Temperature Coefficients of Energy Separations between Ga 3d Core Levels and sp3 Valence-Conduction Bands in GaP

D. E. Aspnes
Bell Laboratories

C. G. Olson
Iowa State University

David W. Lynch
Iowa State University, dlynch@iastate.edu

Follow this and additional works at: http://lib.dr.iastate.edu/physastro_pubs

Part of the Condensed Matter Physics Commons
Temperature Coefficients of Energy Separations between Ga 3d Core Levels and sp3 Valence-Conduction Bands in GaP

Abstract
The measured temperature coefficients of the energy separations between the Ga 3d core levels and the top (Γ8V) and bottom (X6C) of the sp3 valence and conduction bands in GaP between 110 K and 295 K are (+1.0±0.5)×10−4 eV K−1 and (-2.4±0.5)×10−4 eV K−1, respectively. They are described within experimental accuracy by the Debye-Waller, hydrostatic, self-energy, and spatially averaged screened-ion core potential interactions of the sp3 bands alone. No significant core-level contribution is observed.

Keywords
Ames Laboratory, Debye-Waller, screened-ion

Disciplines
Condensed Matter Physics | Physics

Comments
Temperature Coefficients of Energy Separations between Ga 3d Core Levels and sp\(^3\) Valence-Conduction Bands in GaP

D. E. Aspnes

Bell Laboratories, Murray Hill, New Jersey 07974

and

C. G. Olson and D. W. Lynch

Ames Laboratory–ERDA and Department of Physics, Iowa State University, Ames, Iowa 50010

(Received 23 March 1976)

The measured temperature coefficients of the energy separations between the Ga 3d core levels and the top (\(\Gamma_4\)) and bottom (\(X_6^C\)) of the sp\(^3\) valence and conduction bands in GaP between 110 K and 295 K are \((+1.0 \pm 0.5) \times 10^{-4}\) eV K\(^{-1}\) and \((-2.4 \pm 0.5) \times 10^{-4}\) eV K\(^{-1}\), respectively. They are described within experimental accuracy by the Debye–Waller, hydrostatic, self-energy, and spatially averaged screened-ion core potential interactions of the sp\(^3\) bands alone. No significant core-level contribution is observed.

We present the first experimental determination of “absolute” temperature coefficients of valence and conduction bands by determining the energy shift with temperature of the transitions between the Ga 3d\(_{3/2, 5/2}\) core\(_3\) levels and the top (\(\Gamma_4\)) and bottom (\(X_6^C\)) of the valence and conduction bands in GaP. The 3d\(_y^\prime\)–\(\Gamma_4\) separation increases with temperature, showing that the Debye–Waller, \(^1\) self-energy, \(^2\) and spatially averaged screened-ion potential (V\(_{\text{spin}}\) pseudopotential) contributions dominate the hydrostatic component\(^2\) for the upper sp\(^3\) valence bands. The data are explained within experimental accuracy (\(\pm 0.5 \times 10^{-4}\) eV K\(^{-1}\)) by sp\(^3\)-band temperature shifts alone. The magnitudes of the observed coefficients give direct evidence of the validity of the Phillips bond-charge model\(^3\) and spatially dependent dielectric screening for the V\(_{\text{spin}}\) and 3d\(_y\) contributions to the total temperature coefficient. The lack of significant electrostatic shift for the 3d\(_y\) levels suggests that core levels in general may provide good references from which to measure absolute values of small perturbation-induced changes in valence or conduction band energies.

The temperature coefficient of the Ga 3d\(_y\)–X\(_6^C\) energy separation was measured directly by comparing Schottky barrier electroreflectance spectra of the Ga 3d\(_{3/2}\)–X\(_6^C\) and Ga 3d\(_{3/2}\)–X\(_6^C\) critical points taken at 295 K with those taken at 110 K. By 110 K, the strongly nonlinear behavior of the temperature coefficients characteristic of lower temperatures is substantially reduced,\(^5\) so the dominant variation between 110 K and 295 K is linear. Spectra were obtained with undoped (N\(_D\) \(\sim 2 \times 10^{16}\) cm\(^{-3}\)) and Te-doped (N\(_D\) \(\sim 5 \times 10^{17}\) cm\(^{-3}\)) single crystals at several different modulation levels. Measurements were performed at the Synchrotron Radiation Center of the Physical Sciences Laboratory of the University of Wisconsin. Details of the Schottky barrier technique\(^7\) and the experimental apparatus\(^8\) have been given elsewhere. Typical spectra are shown in Fig. 1.

