counting rate. The curvature is parabolic due to the $1/r^2$ dependence of the solid angle.

The source velocity varies linearly as a function of time. A start pulse from the function generator triggers the time-base generator when the source is at its maximum negative (source moving away from absorber) velocity. The time-base generator provides pulses which drive the channel address sequentially so that the analyzer spends equal times in all channels. At the moment channel 200 is addressed, the source has reached its maximum positive velocity. As the channel
address continues to advance, the source velocity decreases so that its maximum negative velocity is reached at channel 399. Mirror spectra are thereby stored in the two halves of the analyzer.

The data are read out of the analyzer directly onto punched paper tape. These tapes are then converted to punched cards for the computer analysis. Permanent records of the data are also made via a typewriter and an x-y recorder.

Once the data are recorded, the problem becomes one of analysis. The resonance lines which make up the spectrum have a well-defined shape, which is determined by the resonant processes. The cross-section for resonant absorption of an incident gamma ray of energy $E$ and wavelength $\lambda$ can be written (46)

$$\sigma(E) = \sigma_0 \frac{\Gamma_\gamma}{4(E-E_\gamma)^2 + \Gamma^2}$$  \hspace{1cm} (30)

where $\Gamma$ is the total width of the absorption line, $\Gamma_\gamma$ its gamma ray width and $\sigma_0$ the maximum resonance cross-section given by

$$\sigma_0 = \frac{2I_B+1}{2I_A+1} 2\pi\lambda^2.$$  \hspace{1cm} (31)

The spins of the ground state and of the excited state are given by $I_A$ and $I_B$, respectively. This cross-section shows a characteristic energy dependence of the form

$$I(E) = \frac{\Gamma}{2\pi} \frac{1}{(E-E_\gamma)^2 + (\Gamma/2)^2}$$  \hspace{1cm} (32)
which is normalized by
\[ \int_0^\infty I(E) dE = 1. \quad (33) \]
The total linewidth \( \Gamma \) and the gamma ray width \( \Gamma_\gamma \) are related by
\[ \Gamma_\gamma = \frac{1}{1+\alpha} \Gamma \quad (34) \]
where \( \alpha \) is the internal conversion coefficient; for \( \text{Tm}^{169}, \alpha = 325 \) (35). The energy distribution of the gamma radiation incident upon the detector is given by Eq. 32. This distribution has a Lorentzian lineshape and leads to Mössbauer effect resonances of the same shape. In the present investigation, the Mössbauer effect spectra consist of two Lorentzian lines.

**B. Analysis and Results**

The data analysis, to be described, was performed on an IBM 360/50 computer. In order to eliminate the geometric curvature (to a first order approximation) the two halves of the data were folded over and summed. The channel address was then converted to velocity units and a function, which consisted of the sum of two Lorentzian lines each multiplied by the background count, was fitted to the data using a \( \chi^2 \) minimization technique developed by Davidon (47). In this fitting procedure the position, width and intensity of each of the two lines as well as the background count could be treated as parameters. Because of poor resolution, however, the widths
of the two lines were constrained to be equal. When a minimum in the value of the function was located, several random steps were taken in an effort to determine whether a relative or an actual minimum had been located. The quadrupole splitting was then given by the difference in the positions (in velocity units) of the two lines. Runs were made at various temperatures between 4.2°K and 300°K with each resulting spectrum analyzed by the procedure outlined above. The temperature dependence of the quadrupole interaction was thus obtained.

The next step in the analysis was to fit Eq. 28 to the temperature dependence using the Davidon minimization technique but with a different function to be minimized. The desired crystal field parameters as well as the parameters \( \rho_1 \) and \( \rho_2' \) were determined by this final fitting.

Initial guesses for the crystal field parameters had to be provided as a starting point for the minimization routine. The parameters remaining in the \( C_{3v} \) symmetry under investigation are: \( C_2^0, C_4^0, C_6^0, C_4^1, C_6^1 \) and \( C_6^3 \). The lattice field-gradient, \( q_{zz}^{(1g)} \), calculated using the plane-wise summation method of de Wette (48) was used to determine \( A_2^0 \) from the relationship defined by Eq. 16. The unshielded parameter \( C_2^0 \) was then evaluated using the value for \( <r^2>_{4f} \) of 0.19 \( \times 10^{-16} \) cm\(^2\), given by Judd and Lindgren (49), and Eq. 11. Lattice sum calculations provided the ratio \( A_4^0/A_6^0 \) which, with the values for \( <r^4>_{4f} \) of 0.069 \( \times 10^{-16} \) cm\(^4\) and for \( <r^6>_{4f} \) of
0.037 \times 10^{-16} \text{ cm}^6 \text{ given by Judd and Lindgren (49), was used to evaluate the ratio } C_4^0/C_6^0. \text{ Ratios between the other crystal field parameters involving the same value of } n \text{ were made using the ordinary lattice sums as given in Eq. 7. Since these sums converge very rapidly for } n > 2, \text{ only ions within a radius of one } c\text{-lattice vector of the central Tm ion were included. For the MgZn}_2 \text{ crystal structure under study this included 155 ions. An upper limit on the ionic energy level separation was set by observing the temperature at which the quadrupole interaction leveled out. Using second-order perturbation theory expressions for the energy levels an estimate of the value of } C_4^0 \text{ or } C_6^0 \text{ was made. From this value, guesses for all the other crystal field parameters could be made using the ratios mentioned above. Guesses for } \rho_1 \text{ and } \rho_2 \text{ were then made using the high and low temperature limits of the quadrupole splitting respectively, i.e.,}

\begin{align*}
(\Delta E)_T^0 &= 2c_2^0\rho_2', \quad T \gg 100^\circ K \\
(\Delta E)_T &= \frac{1}{2}(c_2^0(3J_z^2-J^2)1 + 4c_2^0\rho_2'), \quad T \approx 0^\circ K
\end{align*}

where the average \langle l \mid 3J_z^2-J^2 \mid l \rangle \text{ is the contribution to the field gradient of the lowest lying energy level. In cases where there are two low lying energy levels, this average is replaced by the contributions of both levels. The computer}
fitting program used these guesses as starting values in the minimization routine.

The eigenvalue problem for the Hamiltonian given by Eq. 9 was solved in the fitting routine. This was necessary in order to determine the contribution of each ionic energy level to the nuclear field gradient. The final solution thus includes the ionic energy levels and the associated wave functions.

The intermetallic compounds investigated in this study have the hexagonal Laves phase (Cl4) MgZn$_2$ structure which was first determined by Friauf (50). The space group for this structure is $D^{15}_{6h}$ - $P_{312}$/mmc with 4 formula units per unit cell. The positions of the atoms in the unit cell are (51)

Mg: $\frac{1}{3},\frac{2}{3},z$; $\frac{2}{3},\frac{1}{3},\frac{2}{3}+z$; $\frac{1}{3},\frac{2}{3},\frac{1}{2}-z$; $\frac{1}{3},\frac{2}{3},\frac{1}{2}+z$; $\frac{1}{3},\frac{2}{3},\frac{1}{2}-z$; $x=\frac{1}{16}$

Zn: 0,0,0; 0,0,1/2; x,2x,1/4; 2x,1/4; x,1/4; x,1/4; x,2x,3/4; 2x,3/4; x,3/4; x,3/4; x = -1/6.

We will now present, separately, the data and results for the two compounds studied. In Section V we will discuss the significance of these results.

1. TmRu$_2$

In a study of cubic LnNi$_2$ compounds (MgCu$_2$ structure), Skrabeck and Wallace (6) found that YNi$_2$, LuNi$_2$ and CeNi$_2$ exhibit only Pauli paramagnetism, even at 4.2°K. This result
was interpreted as indicative of the fact that the nickel is nonmagnetic in these phases and that electron transfer had occurred so that the nickel 3d shell had been filled. In a later study, Farrell and Wallace (5) concluded that Ni was nonmagnetic throughout the LnNi$_2$ series.

Ruthenium is also a group VIII element and can be expected to exhibit electronic properties similar to Ni. The electronic configuration of Ru is 4d$^7$5s$^1$. We will make the assumption that the outer 5s electron falls into the 4d shell and in this way the ruthenium enters the lattice as a neutral atom. For this reason, the analysis for TmRu$_2$ was made assuming the Tm ion to be trivalent and the Ru to be neutral.

The de Wette (48) calculation gave a value of $5.41 \times 10^{22}$ cm$^{-3}$ for $q^{(11g)}$. This leads to a value of -300 cm$^{-1}$ for $C_2^0$ using Eqs. 11 and 16. In order to account for the shielding of the outer 5s$^2$p$^6$ electrons, this value for $C_2^0$ was reduced by half to give a value of -150 cm$^{-1}$ for $C_2^0$. The lattice vectors for TmRu$_2$ are $a = 5.246 \ \AA$ and $c = 8.790 \ \AA$ leading to a c/a ratio of 1.676 (52). Lattice sum calculations gave the following values for the ratios between crystal field parameters:

\[
\begin{align*}
C_4^0/C_4^0 & = 28.3 \\
C_4^2/C_4^0 & = 10.1 \\
C_6^2/C_6^0 & = 5.5 \\
C_6^6/C_6^0 & = -12.3.
\end{align*}
\]
The maximum multiplet splitting was assumed to be 100°K. This led to a value of -21 cm\(^{-1}\) for \(C_4^0\). The following initial guesses were made for the parameters:

\[
\begin{align*}
C_2^0 &= -150 \text{ cm}^{-1}, \\
C_6^0 &= -1 \text{ cm}^{-1}, \\
C_4^3 &= -1 \text{ cm}^{-1}, \\
C_6^6 &= 9 \text{ cm}^{-1}, \\
\rho_1 &= -1.76 \times 10^{-6}, \\
\rho_2 &= 4.88 \times 10^{-5}.
\end{align*}
\]

The temperature dependence of the quadrupole interaction in TmRu\(_2\), as determined by the Mössbauer effect, is shown in Fig. 4. The data are presented in Table 1. Points on the graph are data and the solid line is the best fit to the data. The crystal field parameters determined in this fit are illustrated in Table 2. Ionic energy levels and associated wave functions also determined by this fit are shown in Table 3.

2. **TmMn\(_2\)**

The decision as to the charge to place at the manganese site in TmMn\(_2\) was very easy since Mn enters most compounds as a divalent ion. The thulium ion was again assumed to be in the trivalent state. The Mn sublattice contribution in this compound is large as indicated by the value of 4.17 \(\times\) 10\(^{23}\) cm\(^{-3}\) calculated for \(q^{(\text{lig})}_{zz}\). This leads to a value of -2300 cm\(^{-1}\) for \(C_2^0\) using Eqs. 11 and 16. This is considerably larger than the value calculated for TmRu\(_2\). Since it was obvious
Fig. 4. Temperature dependence of the $^{169}$Tm nuclear quadrupole interaction in TmRu$_2$. The solid line is the best fit of Eq. 28 to the data points.
Table 1. Mössbauer effect data for TmRu$_2$

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Linewidth (mm/sec)</th>
<th>Quadrupole splitting (mm/sec)</th>
<th>Intensity$^a_1$ (%)</th>
<th>Intensity$^a_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>65.6</td>
<td>77.0</td>
<td>0.48</td>
<td>0.24</td>
</tr>
<tr>
<td>20.4</td>
<td>43.8</td>
<td>67.8</td>
<td>0.66</td>
<td>0.36</td>
</tr>
<tr>
<td>35.0</td>
<td>52.4</td>
<td>55.7</td>
<td>0.82</td>
<td>0.44</td>
</tr>
<tr>
<td>50.0</td>
<td>55.0</td>
<td>42.8</td>
<td>0.88</td>
<td>0.41</td>
</tr>
<tr>
<td>65.0</td>
<td>40.4</td>
<td>33.0</td>
<td>0.89</td>
<td>0.59</td>
</tr>
<tr>
<td>77.0</td>
<td>52.2</td>
<td>27.0</td>
<td>1.02</td>
<td>0.79</td>
</tr>
<tr>
<td>90.0</td>
<td>32.4</td>
<td>23.1</td>
<td>0.96</td>
<td>0.69</td>
</tr>
<tr>
<td>105.0</td>
<td>38.8</td>
<td>17.5</td>
<td>0.74</td>
<td>0.61</td>
</tr>
<tr>
<td>120.0</td>
<td>24.4</td>
<td>16.8</td>
<td>0.66</td>
<td>0.63</td>
</tr>
<tr>
<td>135.0</td>
<td>41.5</td>
<td>14.8</td>
<td>0.46</td>
<td>0.57</td>
</tr>
<tr>
<td>300</td>
<td>28.9</td>
<td>---</td>
<td>2.25</td>
<td></td>
</tr>
</tbody>
</table>

$^a$The intensities here refer only to the peak heights and not to the area under the curves.
Table 2. Crystal field parameters as determined from a best fit to the temperature dependence of the nuclear quadrupole interaction for both TmRu$_2$ and TmMn$_2$

<table>
<thead>
<tr>
<th></th>
<th>TmRu$_2$</th>
<th>TmMn$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2$</td>
<td>$-79.6$ cm$^{-1}$</td>
<td>$-47.2$ cm$^{-1}$</td>
</tr>
<tr>
<td>$C_4$</td>
<td>$-7.2$ cm$^{-1}$</td>
<td>$-9.7$ cm$^{-1}$</td>
</tr>
<tr>
<td>$C_6$</td>
<td>$-0.8$ cm$^{-1}$</td>
<td>$-4.7$ cm$^{-1}$</td>
</tr>
<tr>
<td>$C_4'$</td>
<td>$-213.3$ cm$^{-1}$</td>
<td>$-100.5$ cm$^{-1}$</td>
</tr>
<tr>
<td>$C_6'$</td>
<td>$-4.1$ cm$^{-1}$</td>
<td>$-6.4$ cm$^{-1}$</td>
</tr>
<tr>
<td>$C_6''$</td>
<td>$9.2$ cm$^{-1}$</td>
<td>$60.4$ cm$^{-1}$</td>
</tr>
<tr>
<td>$\rho_1$</td>
<td>$-6.57 \times 10^{-6}$</td>
<td>$-9.93 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\rho_2$</td>
<td>$1.28 \times 10^{-6}$</td>
<td>$-4.16 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
Table 3. Ionic energy levels and associated wave functions for TmRu$_2$

<table>
<thead>
<tr>
<th>Energy (cm$^{-1}$)</th>
<th>Degeneracy</th>
<th>Wave Function</th>
<th>$&lt;3J_z^2 - J^2&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1</td>
<td>$-0.7051 +6&gt;-0.0621 +3&gt;-0.01910&gt;-0.0621 -3&gt;-0.7041 -6&gt;$</td>
<td>65.3</td>
</tr>
<tr>
<td>0.1</td>
<td>1</td>
<td>$-0.7051 +6&gt;-0.0581 +3&gt;0.0581 -3&gt;0.7051 -6&gt;$</td>
<td>65.5</td>
</tr>
<tr>
<td>37.9</td>
<td>2</td>
<td>$-0.9791 +5&gt;-0.1991 +2&gt;-0.0371 -1&gt;0.0261 -4&gt;$</td>
<td>30.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-0.9791 -5&gt;-0.1991 -2&gt;-0.0371 +1&gt;-0.0261 +4&gt;$</td>
<td></td>
</tr>
<tr>
<td>58.8</td>
<td>2</td>
<td>$0.0501 +5&gt;-0.0671 +2&gt;-0.3251 -1&gt;-0.9421 -4&gt;$</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.0501 -5&gt;-0.0671 -2&gt;-0.3251 +1&gt;-0.9421 +4&gt;$</td>
<td></td>
</tr>
<tr>
<td>70.4</td>
<td>1</td>
<td>$-0.0601 +6&gt;0.6041 +3&gt;0.51410&gt;0.6041 -3&gt;-0.0601 -6&gt;$</td>
<td>-21.6</td>
</tr>
<tr>
<td>79.3</td>
<td>1</td>
<td>$-0.0581 +6&gt;0.7051 +3&gt;-0.7051 -3&gt;0.0581 -6&gt;$</td>
<td>-14.5</td>
</tr>
<tr>
<td>85.3</td>
<td>2</td>
<td>$-0.1911 +5&gt;0.9031 +2&gt;0.3341 -1&gt;-0.1901 -4&gt;$</td>
<td>-27.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-0.1911 -5&gt;0.9031 -2&gt;0.3341 +1&gt;-0.1901 +4&gt;$</td>
<td></td>
</tr>
<tr>
<td>90.0</td>
<td>2</td>
<td>$-0.0501 +5&gt;0.3741 +2&gt;-0.8841 -1&gt;0.2761 -4&gt;$</td>
<td>-34.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-0.0501 -5&gt;0.3741 -2&gt;-0.8841 +1&gt;0.2761 +4&gt;$</td>
<td></td>
</tr>
<tr>
<td>92.3</td>
<td>1</td>
<td>$0.0201 +6&gt;-0.3631 +3&gt;0.85810&gt;-0.3631 -3&gt;0.0201 -6&gt;$</td>
<td>-34.8</td>
</tr>
</tbody>
</table>
that this value of $C_2^0$ would lead to a larger crystal field splitting than was observed, a larger shielding factor ($\sigma_2$) was assumed than was used for TmRu$_2$. The value of $C_2^0$ was set at $-500 \text{ cm}^{-1}$. Lattice vectors for TmMn$_2$ are $a = 5.241 \text{ Å}$ and $c = 8.565 \text{ Å}$ leading to a $c/a$ ratio of 1.634 (53). Lattice sum calculations led to the following ratios between crystal field parameters:

\[
\begin{align*}
C_4^0/C_6^0 &= 13.0 \\
C_4^3/C_4^0 &= 16.9 \\
C_6^0/C_6^0 &= 1.4 \\
C_6^6/C_6^0 &= -2.12.
\end{align*}
\]

An assumed maximum multiplet splitting of $70^\circ \text{K}$ led to a value of $-2 \text{ cm}^{-1}$ for $C_6^0$. The following guesses were then made for the other crystal field parameters:

\[
\begin{align*}
C_2^0 &= -500 \text{ cm}^{-1}, & C_4^0 &= -20 \text{ cm}^{-1}, \\
C_6^0 &= -2 \text{ cm}^{-1}, & C_4^3 &= -346 \text{ cm}^{-1}, \\
C_6^3 &= -3 \text{ cm}^{-1}, & C_6^6 &= 33 \text{ cm}^{-1}, \\
\rho_1 &= -1.36 \times 10^{-5}, & \rho_2 &= 2.8 \times 10^{-5}.
\end{align*}
\]

The temperature dependence of the quadrupole interaction in TmMn$_2$ is presented in Fig. 5. The quadrupole splitting falls off more rapidly with temperature than in TmRu$_2$. The data are shown in Table 4. Crystal field parameters determined
Fig. 5. Temperature dependence of the Tm$^{169}$ nuclear quadrupole interaction in TmMn$_2$. The solid line is the best fit of Eq. 28 to the data points.
Table 4. Mossbauer effect data for TmMn$_2$

<table>
<thead>
<tr>
<th>Temperature ($^\circ$K)</th>
<th>Linewidth (mm/sec)</th>
<th>Quadrupole splitting (mm/sec)</th>
<th>Intensity$_1$ (%)</th>
<th>Intensity$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.0</td>
<td>51.6</td>
<td>64.2</td>
<td>0.76</td>
<td>0.42</td>
</tr>
<tr>
<td>20.4</td>
<td>48.6</td>
<td>54.4</td>
<td>0.81</td>
<td>0.58</td>
</tr>
<tr>
<td>25.0</td>
<td>56.8</td>
<td>47.6</td>
<td>0.55</td>
<td>0.40</td>
</tr>
<tr>
<td>30.0</td>
<td>51.9</td>
<td>41.3</td>
<td>0.65</td>
<td>0.33</td>
</tr>
<tr>
<td>35.0</td>
<td>53.5</td>
<td>33.9</td>
<td>0.60</td>
<td>0.48</td>
</tr>
<tr>
<td>50.0</td>
<td>42.2</td>
<td>23.1</td>
<td>0.90</td>
<td>0.41</td>
</tr>
<tr>
<td>65.0</td>
<td>33.5</td>
<td>16.2</td>
<td>0.73</td>
<td>0.30</td>
</tr>
<tr>
<td>77.0</td>
<td>30.6</td>
<td>14.9</td>
<td>0.92</td>
<td>1.06</td>
</tr>
<tr>
<td>105.0</td>
<td>33.3</td>
<td>14.1</td>
<td>0.50</td>
<td>0.71</td>
</tr>
<tr>
<td>300</td>
<td>34.2</td>
<td>----</td>
<td>2.01</td>
<td></td>
</tr>
</tbody>
</table>

*The intensities here refer only to the peak heights and not to the area under the curves.*
by a best fit to the data are exhibited in Table 2. The ionic energy levels and associated wave functions are shown in Table 5.

C. Shielding Factors

In this section we will introduce the various shielding factors which, up to this point, have been only briefly mentioned. Considerable shielding of the crystal field potential by the outer $5s^2p^6$ electrons is expected. As mentioned earlier, opinions as to the nature and extent of this shielding are varied. However, we will continue our analysis by introducing the usual shielding factors and proceed on the basis that shielding is, indeed, important. No attempt will be made to determine the values of these shielding parameters explicitly since the calculations of the unshielded quantities are uncertain.

The distortion of an ion's closed shells by an external crystalline field and the contributions of such distortions to the electric field gradient at the nucleus of the ion were first investigated by Sternheimer (54, 55, 56, 57). Shielding of the external crystalline electric field at the $4f$-electrons of the rare-earth ion has been shown to be important for the $A_2^0$ crystal field parameter whereas for the other crystal field terms $A_4^m$ with $l > 2$, shielding produces a negligible effect (58). The crystal field parameter $A_2^0$ occurring in the expansion of the crystal field potential differs from the experimentally
Table 5. Ionic energy levels and associated wave functions for TmMn$_2$

<table>
<thead>
<tr>
<th>Energy (cm$^{-1}$)</th>
<th>Degeneracy</th>
<th>Wave Function</th>
<th>$&lt;\text{J}_{z}^{2} - \text{J}^{2}&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1</td>
<td>0.699</td>
<td>+6&gt;+0.047</td>
</tr>
<tr>
<td>0.8</td>
<td>1</td>
<td>-0.707</td>
<td>+6&gt;-0.026</td>
</tr>
<tr>
<td>31.9</td>
<td>2</td>
<td>-0.693</td>
<td>+5&gt;-0.317</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.693</td>
<td>-5&gt;-0.317</td>
</tr>
<tr>
<td>39.2</td>
<td>1</td>
<td>-0.105</td>
<td>+6&gt;+0.345</td>
</tr>
<tr>
<td>41.1</td>
<td>2</td>
<td>-0.575</td>
<td>+5&gt;+0.329</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.575</td>
<td>-5&gt;+0.329</td>
</tr>
<tr>
<td>50.2</td>
<td>2</td>
<td>0.384</td>
<td>+5&gt;+0.351</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.384</td>
<td>-5&gt;+0.351</td>
</tr>
<tr>
<td>51.0</td>
<td>1</td>
<td>0.006</td>
<td>+6&gt;+0.615</td>
</tr>
<tr>
<td>61.6</td>
<td>2</td>
<td>-0.202</td>
<td>+5&gt;+0.817</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.202</td>
<td>-5&gt;+0.817</td>
</tr>
<tr>
<td>68.5</td>
<td>1</td>
<td>0.026</td>
<td>+6&gt;-0.707</td>
</tr>
</tbody>
</table>
determined parameter \( A_2^0 \) due to the electronic shielding. They are related as follows

\[
A_2^0 = A_2^0 (1 - \sigma_2),
\]

the shielding being expressed by the factor \( \sigma_2 \). In their work on the rare-earth trichlorides, Lenander and Wong concluded that "huge" shielding of \( A_2^0 \) occurred (18). Calculations of \( \sigma_2 \) for \( \text{Tm}^{3+} \) ions vary all the way from 0.1 to 0.59 (21, 58, 59). The most recent calculation by Sternheimer gives \( \sigma_2 = 0.48 \) (59). Thus, shielding effects for the \( A_2^0 \) term are large.

Antishielding effects induced in closed shells by an external crystalline field are incorporated in the Sternheimer antishielding factor \( \gamma_\infty \), such that the total electric field gradient at the nucleus is

\[
q'_Z = q_z(1 - \gamma_\infty),
\]

where \( q_z(1) \) is the gradient due to the external environment (60). For ions consisting of other than closed s shells, \( \gamma_\infty \) is negative and large, typically \(-10\) to \(-100\) (61).

The other shielding factor normally introduced is \( R_Q \). An electric field gradient produced by the polarized 4f-electrons is modified by the distortion of the inner closed shells of the ion. The resultant field gradient at the nucleus is then

\[
q'_Z = q_z(1 - R_Q).
\]
This factor is introduced into the calculations by replacing
the $<r^{-3}>_{4f}$ integral by the effective parameter $<r^{-3}>_q$ as
defined in Eq. 25. Recent calculations by Sternheimer (59)
give $\gamma_\infty = -75.3$ and $B_Q = 0.24$ for Tm$^{3+}$ ions.