In comparing these spectra, the effect of small line-shape asymmetry changes with temperature, due to changes in field inhomogeneity,\(^10\) upon the apparent energy of the Ga 3d\(_{3/2}\)–X\(_6^C\) singularity was eliminated by determining the energy shift between spectra by least-squares fitting a combination of a 295 K spectrum, \(\Delta R/R\), and its Kramers–Kronig transform, \(\Delta \theta\), to a 110 K spectrum, \(\Delta R/R\). The energy shift between spectra and a baseline offset were used as third and fourth least-squares parameters. Negligible

![Graph showing the temperature coefficient of GaP](https://example.com/gap-temperature-coefficient.png)

**FIG. 1.** Typical Schottky–barrier electroreflectance spectra of the Ga 3d\(_y\)–X\(_6^C\) critical points of GaP. These spectra were taken on a Te-doped crystal using 103-Hz square-wave modulation from +0.5 V to −6.0 V.
baseline offset was always obtained, providing a check on the procedure.

By this means, we found that the Ga $3d_{3/2}^Y - X_C^C$ energy separation increased by $45 \pm 10$ meV upon cooling from 295 K to 110 K. The temperature coefficient of the Ga $3d_{3/2}^Y - X_C^C$ critical-point energy is therefore $(-2.4 \pm 0.5) \times 10^{-4}$ eV K$^{-1}$. Since the energy increase between $\Gamma^Y_6$ and $X_C^C$ upon cooling from 295 K to 110 K is 63 meV, we obtain in addition a temperature coefficient for Ga $3d_{3/2}^Y - \Gamma^Y_6$ of $(+1.0 \pm 0.5) \times 10^{-4}$ eV K$^{-1}$. Thus the $\Gamma^Y_6$ symmetry point and the $3d^Y$ bands move apart with increasing temperature. These values are summarized in Table I.

To compare these temperature coefficients to theory, it is necessary to include the two extra "absolute" terms that arise from the temperature dependence of the $V_{000}$ form factor (the reference pseudopotential for the $sp^3$ bands) and the electrostatic shift of the $3d^Y$ core levels. In addition, the "relative" $sp^3$ terms arising from the Debye-Waller effect, hydrostatic shift, and electron self-energy must also be included. We discuss each briefly as follows.

The Debye-Waller term describes the weakening of the crystal field with increasing temperature due to ion core vibration, which reduces the crystal-field splitting that gives rise to the fundamental direct gap. This produces a positive contribution to $\Gamma^Y_6$ and a negative contribution to $X_C^C$. The actual values have been calculated recently by Camassel and Auvergne and are given in Table I. There is no Debye-Waller contribution from the $d$ core bands since they are flat to within 0.1 meV. The hydrostatic contribution describes (primarily) the decrease in Fermi energy of the valence electron gas as the crystal expands with increasing temperature, and is therefore negative for both $\Gamma^Y_6$ and $X_C^C$ $sp^3$ symmetry points. We calculate it for $X_C^C$ from the $2 \times 2$ determinant for $X_C^C$ by means of the method of Cardona, using the form factor data from Cohen and Heine. We then relate this value to $\Gamma^Y_6$ by means of the measured pressure dependence of the $\Gamma^Y_6 - X_C^C$ indirect gap, $dE_{\Gamma^Y_6}/dP = -1.1 \times 10^{-6}$ eV bar$^{-1}$, together with the isothermal compressibility $k =$ $1.13 \times 10^{-6}$ bar$^{-1}$, and the linear expansion coefficient $\alpha = 5.8 \times 10^{-6}$ K$^{-1}$. The results, shown in Table I, are almost identical to those obtained by assuming complete free-electron behavior. This is not surprising in view of the insensitivity of valence band structure of groups IV and III-V compounds to pseudopotential form factors in general. There is no hydrostatic contribution from the $d$ core bands.