In the salts investigated by Barnes et al. (3) the com­
plicating effect of the conduction electrons was not present.
This allowed them to determine the ratio $(1 - \gamma_\infty)/(1 - \sigma_2)$
directly from a measurement of $\rho_2$. Values of 250 and 130 were
determined for Tm-ethylsulfate and Tm$_2$O$_3$, respectively.

In the present investigation we are not able to determine
this ratio directly. If we assume that the calculation of $C^0_2$
for TmRu$_2$ is correct and make use of Eqs. 11 and 28, then we
can determine $\sigma_2 = 0.73$. Using Sternheimer's value for $\gamma_\infty$ of
-75.3 (59) we get a value of 282 for this ratio. Then, using
our values for $\rho_2$ and $C^0_2$, the theoretical value of Oleson and
Elbek (62) for $Q = 1.5b$, and Judd and Lindgren's value for
$<r^2>_{4f} = 0.19 \times 10^{-16}$ cm$^2$ (49), we can determine a value for
$q_{zz}^{(c)}$ using Eq. 27. For TmRu$_2$ we have $q_{zz}^{(c)} = -3.82 \times 10^{24}$
cm$^{-3}$. This compares with a value of $5.41 \times 10^{22}$ cm$^{-3}$ calcu­
lated for the lattice contribution. The lattice contribution
must, however, be multiplied by the quantity $(1 - \gamma_\infty)$ for a
direct comparison at the nucleus. This result indicates that
the conduction electron contribution to the electric field
gradient is comparable in magnitude and opposite in sign to
the lattice contribution.
The comparison of the shielding factors for TmMn$_2$ is not so direct. If the calculated value of $C^0$ is correct, a value for $\sigma_2$ of 0.98 must be given. None of the calculations for $\sigma_2$ yield a value of this magnitude as was pointed out earlier. The discrepancies are probably tied up with the conduction electrons. It was assumed that the Tm was a trivalent ion and the Mn was a divalent ion. If the conduction electrons are localized about the ions, the effective charges at the ion site would be reduced. This would reduce the lattice contribution to the field gradient and bring it more in line with what is observed. Since we cannot determine how much localization is present from our experiments, we will assume that $\sigma_2$ is the same as it is in TmRu$_2$ and determine a possible contribution of the conduction electrons in TmMn$_2$. We thus find that $\sigma_{zz}(c) = -2.84 \times 10^{24}$ cm$^{-3}$. This compares with the value of $4.17 \times 10^{23}$ cm$^{-3}$ calculated for the lattice contribution in this compound. It appears that the conduction electron contribution in TmMn$_2$ is less than that in TmRu$_2$, though it is difficult to say anything very quantitative about these results. Here again, the conduction electron contribution is in opposition to the lattice field gradient.
V. DISCUSSION

A. Crystal Field Effects

The main purpose of this study was to investigate crystal field effects in intermetallic compounds. The results of the previous section show clearly that the crystal field effects in these compounds are large, though not as large as in rare-earth salts, and that the Mössbauer effect via the nuclear quadrupole interaction can be used to investigate them.

Maximum quadrupole splittings at low temperatures are quite close to those found by Barnes et al. (3) for Tm-ethyl-sulfate and Tm$_2$O$_3$. Over-all crystal field splittings in the intermetallic compounds are smaller than in these Tm salts, a result which is reflected in a more rapid decrease in the quadrupole splitting with increasing temperature. This is to be expected, since covalent bonds in the salts produce large crystal field effects.

Data for TmRu$_2$ were collected for temperatures down to 4.2°K, however, at this temperature the Mössbauer effect resonances were not well resolved for reasons to be discussed shortly. The quadrupole interaction in TmMn$_2$ was observed only down to 15°K. A magnetic ordering temperature of 12 ±2°K has been reported for TmMn$_2$ (8) and it was desirable to stay above this temperature to avoid the added complications of the exchange interaction. A run was made at 4.2°K in an effort to observe the expected magnetic hyperfine spectrum, however, a
search between velocity limits of ±16 cm/sec revealed no sign of any Mössbauer effect resonances. The reasons for this are not clear, but may be connected with sample inhomogeneities to be discussed later. Most of the quadrupole splittings fall well within experimental error of the fitted lines even though the resonances which compose the Mössbauer effect spectra were not well resolved.

The crystal field parameters determined by this analysis compare quite favorably with the values predicted by the point ion calculations with the values for TmMn₂ showing the largest differences. It is to be noted that the parameter C₄ is dominant in the potential characterizations of both compounds. Margolis (63), in his investigation of PrCl₃ (C₃ᵥ symmetry), found that of the four crystal field parameters necessary to characterize the potential, C₆ was dominant. In calculating parameters for the rare-earth double-nitrates (C₃ᵥ symmetry), Judd (64) found that the important parameters were also of the type C₆. In this respect the analysis showed results very similar to those of Elliott and Stevens (65) for the rare-earth ethylsulfates (C₃ᵥ symmetry) where C₆ and C₆ dominate. In both of these latter cases, the parameter C₂ was found to be small and to play a minor role in the calculations. The findings of Wong and Richman (26) on Tm-ethylsulfate confirm these conclusions. All of these compounds are salts and have no conduction electrons. It is not known exactly how to take
account of the conduction electrons in this static field model, but it would appear that they should affect the $C_2^0$ term most of all. Any field gradient produced by the conduction electrons should be summed with the lattice field gradient and appear in $C_2^0$ through the relation described by Eq. 16. If, however, the conduction electrons are localized about the positive ions, they would reduce the effective charge at the ion sites and affect all of the crystal field parameters through the ordinary lattice sums. It is difficult to determine the exact effect of the conduction electrons from our results.

Throughout this work, it was noted that the fitting procedure was considerably more sensitive to some of the parameters than to others. This is reflected in the fact that some of the parameters were changed only slightly from the initial guesses. For this reason no claim is made as to the uncertainties involved in the final results. The only claim that can be made is that this is certainly a set of parameters which leads to the desired temperature dependence of the quadrupole interaction. It would be very advantageous to be able to reduce the number of independent parameters in some way and get a better determination of those remaining. One possible way of reducing the number of independent parameters was pointed out by Judd (24). Since the ratio $A_2^0/A_0^0$ eliminates the dependence on the 4f-wave functions if the static crystal field model is valid, the theoretical ratio should be maintained in
the experimental values. This idea was used to determine the values of the parameters for the initial guesses in the present study but the constraint was not imposed during the fitting procedure. It is interesting to note that the theoretical ratios for $A^6_6/A^0_6$ and $A^3_6/A^0_6$ were maintained but the ratio $A^3_4/A^0_4$ was not. This was true in both compounds.

Calculations of crystal field effects involving other than point charges are still rather primitive. Hutchings and Ray (66) derive a general expression for the contribution of induced moments of any order on neighboring ions to the crystalline electric field potential at the rare-earth site in PrCl$_3$. This expression was then used to evaluate the contribution of induced dipoles and induced quadrupoles to the crystalline electric potential at the Pr$^{3+}$ site. Although the contribution of the induced moments to the potential was found to be significant, there were still large discrepancies between calculated and experimental values. These discrepancies were attributed to covalency effects and screening of the outer rare-earth electrons.

As indicated in the previous section, the results obtained for TmRu$_2$ seem to be more consistent with the predicted values than those obtained for TmMn$_2$. This may be the result of an incorrect assumption as to the ion charges present in the TmMn$_2$ lattice. Even though it seemed straightforward to assume that the Mn was a divalent ion, this may not be the case.
Neutron diffraction work on TmMn$_2$ by Felcher et al. (8) indicates there is no moment at the Mn site. This is certainly not consistent with the idea that Mn is doubly ionized since it should then be an S state ion with a 3d$^5$ configuration and it should have a large, spin only, moment. It is difficult to imagine a possible electronic configuration which would result in the complete loss of the Mn moment.

Though nothing quantitative can be said about the conduction electron contributions in these two compounds since they are minor contributors to the electric field gradient at the nucleus, it is interesting to note that the sign was negative in both cases and opposite to the lattice contribution. Das and Pomerantz, in discussing nuclear quadrupole interactions in metals (67) tacitly assumed the two contributions to be of the same sign. Hewitt and Taylor (68), however, remarked on the possibility that these contributions might have opposite signs in the case of metallic indium. Torgeson and Barnes (31), in an analysis of hcp lanthanum, found that the conduction electron contribution is opposite in sign to the lattice contribution. Das and Pomerantz (67) show that in many cases, the lattice contribution to the nuclear field gradient may be expected to be much smaller than the contribution of the conduction electrons.
B. Low Temperature Effects on the Mössbauer Resonance

An experimental fact, which may be readily observed in Tables 1 and 4, is the decreasing intensity and associated broadening of the Mössbauer resonance at low temperatures. The minor fluctuations with temperature are not to be considered as significant as they probably originated from experimental inconsistencies, but the large change from room temperature to the low temperatures is significant. This effect was observed in both intermetallic compounds studied and is assumed to be characteristic of them. This is quite the opposite effect expected from basic Mössbauer effect theory which predicts the intensity of the lines should increase as the temperature is decreased due to an increasing recoilless fraction. A comparison of the areas under the curves indicates that the problem is not associated with a decrease in the number of recoilless nuclei. Broadening of the lines due to the exchange interaction is expected to be noticeable only at temperatures near the magnetic ordering temperatures of the compounds. The magnetic ordering temperature of TmRu$_2$ is not known, but it very likely falls below 2°K, since the electronically similar compound TmNi$_2$ appears to order below 2°K (5). The magnetic ordering temperature of TmMn$_2$ is 12 ±2°K (8). Broadening is, however, noticeable in both compounds even at 77°K. This would seem to rule out the exchange interaction as the source of the broadening. These effects are not related to the spectrometer
since the quadrupole splitting in Tm$_2$O$_3$ was observed at 4.2°K using the maximum velocity of the system and showed no anomalous broadening. The spectrum observed at 4.2°K is shown in Fig. 6.

A possible explanation of this strange behavior is that a range of crystal field potentials exists in these compounds. Instead of having a unique value as is tacitly assumed, the crystal potential varies at the Tm$^{3+}$ sites throughout the lattice. Impurities in the lattice, strains and other lattice imperfections could give rise to such variations. Such imperfections are common in metals but can normally be annealed out. However, these are intermetallic compounds which have melting points at approximately 2700°C. In order to properly anneal them a temperature of about 100°C below the melting point should be maintained for at least 2 hours. These compounds undergo a peritectic reaction, so that as they are heated, other phases form at temperatures well below the melting point of the desired compound. In order to maintain a homogeneous compound, the temperature must not be raised above that at which the peritectic reaction takes place. In these compounds the peritectic reaction begins about 1000°C below the melting point. The sample of TmRu$_2$ was annealed at 1650°C for 22 hours. Metallographic analysis showed no inclusions indicating only a single phase to be present. This annealed sample showed no change in the Mössbauer effect resonance.
Fig. 6. Mössbauer effect spectrum of Tm₂O₃ at 4.2°K. The source was Er₂O₃ at 400°C. This spectrum was recorded in an effort to determine whether or not the spectrometer was responsible for the anomalous broadening of the resonances at low temperatures. The lines in this spectrum have half-widths of 23.3 mm/sec and 16.6 mm/sec, thereby showing no broadening at this temperature.
The conclusion which we reached is that the anomalous line broadening and decreasing signal intensity is probably due to a range of crystal field potentials in the sample which could not be effectively annealed out because of a peritectic reaction which occurred at temperatures which were far below the melting point of the compound. The Mössbauer effect measurements then effectively measured an average quadrupole interaction of the nucleus.

C. Asymmetries

An asymmetry in the intensities of the two lines of the Mössbauer effect spectrum was also noted. Goldanskii was the first to give a plausible explanation for this phenomenon (69). In cases where the symmetry of a crystal lattice is less than cubic, the recoil-free fraction may be anisotropic, i.e., the bonds which hold the atom in the lattice may be stronger in one crystal direction than in another. This anisotropic recoil-free fraction, when averaged over all possible crystal orientations, leads to an asymmetry in line intensity. This asymmetry is enhanced at high temperatures.

More recently, Blume has shown that asymmetries in Mössbauer effect quadrupole resonances can arise due to paramagnetic relaxation effects (70). These effects are due to finite relaxation times of the ionic states. Magnetic exchange effects average out completely only if the relaxation is infinitely fast compared with the lifetime of the excited
nuclear state. In many cases, however, especially at low temperatures, this condition is not met. The magnetic interaction is not completely averaged out and begins to broaden the lines. Bradford and Marshall have recently extended Blume's work and have shown that the line which is due to the $^{3/2} \rightarrow ^{1/2}$ transition is broader and less intense than the $^{1/2} \rightarrow ^{1/2}$ line (71). This type of asymmetry would become more pronounced at low temperatures.

It is difficult to explain our results in terms of relaxation time effects because in metals the direct spin-lattice relaxation between the atomic spins and the conduction electrons is usually so effective that the relaxation time is too fast to permit observing this effect. Bradford and Marshall had to consider dilute materials in order to make the relaxation time long enough to make their effect observable.

The temperature dependence, if any, is not clear in our case because of the added complication of line broadening and decreasing intensity due to other effects already considered. The only justifiable conclusion at this point is that the asymmetry is probably due to an anisotropic recoil-free fraction.
VI. LITERATURE CITED


55. Sternheimer, R. M., Phys. Rev. 84, 244 (1951).
VII. ACKNOWLEDGMENTS

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VIII. APPENDIX A

We include the details of the calculations of the lattice electric field gradient by the plane-wise summation method of de Wette (48). As pointed out in Section IV, the MgZn$_2$ crystal structure under investigation has four formula units per unit cell. The volume of the unit cell is $(\sqrt{3}/2)a^2c$. The analysis for the two compounds studied, TmRu$_2$ and TmMn$_2$, is slightly different. Thulium was assumed to be trivalent in both compounds. However, Ru was assumed to be neutral and Mn was assumed to be divalent in TmRu$_2$ and TmMn$_2$ respectively.

The sums to be considered are $S_{0,0,0}$; $S_{0,0,3/8}$; $S_{1/3,1/3,1/2}$; $S_{1/3,1/3,1/2}$; $S_{1,2,1/2,3/16}$; $S_{1,2,0,3/16}$; $S_{0,1/2,3/16}$; $S_{5/6,5/6,11/16}$; $S_{5/6,1/3,11/16}$; $S_{1/3,5/6,11/16}$; $S_{2/3,2/3,3/15}$; $S_{2/3,2/3,15/16}$; $S_{2/3,2/3,7/15}$; $S_{2/3,2/3,7/16}$; $S_{5/6,2/3,15/16}$; $S_{5/6,2/3,7/16}$; $S_{1/3,1/3,1/2}$; $S_{1/3,1/3,1/2}$; $S_{1,2,1/2,3/16}$; $S_{1,2,0,3/16}$; $S_{0,1/2,3/16}$; $S_{5/6,5/6,11/16}$; $S_{5/6,1/3,11/16}$; $S_{1/3,5/6,11/16}$; $S_{2/3,2/3,3/15}$; $S_{2/3,2/3,15/16}$; $S_{2/3,2/3,7/15}$; $S_{2/3,2/3,7/16}$. For a definition of these terms, see Ref. 48. They may be written in the following forms for these calculations

$$S_{0,0,0} = \frac{1}{a^3} \left[ -11.0341754 + \frac{8\pi^2}{\sqrt{3}} \sum \frac{n_1 h_1 e^{\alpha n_1 h_1}}{\sinh(h_1 \pi a)} \right]$$

$$S_{0,0,3/8} = \frac{8\pi^2}{\sqrt{3} a^3} \left[ \sum n_1 h_1 \cosh(h_1 \pi a/4) \right]$$
\[ S_{1/3, 1/3, 1/2} = \frac{8\pi^2}{\sqrt{3a^3}} \left[ \sum_{n} \frac{n_i h_i c_i}{\sinh(h_1 \pi \alpha)} \right] \]  

\[ S_{1/3, 1/3, 7/8} = \frac{8\pi^2}{\sqrt{3a^3}} \left[ \sum_{n} n_i h_i c_i \frac{\cosh(3/4 h_1 \alpha)}{\sinh(h_1 \pi \alpha)} \right] \]  

\[ S_{1/3, 1/3, 7/8} = S_{1/2, 1/2, 3/16} = S_{0, 1/2, 3/16} \]

\[ = \frac{8\pi^2}{\sqrt{3a^3}} \left[ \sum_{n} n_i h_i c_i \frac{\cosh(3/4 h_1 \alpha)}{\sinh(h_1 \pi \alpha)} \right] \]  

\[ S_{5/6, 5/6, 11/16} = \frac{8\pi^2}{\sqrt{3a^3}} \left[ \sum_{n} n_i h_i b_i \frac{\cosh(3/4 h_1 \alpha)}{\sinh(h_1 \pi \alpha)} \right] \]  

\[ S_{5/6, 1/3, 11/16} = S_{1/3, 5/6, 11/16} \]

\[ = \frac{8\pi^2}{\sqrt{3a^3}} \left[ \sum_{n} n_i h_i b_i \frac{\cosh(3/4 h_1 \alpha)}{\sinh(h_1 \pi \alpha)} \right] \]  

\[ S_{2/3, 2/3, 15/16} = \frac{8\pi^2}{\sqrt{3a^3}} \left[ \sum_{n} n_i h_i c_i \frac{\cosh(7/8 h_1 \alpha)}{\sinh(h_1 \pi \alpha)} \right] \]  

\[ S_{2/3, 2/3, 7/16} = \frac{8\pi^2}{\sqrt{3a^3}} \left[ \sum_{n} n_i h_i c_i \frac{\cosh(1/8 h_1 \alpha)}{\sinh(h_1 \pi \alpha)} \right] \]  

For TmRu$_2$ these sums are combined as follow:

\[ q^{(lig)} = 8\pi v + \sum_{n} \left[ S_{0, 0, 0} + S_{0, 0, 3/8} + S_{1/3, 1/3, 1/2} + S_{1/3, 1/3, 7/8} \right] = 5.41 \times 10^{22} \text{ cm}^{-3} \]
where \( v = \left(\frac{\sqrt{3}}{8}\right)c a^2 \) is the volume per ion and \( Z \) is the charge per ion. For \( \text{TmMn}_2 \) the sums are combined as follows

\[
q(\text{lig}) = 8Z_1 \frac{\pi}{3} v_1 + Z_1 \left[ S_{0,0,0} + S_{0,0,3/8} + S_{1/3,1/3,1/2} + S_{1/3,1/3,7/8} + 8Z_2 \frac{\pi}{3} v_2 + Z_2 \left[ S_{1/2,1/2,3/16} + S_{1/2,0,3/16} + S_{0,1/2,3/16} + S_{5/6,5/6,11/16} + S_{5/6,1/3,11/16} + S_{1/3,5/6,11/16} + S_{2/3,2/3,15/16} + S_{2/3,2/3,7/16} \right] \right] = 4.17 \times 10^{23} \text{ cm}^{-3}
\]

where \( v_1 = \left(\frac{\sqrt{3}}{8}\right)c a^2 \) is the volume per Tm ion, \( v_2 = \left(\frac{\sqrt{3}}{16}\right)c a^2 \) is the volume per Mn ion and \( Z_1 \) and \( Z_2 \) are the ionic charges on the Tm and Mn ions respectively.
IX. APPENDIX B

The computations involved in the analysis of experimental data presented in this paper were carried out with the aid of an IBM 360/50 computer. This section contains the listings of the Fortran computer programs that were used. The analysis involved two major steps.

1) VMMIN... A least squares fitting to the experimental Mössbauer effect data of two Lorentzian lines using the method of Davidon (47).

2) VMM... A least squares fitting of Eq. 28 to the experimentally determined variation of the nuclear quadrupole interaction with temperature also using the method of Davidon (47).

Some of the programs used are available in the SHARE library and are not included here.
The required decks are:

1. MAIN1
2. PREP
3. FCN
4. MATMPY
5. READY
6. AIM see SHARE No. 980
7. FIRE ZO ANFZ013
8. DRESS
9. STUFF

The listings of decks 1-3 follow.
MAIN...

THIS IS THE CONTROLLING PROGRAM FOR THE MINIMIZATION ROUTINE WHICH FITS
LINES OF PRESCRIBED SHAPES TO THE MOSSBAUER EFFECT DATA. COMMUNICATION
WITH SUBPROGRAMS IS VIA COMMON.

INPUT DATA
TITLE(I)=DESIGNATION OF PARTICULAR RUN
NJ=NUMBER OF LINES BEING FITTED
NP=TOTAL NUMBER OF DATA POINTS INVOLVED IN THE FITTING
NC=NUMBER OF CONSTRAINTS ON PARAMETERS
NL=INDICATES WHETHER OR NOT GEOMETRIC EFFECT IS TO BE CORRECTED
K=NUMBER OF RANDOM STEPS AT END OF MINIMIZATIÖN
ID=PARAMETER WHICH INDICATES WHETHER LORENTZIAN OR GAUSSIAN LINE-
SHAPES ARE TO BE FITTED TO THE DATA
NR,NS,NU, AND NV ARE PARAMETERS USED TO INDICATE VARIOUS OPTIONS FOR
PUTTING OUT RESULTS OF CALCULATION
E=PARAMETER USED TO INDICATE WHEN MINIMUM HAS BEEN REACHED
P=RANDOM STEP SIZE
XI(I)=ARE GUESSES FOR PARAMETERS TO BE DETERMINED IN MINIMIZATION

PROCEDURE
VARIABLE METRIC MINIMIZATION METHOD APPLIED TO MOSSBAUER EFFECT DATA
TA. REVISED OCT. 1965, D.J. GENIN

DIMENSION H(40,40),X(40),G(40),S(40),XP(40),GP(40),T(40),GB(40),CI
140,25),XD(400),YD(400),TITLE(40),YC(400)

COMMON H,X,G,S,XP,GP,T,GB,XD,YD,M0,NS,LS,ML,MS,NS,IT,GS,GSP,GTP
1,GSS,GT,GGB,F,FP,F0,EP,K,T0,RS,SL,S,SA,EL,DELTA,NC,IP,ID,NJ,
2,J1,J2,J3,J4,J5,NU,NV,XR,NL,J3,J6,YC