The self-energy term (intraband virtual scattering of electrons by phonons) is of second order in the electron-phonon interaction, causing the gap to decrease as the phonon population increases with increasing temperature. The result of Baumann's calculation for $\Gamma^Y_6$ is given in Table I. The value for $X_C^C$ is expected to be substantially less because the density-of-states effective mass for $X_C^C$ is 0.45 that of the heavy hole, and longitudinal acoustic-mode scattering accounts for only a fraction of the electron-lattice coupling. There is no self-energy contribution from the $d$ core bands.

We consider finally the "absolute" contributions

<table>
<thead>
<tr>
<th>Term</th>
<th>$3d^Y, \Gamma^Y_6$</th>
<th>$3d^Y, X_C^C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye-Waller</td>
<td>$+2.0^a$</td>
<td>$-1.25^a$</td>
</tr>
<tr>
<td>Hydrostatic</td>
<td>$-1.4^b$</td>
<td>$-1.6^b$</td>
</tr>
<tr>
<td>Self-energy</td>
<td>$+0.6^c$</td>
<td>(negligible)$^b$</td>
</tr>
<tr>
<td>$V_{000}$</td>
<td>$+0.5^b$</td>
<td>$+0.5^b$</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>$&lt;0.1^b$</td>
<td>$&lt;0.1^b$</td>
</tr>
<tr>
<td>$d$(bond charge)$/dT$</td>
<td>(negligible)$^b$</td>
<td>(negligible)$^b$</td>
</tr>
<tr>
<td>Total ($sp^3-3d^Y$)</td>
<td>$+1.7$</td>
<td>$-2.4$</td>
</tr>
<tr>
<td>Expt.</td>
<td>$+1.0 \pm 0.5$</td>
<td>$-2.4 \pm 0.5$</td>
</tr>
</tbody>
</table>

$^a$Camassel and Auvergne, Ref. 11. $^b$Baumann, Ref. 4. $^c$See text.
to the temperature coefficients. The $V_{00}$ contribution arises from the change in $sp^3$ reference potential as the spatially averaged screened-ion core potential $V_{00} = -\frac{3}{2}E_{F0} - \Omega^{-2/3}$ decreases with thermal expansion. Here, $\Omega$ is the unit cell volume and (for metals) $E_{F0}$ is the Fermi energy of the free-electron gas. Thus $dV_{00}/dT = -3\Delta E_{F0}$.

By the Phillips bond-charge model, which explains well phonon dispersion in these materials, only the bond charge, $\rho_b = \rho_{VB}/\epsilon_0$, is free to move and hence only it contributes to volume-induced changes in $V_{00}$. Here, $n_{VB} = -32/a^3$, where $a = 10.300 a_0^{22}$ is the valence-band charge density, and $\epsilon_0 = 9.1^{23}$ is the dielectric constant. The calculated value is shown in Table I.

The 3$d^7$ levels are affected primarily by the changes in the electrostatic interaction between screened bond and core charges, and by the decrease$^{24}$ (redistribution) of the bond charge with increasing temperature. Both effects are quite small. This can be shown from the dielectric model, where the local screening is given by the position-dependent dielectric function, $\epsilon(r_b)$, as calculated by Wang and Kittel.\$ If we assume point charges and a midpoint bond for simplicity, the first two charge distributions outside Ga are the four bond charges $-2e/\epsilon_0$ at $r_b = \sqrt{3}a_0/8$ with $\epsilon(r_b) = 4.9$, and the four P core charges $+4e/\epsilon_0$ at $r_p = \sqrt{3}a_0/4$ with $\epsilon(r_p) = 7.9$. By direct calculation of the electrostatic potential, the contribution from thermal expansion is $-0.13 \times 10^{-4}$ eV K$^{-1}$ from the bond charge and $+0.08 \times 10^{-4}$ eV K$^{-1}$ from the P cores. These are intrinsically small and compensating. The Madelung contribution from remaining charge shells is similarly negligible.

The decrease$^{24}$ (redistribution) of bond charge alone with increasing temperature according to $\delta = -2e/\epsilon_0$ and $\epsilon^{-1}/\epsilon_0 = 1.6 \times 10^{-5}$ K$^{-1}$ leads to a $3d$ contribution $-1.6 \times 10^{-4}$ eV K$^{-1}$. Although this is comparable to the larger $sp^3$ contributions in Table I, the redistribution of this charge (in part to Ga orbitals) will substantially reduce this. It is not possible to calculate accurately the total change in this crude model, but realistic estimates of redistribution show that the net effect of redistribution should be less than one fourth of the contribution of the bond charge itself. This is less than the experimental error. We conclude that the $3d^7$ effects are negligible compared to those of the $sp^3$ valence-conduction bands.