100 MS=0
101 IX=0
104 READ (1,11) I,1=1,40
105 READ (1,2) NJ,NP,NC,NL,K,ID,NS,NU,NV,E,P
106 IF (NJ) 107,107,108
107 STOP 88
108 N=3*NJ+1+NL
109 DELTA=1.0
110 XR=0.5
111 NNFH=0
112 NTSD=0
114 IF (E)115,115,116
115 E=1.0E-3
116 IF (P)119,119,117
117 P=SQRT(FLOAT(NP))
118 P=SQRT(2.0*P)
119 IF (K)121,120,121
120 K=3
121 J1=NJ+1
122 J2=J1+NJ
123 J4=J2+NJ
124 J5=J2+1
125 DO 127 I=1,N
126 DO 127 J=1,N
127 H(I,J)=0.0
128 IF (NS)129,131,140
129 READ (1,3) X(J),J=J5,J3)
167  YXI=YO(I)
169  XIJA=1.0-YXI/X(1)
170  YT=(YXI+X(1))/2.0
171  IJ=I-1
172  GO TO 174
173  IJ=IJ-1
174  IF (YD(IJ)-YT)173,173,175
175  X2=XD(IJ)
176  IJ=I+1
177  GO TO 179
178  IJ=IJ+1
179  IF (YD(IJ)-YT)178,178,180
180  XI=XD(IJ)
181  XIJB=XI-X2
182  H(JA,JA)=1.0/(X(IJB)*YXI)
183  H(JB,JB)=X(IJB)/X(JA)**2/YXI
185  H(JX,JX)=H(JB,JB)
186  IF (NL)186,186,94
94  DO 81 J=1,NL
95  JC=3*NJ+1+J
81  H(JC,JC)=(0.003*X(JC))**2
186  WRITE (3,7)
187  WRITE (3,5)(TITLE(I),I=1,40)
188  WRITE (3,8)(NJ,NP,NC,K,IT,ID*NR,NS,NU,NL,EG,E,P)
189  IF (IX1192,192,190
190  WRITE (3,32)(X(JX))
191  GO TO 100
192  WRITE (3,9)X(1)
193  WRITE (3,10)(X(J),J=2,J1)
194  WRITE (3,11)(X(J)),J=J4,J2)
195  WRITE (3,12)(X(J)),J=J5,J3)
196  WRITE (3,13)(X(J)),J=J6,N)
197  WRITE (3,14)H(I,1)
198  WRITE (3,10)(H(I,I),I=2,J1)
199  WRITE (3,11)(H(I,I),I=J4,J2)
200  WRITE (3,12)(H(I,I),I=J5,J3)
201  WRITE (3,13)(H(I,I),I=J6,N)
202  M1=1
203  F=0.0
204  CALL FCN(N,G,F,X,M1)
205  L=1
206  WRITE (3,15)IT,MS,F
207  WRITE (3,16)
208  IF (NC)217,217,209
209  DU 216 JJ=1,NC
210  CALL MATPY(N,NH,C(I,JJ),T)
211  CALL MATPY(N,N,T,C(I,JJ),T)
212  IF (TU-E)216,216,213
213  DU 219 JJ=1,N
214  DU 215 JJ=1,N
215  H(I,J)=H(I,J)-T(I)*T(J)/TU
216  CONTINUE
CALL READY
L=L
GO TO (241,239,237,222),L
L=2
GO TO 208
CALL AIM
L=L
GO TO (225,235,237),L
CALL FIRE
L=L
GO TO (235,228,222),L
L=1
CALL DRESS
L=L
GO TO (250,232),L
MJMP=3
NTSH=1
GU TO 257
L=2
GO TO 229
L=3
GO TO 229
L=4
GO TO 229
IF (NV)242,242,243
WRITE (3,17)0£LTA
IF (K)244,244,247
CALL STUFF
L=L
GO TO (201,260),L
MJMP=4
IF (NR-1)280,280,263
L=2
GO TO 229
L=3
GO TO 229
L=4
GO TO 229
WRITE (3,18)(X(I),I=1,N)
WRITE (3,17)DELTA
CALL SLITET(4,J)
GO TO (255,220),J
WRITE (3,20)
MJMP=1
IF (NV)258,258,263
WRITE (3,17)0£LTA
GO TO 263
WRITE (3,21)
MJMP=2
IF (NR)280,280,263
IF (NTSH)264,264,268
DO 266 I=1,N
DO 266 J=1,N
H(I,J)=2.0#H(I,J)
NTSH=1
NTSD=1
WRITE (3,22)
DO 275 I=1,N
271 WRITE (3,23)I,((I,J),J=2,J1)
272 WRITE (3,24)I,((I,J),J=2,J1)
273 WRITE (3,25)I,((I,J),J=2,J1)
274 WRITE (3,26)I,((I,J),J=J4,J3)
   IF (NL)275,275,91
275 CONTINUE
276 WRITE (3,28)G(I)
277 WRITE (3,10)(G(I),I=2,J1)
278 WRITE (3,11)(G(I),I=J4,J2)
279 WRITE (3,12)(G(I),I=J5,J3)
   IF (NL)280,280,90
280 WRITE (3,13)(G(I),I=J6,N)
281 DO 282 1=1,N
282 H(I,1)=2.0*H(I,I)
283 NTS0=1
284 WRITE (3,14)H(I,1)
285 WRITE (3,10)(H(I,I),I=2,J1)
286 WRITE (3,11)(H(I,I),I=J4,J2)
287 WRITE (3,12)(H(I,I),I=J5,J3)
   IF (NL)288,288,89
288 MJMP=MJMP
289 GO TO (290,290,300,300,290,MJMP
290 IF (NTSH)296,296,291
291 U(I,J)=U(I,J)/2.0
292 NTS1=0
293 GO TO 299
294 IF (NTS0)300,300,297
295 DO 298 1=1,N
298 H(I,1)=H(I,1)/2.0
299 NTS0=0
300 WRITE (3,29)F,GS
301 WRITE (3,9)X(I)
302 WRITE (3,10)(X(I),I=2,J1)
303 WRITE (3,11)(X(I),I=J4,J2)
304 WRITE (3,12)(X(I),I=J5,J3)
   IF (NL)305,305,88
305 MJMP=MJMP
306 GO TO (308,308,308,308,244),MJMP
307 MJMP=2
308 WRITE (3,19)M1=3
310 CALL FCHNIN(G,F,X,M1)
311 MJMP=MJMP
312 GO TO (313,100),MJMP
313 NS=2
314 WRITE (3,8)NJ,NS,N,NC,K,10,NS,NV,E,P
315 WRITE (3,9)X(I)
316 WRITE (3,10)(X(I),I=2,J1)
317 WRITE (3,11)(X(I),I=J4,J2)
318 WRITE (3,12)(X(I),I=J5,J3)
   IF (NL)319,319,87
91

37 WRITE (3,13) (X(I,1), I=1,N)
319 DO 320 I=1,N
320 WRITE (3,31) (H(I,J), J=1,N)
321 WRITE (2,6) (XD(I),YD(I), I=1,NPI
322 GO TO 100

C
1 FORMAT (20A4)
2 FORMAT (4I4,6I2,E10.4,E8.4)
3 FORMAT (12E6.0)
4 FORMAT (6E12.0)
5 FORMAT (1OH0,20A4/1X,20A4)
6 FORMAT (3(E8.4,E12.6))
7 FORMAT (SIMILAR SHAPE FITTING BY VARIABLE METRIC MINIMIZATION)
8 FORMAT (4H0Nj=11,5H NP=I3,5H NC=I2,4H K=I2,5H ID=11,5H NR=11,5H NS=11,5H NL=11,5H EG=1PE8.2/3H0E=1PE13.5
2,4H P=1E13.5)9 FORMAT (11HPARAMETERS/7HO Y(O)1PE14.5)
10 FORMAT (7HO OR G,1P8E14.5)
11 FORMAT (7HO OR G,1P8E14.5)
12 FORMAT (7HO XIJ,1P8E14.5)
13 FORMAT (7HO KIL,1P8E14.5)
14 FORMAT (34HDIAGONAL ELEMENTS OF ERROR MATRIX/7HO Y(O)1PE14.5)
15 FORMAT (4HOIT=14,6M STEP14,4H F=1PE14.5)
16 FORMAT (20HO= - - - - - - - - - - - - - - - - - - -)
17 FORMAT (7HODELTA=1PE14.5)
18 FORMAT (3HOX=1PE8E14.5/3HO 8E14.5)
19 FORMAT (20HOEND OF MINIMIZATION)
20 FORMAT (20HOPROCESS INTERRUPTED/21HOPRESENT VALUES * * *)
21 FORMAT (13HOFINAL VALUES)
22 FORMAT (13HERROR MATRIX)
23 FORMAT (5HOY(O),13,1PE14.5)
24 FORMAT (5HO A-G,13,1PE14.5)
25 FORMAT (5HO B-D,13,1PE14.5)
26 FORMAT (5HO XIJ,13,1PE14.5)
27 FORMAT (5HOK(L),13,1PE14.5)
28 FORMAT (3HOGRADIENT/7HO Y(0),1PE14.5)
29 FORMAT (3HOE=1PE4.5,5H GS=1PE14.5)
31 FORMAT (1HO,1PE12.5)
32 FORMAT (6HOP* * IN CALCULATING GUESSES - NO X(I) CAN BE FOUND EQ
31UAL TO1PE14.5)33 FORMAT (1H1,20A4/1X,20A4)
END
PREP...
THIS ROUTINE PREPARES THE DATA FROM THE MULTICHANNEL ANALYZER FOR
ANALYSIS BY THE FITTING ROUTINE. IT FOLDS AND SUMS THE TWO HALVES OF THE
DATA. THEN IT CONVERTS CHANNEL NUMBER TO VELOCITY UNITS.

INPUT DATA
IP=PARAMETER WHICH INDICATES WHETHER OR NOT PREPROCESSING WILL BE
DONE
I0=NUMBER OF DATA SETS TO BE HANDLED
NM=TOTAL NUMBER OF DATA POINTS IN EACH DATA SET
IX10=ZERO VELOCITY FOR THE FIRST HALF OF THE DATA
IX20=ZERO VELOCITY FOR SECOND HALF OF DATA
IR=NUMBER OF DATA POINTS ON EITHER SIDE OF ZERO VELOCITY TO BE
INCLUDED IN ANALYSIS
GA(I)=NUMBER OF HUNDRED THOUSANDS TO BE ADDED TO COUNTS AT EACH
DATA POINT
HA(I)=NUMBER OF MILLIONS TO BE ADDED TO COUNTS AT EACH DATA POINT
XADD(I)=CHANNEL NUMBER OF EACH DATA POINT
YDATA(I)=TOTAL COUNTS AT EACH DATA POINT

DATA PREPROCESSING ROUTINE
OCT. 1965, D.J. GENIN

DIMENSION XD(400), YD(400), XADD(400), YDATA(400), CH(400), Y2(400),
IX(400), E(6), GA(7), HA(7)

10 WRITE (3,1)
11 READ (1,2) IP, I0, NM, IX10, IX20, IR
12 READ (1,8) (GA(I), HA(I), I=1, I0)
13 Th=1.0E+05
14 TM=1.0E+06
15 IF (IP)59,15,59
16 DU 16 I=1,NM
17 DO 21 J=1, I0
18 READ (1,3) (XADD(I), YDATA(I), I=1, NM)
19 DO 21 I=1, NM
20 CH(I)=XADD(I)
21 YD(I)=YU(I)+YDATA(I)+GA(I)*TH+HA(I)*TM
22 IF (IX10-200)22,23,9
23 IA=IX10-IR-200
24 IB=IX10+IR-200
25 GO TO 24
26 IA=IX10-IR
27 IB=IX10+IR
28 IF (IX20)33,33,25
29 IC=IX20-IR
30 ID=IX20+IR
31 DO 28 I=IC, ID
32 Y2(I)=YD(I)
33 Y2(I)=YD(I)
34 INVERT SECOND HALF OF DATA AND ADD TO FIRST HALF
35 DU 32 J=IA, IB
36 L=IX10+IX20-J
31 Y2(J)=Y2(L)
32 YD(J)=YD(J)+Y2(J)
C
CONVERT TO VELOCITY
C
33 READ (1,4)C,XNW,(E(I),I=1,6)
34 UD 4 I=IA,IB
35 X10=IX10
36 Z(I)=CM(I)-X10E1.0
37 IF (XNW)38,40,38
38 X0(I)=C*XNW*SIN(Z(I)/XNW)
39 GO TO 41
40 X0(I)=C*Z(I)*(1.0+E(1)*Z(I)+E(2)*Z(I)**2+E(3)*Z(I)**3+E(4)*Z(I)**4)
   1+E(5)*Z(I)**5+E(6)*Z(I)**6
41 CONTINUE
C
WRITE TABLE OF RESULTS
C
50 WRITE (3,5)
51 WRITE (3,6)IR,C,I,X0(1),X10(1),X20(1),Z(I),XD(I),YD(I),I=1,18
52 J=1+IA-1
53 X0(J)=X0(I)
54 Y0(J)=Y0(I)
55 RETURN
57 READ (1,7)XD(I),YD(I),I=1,18
58 GO TO 57
C
1 FORMAT (20HSTART PREPROCESSING)
2 FORMAT (6I6,2E6.0)
3 FORMAT (5(F4.1,F9.3))
4 FORMAT (8E8.4)
5 FORMAT (25HRESULTS OF PREPROCESSING)
6 FORMAT (4H0IR=I3,4X,2HC=F8.5,4X,6HX(10)=I3,4X,6HX(20)=I3//5X,7HX-X
   110)=,10X,2HW=,10X,2HY=//1H,6X,F4.0,5X,F12.4,3X,E12.6)<
7 FORMAT (3(I8.4,E12.6))
8 FORMAT (14E5.0)
END
FCN

THIS ROUTINE CALCULATES THE FUNCTION TO BE MINIMIZED AS WELL AS ITS FIRST DERIVATIVE. NO INPUT DATA ARE REQUIRED AS THEY ARE PROVIDED BY THE MAIN ROUTINE.

FUNCTION EVALUATION, OCT. 1965, D.J. GENIN

SUBROUTINE FCN(N,G,F,X,M1)

DIMENSION H(40,40),XA(40),GC(40),S(40),XP(40),GP(40),T(40),GB(40),
LC(40),XO(40),YO(40),YC(40),FUNC(40),FF(40),SD(40),XPM(13)
1,XT(13),EX(13),EF(13),D(40),S2(400),FC(400),XLAB(15),YLAB(15),
3ULAB(15),GLAB(15),X(40),G(40),S3(400),FAC(400),S4(400)
COMMON H,XA,GC,XP,GP,T,GB,XD,YD,ZD,MD,NS,IT,GS,GS2,
1Q1P,GS,YT,GS2,FD,Fp,FB,FB,Es,KP,T0,RS,SL,SLR,AL,EL,DELTA,NC,NP,1D
2,NJ,J1,J2,J4,J5,J6,JN,J3,J6,YC

10 IF (M1-2)11,11,80
11 F=0.0

12 DO 19 J=1,NJ
13 K1=J+1
14 X(J)=0.0
15 K2=K1+NJ
16 IF (10)17,17,18
17 XJT(J)=0.5*X(J2)
GO TO 19
18 XJT(J)=0.5*X(J2)**2
19 CONTINUE

DO 20 JJ=1,N
20 G(JJ)=0.0

DO 54 I=1,NP
22 FAC(I)=0.0
23 DO 35 J=1,NJ
24 K=J+1
25 K2=K1+NJ
26 K3=K2+NJ
27 XPM(J)=X(DJ-X(K3)
28 IF (10)29,29,32
29 EXF(J)=XPM(J)**2+XJT(J)**2
30 EX(J)=X(JT(J)/EXF(J)
31 FAC(I)=FAC(I)+X(K1)*EX(J)*XJT(J)
GO TO 35
32 EXF(J)=XPM(J)/XJT(J)
33 EX(J)=EXP(-XPM(J)/EXF(J)
34 FAC(I)=FAC(I)+X(K1)*EX(J)
35 CONTINUE

36 FAC(I)=1.0-FAC(I)

IF (NL)37,37,150
150 YC(I)=X(I)*FAC(I)*(1.0*X(IN)*XD(I))**2
GO TO 38
37 YC(I)=X(I)*FAC(I)
38 FUNC(I)=YD(I)-YC(I)
39 FFF(I)=FUNC(I)/YD(I)
40 SD(I)=FFF(I)*FUNC(I)
41 F=F+SD(I)

C CALCULATE DERIVATIVES
CALL GRAPH(NP, XD, S2, 0, 2, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0)

CALL GRAPH(NP, XD, S3, 0, 2, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0)

CALL ORGIE(0.0, 0.0, 1)

CALL GRAPH(NP, XD, FC, 0, 2, XSIZE, 4.0, 0.0, XMIN, 0.0, 0.0, XLAB, YLAB, GLAB1, GLAB2)

CALL ORGIE(0.0, 5.0, 1)

CALL GRAPH(NP, XD, FUNC, 0, 2, XSIZE, 4.0, 0.0, XMIN, 0.0, -5.0, XLAB, YLAB, GLAB1, GLAB2)

CALL ORGIE(15.0, 0.0, 0)

CALL GRAPH(NP, XD, S4, 1312833600, 7, XSIZE, 9.0, 0.0, XMIN, 0.0, 0.0, XLAB, YLAB, GLAB1, GLAB2)

CALL GRAPH(NP, XD, S3, 0, 2, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0)

FORMAT (12H0 CONSTRAINTS)

FORMAT (IHO12, 8E14.5)

FORMAT (1H02X, 8E14.5)

FORMAT (15H0 CONSTRAINTS)

FORMAT (12H0 START TABLE//13H0 VELOCITY, 7X, 6H COUNTS, 6X, 11H CALC C COUNTS, 8X, 6H DIFF, 9X, 7H DIFF**2, 3X, 10H1-CTS/Y(0), 3X, 15H1-CALCCTS/Y(0 2))

FORMAT (1H0, 7E14.5)

FORMAT (2F6.2)

FORMAT (20A4)

END
The required decks for this routine are:

1. MAIN2
2. FCN
3. EIGEN
4. TRIDI
5. EIGVAL
6. VECTR1
7. VECTR2
8. READY
9. AIM
10. FIRE
11. DRESS
12. STUFF
13. MATMPY

The listings for decks 1-7 follow.
MAIN2...

THIS IS THE CONTROLLING ROUTINE FOR THE FIT TO THE TEMPERATURE DEPENDENCE
OF THE QUADRUPOLE SPLITTING. COMMUNICATION WITH SUBROUTINES IS VIA COMMON
INPUT DATA

TITLE(I)=DESIGNATION OF PARTICULAR RUN
NP=NUMBER OF DATA POINTS USED IN FIT
K=NUMBER OF RANDOM STEPS
E=PARAMETER USED TO INDICATE WHEN MINIMUM HAS BEEN REACHED
P=RANDOM STEP SIZE
ITAPE2 AND ITAPE2 ARE SCRATCH TAPES
X(J)=GUESSES FOR PARAMETERS DETERMINED BY FIT
XU(I)=TEMPERATURES OF DATA POINTS
YD(I)=QUADRUPOLE SPLITTING AT EACH DATA POINT

VARIABLE METRIC MINIMIZATION METHOD APPLIED TO CALCULATION OF CEF
PARAMETERS FROM TEMPERATURE DEPENDENCE OF QUADRUPOLE INTERACTION.

DIMENSION H(10,10),X(10),G(10),S(10),XP(10),GP(10),T(10),GB(10),
1XD(40),YD(40),AC(10),DE(19,6),TITLE(40),R(1)

COMMON H,X,G,S,XP,GP,T,GB,XD,YD,AC,DE,MO,LS,M,L,IT,GS,GP,TG,
1GS,GTT,GSB,F,FP,F0,EL,P,TU,SL,Z,Q,AL,DE,LS,M,L,F,FP,FB,FU,
2ITAPE1,ITAPE2

100 MS=0
READ (1,1)(TITLE(I),I=1,40)
READ (2,2)NP,K,E,P IF (NP)107,107,103
107 STOP aa
108 DELTA=1.0
READ (1,19)ITAPE1,ITAPE2
XR=0.5
NSH=0

IF (E) 115,115,116
115 F=0.0
116 E=1.0E-7
117 P=SQRT(FLOAT(NP))
P=SQR(2.0*P)
119 IF (K) 120, 120, 121
120 K=0
121 DU 127 I=1,8
128 W(I) 127 J=1,8
127 H(I,J)=0.0
READ (1,3)(X(J),J=1,8)
READ (1,4)XD(I),YD(I),I=1,10
EG=0.3
DO 140 J=1,8
140 H(J,J)=(EG*G(J))**2
WRITE (3,5)
WRITE (3,6)(TITLE(I),I=1,40)
WRITE (3,7)NP,K,E,P
WRITE (3,8)(X(J),J=1,8)
WRITE (3,9)(H(I,1),I=1,8)

MI=1
201 P=0.0
CALL HLN(U,F,X,MU)

IF (F) 241, 241, 204

L = 1
IT = 0
WRITE (1,10) IT, MS, F
WRITE (1,11)

C

217 CALL READY
L = L
GO TO (1, 241, 239, 237, 229), L

220 L = 2
221 GO TO 217
222 CALL AIR
L = L
GO TO (1, 25, 239, 237), L

225 CALL FIRE
L = L
GO TO (1, 235, 228, 222), L

228 L = L
229 CALL DRESS
L = L
GO TO (1, 250, 232), L

C

232 MJMP = 3
NISH = L
GO TO 257

C

235 L = 2
GO TO 239

237 L = 3
GO TO 239

239 L = 4
GO TO 239

241 WRITE (1, 12) DELTA
IF (K) 244, 244, 247

244 CALL SFF
L = L
GO TO (1, 201, 260), L

247 MJMP = 4
GO TO 240

C

250 WRITE (1, 11)
GO TO 250

251 WRITE (1, 12) DELTA
GO TO 250

C

260 WRITE (1, 13)
MJMP = 2

263 IF (J) 1264, 1264, 1268

264 JJ 266 = 1, B
JJ 266 = -1, A

266 H(J,J) = .5491(J+J)
NISH = 1

269 NISH = 1
WRITE (1, 14)
GO TO 269

275 WRITE (1, 19) I, H(J,J), J = 1, B
WRITE (1, 16) (I(I)), I = 1, B
IF (NTS0) 281, 281, 284
281 UU 282 I=1,8
282 H(I,1)=2.0*H(I,1)
284 WRITE (3,9)(H(I,1),I=1,8)
285 GO TO (290,290,300,290), MJMP
290 IF (NTSH) 296, 296, 291
291 DU 293 I=1,8
292 J=1,8
293 H(I,J)=H(I,J)/2.0
294 NTSH=0
295 GO TO 299
296 IF (NTS0) 300, 300, 297
297 DU 298 I=1,8
298 H(I,1)=H(I,1)/2.0
299 NTSD=0
300 WRITE (3,17)F,US
301 WRITE (3,8)(X(I),I=1,8)
302 MJMP=MJMP
303 GO TO (308,308,307,244), MJMP
307 MJMP=2
308 WRITE (3,18)
309 MI=3
310 CALL FCN(G,F,X,M1)
311 GO TO 100
C
1 FORMAT (20A4)
2 FORMAT (14,12,2E8.4)
3 FORMAT (8E10.4)
4 FORMAT (10E8.4)
5 FORMAT (5H12FE PARAMETERS CALC BY VARIABLE METRIC MINIMIZATION)
6 FORMAT (1HO,20A4/1X,20A4)
7 FORMAT (4HNP=I3,4H K=I2,4H E=1PE13.5,4H P=1PE13.5)
8 FORMAT (11H0PARAMETERS//1PE8.5)
9 FORMAT (3H0DIAGONAL ELEMENTS OF ERROR MATRIX//1PE8.5)
10 FORMAT (4H0IT=I4,6H STEPI4,4H F=1PE4.5)
11 FORMAT (20H0-- -- -- -- -- --)
12 FORMAT (7H0MODELTA=1PE4.5)
13 FORMAT (13H0FINAL VALUES)
14 FORMAT (13H0ERRR MATRIX)
15 FORMAT (1HO,13,1PE4.5)
16 FORMAT (9H0GRADIENT//1PE4.5)
17 FORMAT (3HOF=1PE4.5,5H GS=1E4.5)
18 FORMAT (2H0END OF MINIMIZATION)
19 FORMAT (213)
END
FCN...

This routine calculates the function to be minimized as well as its first derivative.

Function evaluation for determination of CEF parameters from temperature dependence of quadrupole splitting.

Routine FCN0, F, XM11

Dimension H(10,10), XA(10), GC(10), S(10), XP(10), GP(10), T(10), GB(10), 
XU(10), YU(10), FUNC(40), FFF(40), SU(40), FC(10), XLAB(5), YLAB(5), 
ZLAB(5), GLAB(5), FAC(10), EN(10), AG(10), X(10), G(10), DE(9,6), 
SDP(11), JSF(10), FUN(40), SFUN(40,10), AD(5,5), R(11), EV(9), AV(9,9), 
4AS(9,9), AB(9,9), JS(9), SP(9)

Common H, XA, GC, S, XP, GP, T, GB, XD, AL, DE, MU, LS, MS, IF, GS, GSP, 
1GF, 5U, GI, 5B, 1U, FX, FB, FD, EX, PX, LS, SL, Z, AX, EL, DELTA, NP, XR, 
2ITAPE1, ITAPE2, R

IF (M1-2)99,99,99

34 F=0.0

BK=0.09501

ITAPE1=ITAPE1

ITAPE2=ITAPE2

Set up matrix to be diagonalized.