The sum of the theoretical terms gives good agreement with the experimental temperature coefficients for both $\Gamma^5$ and $X^5$ critical points.

Since the theoretical contributions arise entirely with the $sp^3$ valence and conduction bands, this agreement clearly shows that these core levels provide accurate references from which to measure absolute values of perturbation-induced changes in the valence and conduction bands. The results further demonstrate the validity of the Phillips dielectric model$^7$ with respect to the magnitude of the bond charge. Finally, we have shown that the pseudopotential approach yields good absolute values of temperature-induced shifts of valence and conduction band energies, thus complementing previous calculations of temperature$^{54,11,12}$ and pressure$^{27}$ coefficients of $sp^3$ band-to-band transitions.

One of us (D.E.A.) wishes to thank J. C. Phillips, E. O. Kane, and J. R. Chelikowsky for useful discussions. We also acknowledge the cooperation of E. M. Rowe and the Synchrotron Radiation Center Staff. The Synchrotron Radiation Center was supported by the National Science Foundation under Grant No. DMR-74-15089.

$^{1}$S. C. Yu and H. Brooks, unpublished.
$^{5}$J. C. Phillips, Phys. Rev. 166, 832 (1968), and 168, 905, 912, 917 (1968).
$^{9}$D. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. B 12, 2527 (1975), and to be published.
Test for Band Ferromagnetism in hcp Cobalt: Knight Shift in the Ferromagnetic Phase of Cobalt

D. Fekete, A. Grayevsky, and D. Shaltiel
The Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

and

U. Goebel and E. Dormann
Institut für Festkörperphysik II Technisches Hochschule Darmstadt, Darmstadt, West Germany

and

N. Kaplan
The Hebrew University, Jerusalem, Israel, and Technische Hochschule Darmstadt, Darmstadt, West Germany

(Received 8 April 1976)

A high-field Knight-shift measurement in a single crystal of hcp cobalt, $K = 0.0186$, is used to derive the spin susceptibility $\chi_s = 1.8 \times 10^{-6}$ emu/mole and the orbital susceptibility $\chi_{ov} = 2.2 \times 10^{-6}$ emu/mole. Comparing the results with predictions of the ferromagnetic band model, we conclude that hcp cobalt is a weak itinerant-electron ferromagnet.

It is now believed on general grounds that the ferromagnetic 3d metals—iron, nickel, and cobalt—are itinerant-electron ferromagnets. However, while models of band ferromagnetism could account for some observations in cubic iron and nickel, so far very little conclusive evidence was presented connecting properties of hcp cobalt with band ferromagnetism. In the present Letter a high-field "Knight-shift" study in a single crystal of hcp cobalt, in the ferromagnetic phase, is described and the results utilized to test in a critical manner the predictions of the band model of ferromagnetism concerning the spin susceptibility, $\chi_s$, in cobalt. Simultaneously, an experimental value of the orbital susceptibility, $\chi_{ov}$, in the ferromagnetic phase of hcp cobalt is determined.

First, a brief review of existing information relevant to the present study. As is well known, a prediction of the ferromagnetic band model can be tested directly by measuring the high-field spin susceptibility $\chi_s$, high-field meaning applied magnetic fields well above technical saturation. The model prediction $\chi_s$ in the low-temperature limit is

$$\chi_s = 4\mu_0^2/[2[N_{min}(E_F)]^{-1} + [N_{maj}(E_F)]^{-1} - 2I]. \ (1)$$

Based on results of two independent pioneering band-structure calculations available at the time it was concluded that hcp cobalt is a so-called "strong" itinerant-electron ferromagnet, i.e., one in which the majority-spin sub-band is fully occupied. As a result, in accordance with Eq. (1), only a small $\chi_s$ value $[20-25] \times 10^{-6}$ emu/mole was predicted. In a more recent band calculation, based on hcp interpolation schemes and claiming improved accuracy, it is found that neither sub-band is yet fully occupied, delineating hcp cobalt as a "weak" itinerant-electron ferromagnet with $\chi_s$ being 3 times larger than the predictions based onRefs. 6 and 7. Some time later the total high-field susceptibility of hcp cobalt...