DO 50 J=1,6

DO 51 J=1,9

DO 51 J=1,9

AV(J,1)=0.0

AV(1,1)=.6667*X(1)+.9697*X(2)+.9324*X(3)

AV(1,2)=-.3269*X(4)-.12572*X(5)

AV(1,3)=.06135*X(6)

AV(2,1)=-.1515*X(1)-.5289*X(2)-.822*X(3)

AV(2,2)=.09119*X(4)-.2256*X(5)

AV(2,3)=-.16993*X(6)

AV(3,1)=-.4242*X(1)+.8228*X(2)+.695*X(3)

AV(3,2)=AV(2,1)

AV(3,3)=AV(2,2)

AV(4,1)=AV(4,2)

AV(4,3)=AV(4,2)

AV(5,1)=AV(5,2)

AV(5,3)=AV(5,2)

AV(6,1)=AV(6,2)

AV(6,3)=AV(6,2)

Set up partial derivatives

UA1=AV(1,1)-AV(1,2)

UA2=UNUN2

UA2=AV(1,1)-AV(1,3)

UN2=UNUN2

OU3=UA2-OU(4,1)

OU4=UA2-OU(4,2)

OU5=UA2-OU(4,3)

OU6=UA2-OU(4,3)

OU7=OU(4,3)
DN2 = DN6 ** 2
DN7 = AN(1, 4)

C

UE(1, 1) = .6667 * .8182 * DN42 / DN12 - 1.0909 * DN52 / DN22
UE(1, 2) = -.1515 * .8182 * DN42 / DN12 - 2.7273 * DN62 / DN32
UE(1, 3) = -.4242 * .2186 * DN52 / DN22 + .5454 * DN62 / DN32
UE(1, 4) = DE(1, 1)
UE(1, 5) = DE(1, 1)
DE(1, 1) = .9667 - 1.4986 * DN42 / DN12 - 1.4694 * DN52 / DN22
DE(1, 2) = - .5489 * 1.4769 * DN42 / DN12 + 1.3571 * DN62 / DN32
DE(1, 3) = .6280 * .2938 * DN52 / DN22 - 2.1034 * DN62 / DN32
DE(1, 4) = DE(1, 2)
DE(1, 5) = DE(1, 2)

DE(2, 1) = -.9324 - .8896 * DN42 / DN12 + 2.6274 * DN52 / DN22
DE(2, 2) = - 1.8222 + .8896 * DN42 / DN12 + 3.5170 * DN62 / DN32
DE(2, 3) = 1.6955 - 2.5468 * DN52 / DN22 - 1.0340 * DN62 / DN32
DE(2, 4) = DE(2, 3)
DE(2, 5) = DE(2, 3)

DE(3, 1) = -.2514 * DN42 / DN12
DE(3, 2) = 2.5144 * DN42 / DN12 - 2.4512 * DN62 / DN3
DE(3, 3) = -.49024 * DN62 / DN3
DE(3, 4) = DE(3, 5)
DE(3, 5) = DE(3, 5)

DE(4, 1) = -.2514 * DN42 / DN12
DE(4, 2) = 2.5144 * DN42 / DN12 - 2.4512 * DN62 / DN3
DE(4, 3) = -.49024 * DN62 / DN3
DE(4, 4) = DE(4, 5)
DE(4, 5) = DE(4, 5)

DE(5, 1) = DE(1, 1)
DE(5, 2) = DE(2, 1)
DE(5, 3) = DE(3, 1)
DE(5, 4) = DE(4, 1)
DE(5, 5) = DE(5, 1)

KCWIN: ITAPE1
KCDWIN: ITAPE2

DO 10 I = 1, 5
10 WHITE (ITAPE1)(AD(1, J), J = 1, 5)
CALL (IDEN(5, - 5), ITAPE1, ITAPE2)
KCDWIN: ITAPE2
KCDWIN: (EVAL(1, I), I = 1, 5)
DU = 0
LJ = 1, 5
60 CAD (ITAPE2)(AV(J, I), J = 1, 5)
DU = 1
LJ = 1, 5
61 AD(1, I) = 0.
AD(1, I) = 3.3333 * X(I) - .4665 * X(2) + 2.331 * X(3)
AD(1, I) = .0449 * X(4) - .0363 * X(5)
AD(1, I) = .11477 * X(6)
AD(2, I) = -.3030 * X(I) + .1477 * X(2) - .9324 * X(3)
AD(2, I) = .0166 * X(4) - .0402 * X(5)
AD(2, I) = -.15476 * X(6)
AD(3, I) = -.3939 * X(11) + .6269 * X(2) + .876 * X(3)
AD(3, I) = .0241 * X(4) + .0617 * X(5)
AD(3, I) = .0606 * X(1) - .9403 * X(2) - .391 * X(3)

C
C
C
C

DN1 = AD(1, 1) - AD(2, 2)
DN12 = -0192
ON2 = A0(i,i) - A1(3,3)

DN3 = A0(2,2) - A1(3,3)

ON32 = ON3 * ON3

DN2 = DN5 * DN6

DN9 = A0(2,4)

DN92 = DN9 * DN9

DN11 = DN3 * DN12

DN112 = DN11 * DN12

C

DE(1,1) = 0.333 * -6363 * DN62 / DN12 + .7272 * DN72 / DN22

DE(1,1) = 0.309 * .3636 * DN62 / DN12 - .0909 * DN82 / DN32 + .3636 * DN92 / DN42

DE(1,1) = 0.196 * .7272 * DN72 / DN22 + .0909 * DN82 / DN32 + .4545 * DN112 / DN52

DE(1,1) = 0.061 * -4545 * DN112 / DN52 - .3636 * DN92 / DN42

DE(1,2) = -0.445 * .7543 * DN62 / DN12 + .5192 * DN82 / DN32 - 1.0480 * DN92 / DN42

DE(1,2) = -0.626 * .1273 * DN72 / DN22 - .5192 * DN82 / DN32 + 1.5672 * DN112 / DN52

DE(1,2) = -0.943 * .5672 * DN112 / DN52 + 1.0480 * DN92 / DN42

DE(1,3) = -2.331 * 1.3986 * DN62 / DN12 + 1.3786 * DN72 / DN22

DE(1,3) = -9.324 * 1.3986 * DN62 / DN12 + 1.3786 * DN72 / DN22

DE(1,4) = -0.470 * -1.0807 * DN72 / DN22 - 1.7800 * DN82 / DN32 - 1.1867 * DN112 / DN52

DE(1,4) = -3.391 * 1.1867 * DN112 / DN52 + 5.933 * DN92 / DN42

DE(1,4) = -0.0845 * DN62 / DN11

DE(1,4) = -DE(6,4) * 0.0168 * DN8 / DN3

DE(1,4) = 0.0168 * DN8 / DN3 + 0.0482 * DN11 / DN5

DE(1,4) = 0.0166 * DN11 / DN5

DE(1,4) = -0.045 * -DN6 / DN1

DE(1,4) = -DE(6,4) * 0.045 * 0.045 * DN6 / DN1

DE(1,4) = -0.045 * 0.045 * DN6 / DN1

DE(1,4) = -0.045 * 0.045 * DN6 / DN1

DE(1,4) = -0.045 * 0.045 * DN6 / DN1

DE(1,4) = -0.045 * 0.045 * DN6 / DN1

DE(1,4) = -0.045 * 0.045 * DN6 / DN1

DE(1,4) = -0.045 * 0.045 * DN6 / DN1

C

REWIND ITAPE1
REWIND ITAPE2
WRITE (ITAPE1) (A0(I,J), J=1,4)
CALL EULNC1,-4,ITAPE1,ITAPE2
REWIND ITAPE2
READ (ITAPE2) (EVII,I=6,9)
DO 63 I=6,9
C
REWIND ITAPE2
READ (ITAPE2) (AV(J,J), J=6,9)
C
IF (EVII-EVJ6>) 100, 103, EV6)
EV6), AND LABEL IT EV7.
C
IF (EV11-EVJ6) 100, 106, 101
101 B=EV11
```
EV(1) = EV(6) 
EV(6) = h 
DO 64 J = 1, M 
    B = AV(J, 1) 
    AV(J, 1) = AV(J, 6) 
    AV(J, 6) = B
64 CONTINUE
100 CONTINUE

NORMALIZE ENERGY LEVELS MAKING EV(1) = 0.

EB = EV(1)
DO 102 J = 1, 9
102 EV(J) = EV(1) - EB

RELABEL EIGENVALUES SO THAT EV(1) CORRESPONDS TO MJ = +6, EV(2) CORRESPONDS TO MJ = +3 ETC.

CALL PUMP(EV(1), EV(9), 5, AV(1, 1), AV(9, 9), 5)
DO 65 I = 1, 9
    DO 64 J = 1, M
        AS(J, I) = 0.
64 EN(J) = 0.
65 EN(I) = 0.
66 AS(J, 1) = AV(J, 1) ** 2
67 CONTINUE
N = 1
68 DO 66 J = 1, 9
69 N = J
    IF (AS(J, 1) - AS(J, 1)) 69, 68
    AS(J, 1) = AS(J, 1)
70 CONTINUE
GOTO (301, 302, 302, 302, 300), N
120 IF (AB(J, 1)) 128, 124, 125
121 EN(2) = EV(1)
122 AB(J, 2) = AV(J, 1)
123 GOTO 67
124 IF (AB(J, 2)) 132, 132, 134
125 EN(3) = EV(1)
126 AB(J, 3) = AV(J, 1)
127 GOTO 67
128 IF (AB(J, 3)) 140, 140, 143
129 AB(J, 4) = AV(J, 1)
130 GOTO 67
132 IF (AB(J, 4)) 150, 150, 153
133 EN(4) = EV(1)
134 AB(J, 5) = AV(J, 1)
137 GOTO 67
140 IF (AB(J, 5)) 160, 160, 163
143 EN(5) = EV(1)
148 AB(J, 6) = AV(J, 1)
160 GOTO 67
150 IF (AB(J, 6)) 170, 170, 173
153 EN(6) = EV(1)
165 AB(J, 7) = AV(J, 1)
170 GOTO 67
163 IF (AB(J, 7)) 180, 180, 183
173 EN(7) = EV(1)
178 AB(J, 8) = AV(J, 1)
180 GOTO 67
183 EN(8) = EV(1)
190 AB(J, 9) = AV(J, 1)
200 GOTO 67
215 EN(9) = EV(1)
220 AB(J, 10) = AV(J, 1)
230 GOTO 67
240 EN(10) = EV(1)
250 AB(J, 11) = AV(J, 1)
260 GOTO 67
270 EN(11) = EV(1)
280 AB(J, 12) = AV(J, 1)
290 GOTO 67
283 EN(12) = EV(1)
293 AB(J, 13) = AV(J, 1)
300 GOTO 67
305 AB(J, 1) = AV(J, 1)
```
304 IF (AB(5,5)) 301, 311, 301
311 EN(5) = EV(1)
306 AB(J,4) = AV(J,1)
307 IF (AB(2,2)) 308, 307, 308
308 EN(2) = EV(1)
309 AB(J,2) = AV(J,1)
311 J=6,9
310 AB(J,4) = AV(J,1)
302 IF (AB(3,3)) 320, 380, 320
380 EN(3) = EV(1)
307 J=6,9
70 AB(J,3) = AV(J,1)
67 CONTINUE
70 AB(J,3) = AV(J,1)
71 AS(J,1) = AV(J,1)**2
72 J = 6,9
73 CONTINUE
74 N=J
75 AS(J,1) = AS(J,1)
350 IF (EN(6)) 351, 351, 352
351 EN(6) = EV(1)
353 J=6,9
355 AB(J,6) = AV(J,1)
352 IF (EN(9)) 354, 354, 355
354 EN(9) = EV(1)
356 J=6,9
358 AB(J,9) = AV(J,1)
355 IF (EN(7)) 357, 357, 358
357 EN(7) = EV(1)
359 J=6,9
359 AB(J,7) = AV(J,1)
360 EN(J) = EV(J)
358 J=6,9
360 AB(J,8) = AV(J,1)
361 IF (EN(7)) 362, 362, 363
362 EN(7) = EV(1)
364 J=6,9
364 AB(J,7) = AV(J,1)
365 EN(8) = EV(1)
367 J=6,9
367 AB(J,8)=AV(J,1)
GO TO 72
366 IF (EN(6))368,368,369
368 EN(6)=EV(I)
DU 370 J=6,9
370 AB(J,6)=AV(J,1)
GO TO 72
369 EN(9)=EV(I)
DU 371 J=6,9
371 AB(J,9)=AV(J,1)
72 CONTINUE
CALL PDUMP(EN(1),EN(9),5,AB(1,1),AB(9,9),5)

C DETERMINE THE CONTRIBUTIONS OF EACH LEVEL TO THE FIELD GRADIENT.
C
DO 76 I=1,9
76 QA(I)=0.
QA(1)=66.
QA(2)=15.
QA(3)=42.
QA(4)=15.
QA(5)=66.
QA(6)=33.
QA(7)=30.
QA(8)=39.
QA(9)=6.
DU 77 I=1,9
AC(I)=0.
DU 78 J=1,9
78 SP(J)=QA(J)*AB(J,1)
DU 77 J=1,9
77 AC(I)=AC(I)+AB(J,1)*SP(J)
CALL PDUMP(AC(1),AC(9),5)

C CALCULATE F
C
DO 103 J=1,8
103 G(J)=0.
DO 104 L=1,NP
SFC=0.
SFAC=0.
DU 105 L=1,9
GU TO (79,79,79,79,79,80,80,80,80),1
79 FC(I)=EXP(-EN(I)/IBK*XDIL)
GO TO 81
80 FC(I)=2.*EXP(-EN(I)/(BK*XDIL))
DU TO 81
81 FAC(I)=AC(I)*FC(I)
SFC=SFC+FC(I)
105 SFAC=SFAC+FAC(I)
CALL PDUMP(FC(I),FC(9),5,FAC(1),FAC(9),5)
SF=SFAC/SFC
FAC(L)=YD(L)*.000225-FUNC(L)
FUNC(L)=FUNC(L)/(YD(L)*.000225)
SD(L)=FUNC(L)*FFF(L)
F=F+SD(L)

C CALCULATE G(I)
C
DO 107 J=1,6
    DFAC(J)=0.
    DFC(J)=0.
    DU 107 I=1,9
    DFAC(J)=DFAC(J)+DE(I,J)*FAC(I)
107   DFC(J)=DFC(J)+DE(I,J)*FC(I)
    CFUN=X(I)*X(7)/(2.*BK*XDCL)*SFC
    DFUN(I,J)=FUN(L)/X(I)+CON*(DFC(I)*SF-DFAC(I))
    DU 82 J=1,6
82   DFUN(L,J)=CON*(DFC(J)*SF-DFAC(J))
    DFUN(L,7)=X(I)*SF/2.
    DFUN(L,8)=2.*X(I)
    DU 104 J=1,8
104  G(J)=G(J)+FFPIL)*DFUN(L,J)
    DU 108 J=1,8
108  G(J)=G(J)*FFPIL)*DFUN(L,J)
    CALL PDUMPFF,F,5,G(I),G(8),5
    GO TO 110

C      PRINT RESULTS
C
98 WRITE (3,1)
    DU 109 I=1,NP
    FUN(I)=FUN(I)+4444.44
109 WRITE (3,2)XU(I),Y0(I),FUN(I)
    DU 200 J=1,9
200 WRITE (3,3)EN(J),(AB(I,J),I=1,9)

C      GENERATE PLOT
C
READ (1,3)XSIZE
READ (1,4)XLAB,YLAB,GLAB1,GLAB2
    CALL GRAPHPNP,XD,YD,1312833000,7,XSIZE,9,0,0,0,XMIN,0,0,0,0,0,0
    CALL GRAPHPNP,XD,FUN,0,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
    READ (1,4)XLAB,YLAB,GLAB1,GLAB2
    CALL GRAPHPNP,XD,50,2,XSIZE,6,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
    CALL GRAPHPNP,XD,50,2,XSIZE,6,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
    READ (1,4)XLAB,YLAB,GLAB1,GLAB2
110 RETURN

C      FORMAT (17HOTABLE OF RESULTS/12HOTEMPERATURE,8X,4HDATA,9X,4HCALC)
2 FORMAT (1H0,3E14.5)
3 FORMAT (F6.2)
4 FORMAT (20A4)
5 FORMAT(34HENERGY = " WAVE FUNCTION =/(F12.2,9F13.3))
END
SUBROUTINE EIGEN(N,L,ITAPE1,ITAPE2)
MATRIX DIAGONALIZATION SUBROUTINE FOR REAL SYMMETRIC MATRICES.
HOUSEHOLDER'S METHOD

THE UPPER TRIANGULAR ELEMENTS ARE ASSUMED STORED ON TAPE ITAPE1.
N=SIZE OF MATRIX.  L=NUMBER OF EIGENVECTORS TO BE CALCULATED.

IF L IS EQUAL TO OR GREATER THAN ZERO, EIGENVALUES WILL BE GIVEN
IN DECREASING ORDER.
IF L IS LESS THAN ZERO, EIGENVALUES WILL BE GIVEN IN INCREASING
ORDER.

EIGENVALUES OR EIGENVALUES + VECTORS ARE RETURNED ON TAPE ITAPE2.

THIS PROGRAM HAS BEEN REVISED FOR THE IBM 360 SERIES.

DIMENSION DIAG(175),OFFDI(175),W1(175),W2(175),E(175),V(175)
REWIND ITAPE1
5 CALL TRIDKIN,ITAPE1,DIAG,OFFDI,W1,W2)
CALL EIGVAL(N,L,E,DIAG,OFFDI,W1,W2)
REWIND ITAPE2
WRITE (ITAPE2)(E(K),K=1,N)
M=IABS(L)
IF (M8,8,6
6 DO 7 I=1,M
CALL VECTR1(N,DIAG,OFFDI,E(I),V,W1,W2)
CALL VECTR2(N,V)
7 WRITE (ITAPE2)(V(K),K=1,N)
8 REWIND ITAPE1
RETURN
END
SUBROUTINE TRIDI(N,ITAPl,AA,BfW,QB)

COMMON HfXfGiS,XPtGPfT,GB,XO,YD,AC,DE,MD,Ls,ML,MS,IT,GS,GSP,GTp,
1GS,STT,GSb,F,FP,Fb,Fc,E,K,P,TO,Ks,SL,2,Q,A,EL,DELTA,NP,XR,
2ITAPE1,1TAPE2,R

C STORE ELEMENTS OF UPPER TRIANGLE BY ROWS IN R.
REWIND ITAPl
NP1=N+1
NL=N*NP1/2
NM1=N-1
NP2=N+2
KU=0
DO 5 I=1,N
KL=KU+1
READ (ITAPl) (RU) ,J=KL,KU)
C STORE ORIGINAL DIAGNOL IN AA.
L=-N
DO 10 I=1,N
L=L+NP2-1
10 AA(I)=R(L)
B(1)=0.
IF (N-2)99,6e>,15
lb KK=0
KU=KK+1
C PERFORM (N-2) TRANSFORMATIONS.
DO 55 KA=2,NM1
KL=KU+2
KU=KL+N-KA
KJ=KA*1
C CALCULATE AND STORE MODIFIED COLUMN MATRIX W
SUM=0.0
KL1=KL+1
DO 20 J=KL1,KU
20 SUM=SUM+R(J)**2
C TEST TO SEE IF TRANSFORMATION IS NECESSARY.
IF (SUM)22,22,25
b(KA)=R(KL)
R(KL)=0.
GO TO 55
25 SA=SQR(T(SUM+R(KL)**2))
B(KA) =SIGN(SA,-R(KL))
SA=1./SA
W(KA)=SQR(T(ABS(R(KL))**SA+1.))
XA=SIGN(SA/W(KA),R(KL))
R(KL)=W(KA)
C RETURN NEW FIRST OFF DIAGONAL IN B
C THIS PROGRAM IS FOR THE IBM 360/40.
C
DO 30 I=KJ,N
JJ=J*KK
W(I)=XA*R(JJ)
30 R(JJ)=W(I)

C CALCULATE NEW R MATRIX WITH ROW KA-1 NOW HAVING ZEROS OFF 2ND DIAGONAL
DO 35 J=KA,N
JJ=J+1
QB(J)=0.0
L=KK*J
DO 33 I=KA,J
L=L+NPI-L
33 QB(J)=QB(J)+R(L)*W(I)
IF (JJ-N)34,34,36
34 DO 35 I=JJ,N
L=L+1
35 QB(J)=QB(J)+R(L)*W(I)
36 XA=0.0
DO 40 J=KA,N
40 XA=XA+W(J)*QB(J)
XA=.5*XA
DO 45 I=KA,N
45 QB(I)=XIW(I)-QB(I)
L=KU
DO 50 I=KA,N
50 QB(I)=QB(I)+W(I)*QB(J)
55 KK=KK+NPI-KA
C Sort output for desired return.
L=1
DO 60 I=1,N
AA(I)=R(L)
60 L=L+NPI-L
65 B(N)=R(NL-1)
99 RETURN
END
SUBROUTINE EIGVAL(N,L,E,A,B,F,W)

END IF input data sensed
THIS SUBPROGRAM CALCULATES THE EIGENVALUES OF THE REAL SYMMETRIC
TRIDIAGONAL MATRIX WHOSE DIAGONAL ELEMENTS ARE STORED IN A,
AND WHOSE OFF DIAGONAL ELEMENTS ARE STORED IN B.

ORTEGA'S METHOD OF STURM SEQUENCES IS USED.

THE EIGENVALUES ARE RETURNED IN E.

DIMENSION A(101),B(101),E(101),F(101),W(101)

FIND UPPER AND LOWER BOUNDS AND NORMALIZE INPUT
NM1=N-1
BD=ABS(B(N))+ABS(A(N))
DO 1=1,NM1
5 BD=AMAX(BD,ABS(B(I))+ABS(A(I))+ABS(B(I+1)))
DO 6 I=1,N
A(I)=A(I)/BD
B(I)=B(I)/BD
W(I)=1.
6 E(I)=-1.
DO 8 I=1,N
8 IF(W(I))102,104,104
102 S1=-1.
M=0
GO TO 105
104 S1=1.
M=1
105 DD 120 I=2,N
106 IF (B(I))106,113,106
107 IF (ABS(F(I-1))+ABS(F(I-2))-1.0E-15)<110,112,112
110 F(I-1)=F(I-1)+1.0E15
F(I-2)=F(I-2)+1.0E15
112 F(I)=(A(I)-X)*F(I-1)-B(I)**2*F(I-2)
GO TO 115
113 F(I)=(A(I)-X)*S1
GO TO 115
114 F(I)=(A(I)-X)*F(I-1)-B(I)**2*S2
115 S2=S1
IF (F(I))116,117,116
116 S1=SIGN(1.,F(I))
117 M=M+1
120 CONTINUE

TRAP EIGENVALUES IN SMALLER AND SMALLER BOUNDS
IF(M)13,14,11
11 DD 12 J=K,M
12 E(J)=AMAX1(E(J),X)
13 M=M+1
1 IF(N-M)18,14,14
14 DO 15 J=M,N
15 W(J)=AMIN(W(J),X)
   GO TO 8
50 CONTINUE
C
C RESTORE INPUT AND ORDER EIGEN VALUES
   DO 60 I=1,N
      A(I)=A(I)+BD
      B(I)=B(I)+BD
   60 F(I)=(W(I)+E(I))*BD/2.
      IF(ISIGN(1,L))70,63,63
63 DO 65 I=1,N
65 E(I)=F(I)
   GO TO 80
70 J=N
   DO 75 I=1,N
      E(J)=F(I)
75 J=J-1
80 RETURN
   END
SUBROUTINE VECTRI(N,A,B,E,V,P,Q)

C THIS SUBPROGRAM CALCULATES THE EIGENVECTOR OF THE TRIDIAGONAL
C MATRIX WHICH CORRESPONDS TO THE EIGENVALUE E.
C
DIMENSION A(T),B(T),V(T),P(T),Q(T)

C SET UP SIMULTANEOUS EQUATIONS FOR EIGEN VECTOR WITH EIGEN VALUE E

X=A(1)-E
Y=B(2)
LPl=N-1
D0 210 I=1,LPl
IF (ABS(X)-ABS(B(I+1)))>204,206,208
204 P(I)=B(I+1)
Q(I)=A(I+1)-E
V(I)=B(I+2)
Z=X/P(I)
X=Z*Q(I)+Y
IF (LPl-I)>.205,210,205
205 Y=2*V(I)
GO TO 210
206 IF (X)>.208,207,208
207 X=1.0E-10
208 P(I)=X
Q(I)=Y
V(I)=A(I+1)-(B(I+1)/X*Y)+E
Y=B(I+2)
210 CONTINUE

C SOLVE SIMULTANEOUS EQUATIONS FOR EIGEN VECTOR OF TRI-DIAGONAL MATRIX

220 IF (X)>.221,228,221
221 V(N)=1./X
222 I=LPl
V(I)=1.-Q(I)*V(N)/P(I)
X=V(N)*Z+V(I)**2
225 I=I-1
IF (I)=226,230,226
226 V(I)=1.-Q(I)*V(I+1)+V(I)*V(I+2))/P(I)
X=X+V(I)**2
GO TO 229
228 V(N)=1.0E10
GO TO 222
230 X=SQR(T(X))
D0 231 I=1,N
231 V(I)=V(I)/X
RETURN
END
SUBROUTINE VECTR2(N,V)

C THIS SUBPROGRAM TRANSFORMS THE EIGENVECTORS OF THE TRIDIAGONAL
C MATRIX INTO THE EIGENVECTORS OF THE ORIGINAL MATRIX.

DIMENSION H(10,10),X(10),G(10),S(10),XP(10),GP(10),T(10),GB(10),
1X0(40),YD(40),AC(10),DE(9,6),R(I),V(I)
COMMON H,X,G,S,XP,GP,T,GB,XD,YD,AC,DE,M0,L,LS,M1,MS,IT,GS,GSP,GTP,
LGSS,GT,GSB,F,FP,FB,FO,E,K,P,T0,RS,SL,Z,Q,A,EL,DELA,NP,XR,
2ITAPE1,ITAPE2,R
J=(N*N-N-2)/2
KA=N
NP1=N+1
GO TO 42
32 KA=KA-1
J=J+KA-NP1
Y=0.0
DO 35 I=KA,N
L=J+I
35 Y=Y+V(I)*R(L)
DO 40 I=KA,N
L=J+I
40 V(I)=V(I)-Y*R(L)
42 IF I(J)
44 RETURN
END