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²²The $A_{\frac{1}{2}}^{\nu}$ and $A_{\frac{3}{2}}^{\nu}$ expressions given here are, of course,

valid for all atomiclike functions, including the lower-lying $C_{\frac{1}{2}}$.

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Electron Energy Levels in LaSn_3 . II. Relativistic Connections Using Perturbation Theory

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In a separate paper, electron energy levels in perfectly ordered LaSn_3 were calculated non-relativistically for the equivalent of 64 points in the reciprocal-space lattice using a modified orthogonalized-plane-wave method. We now use perturbation theory to determine the relativistic corrections. Starting with Dirac's theory of the relativistic spinning electron and following Slater we write the final $E(\vec{k})$ as $E^0(\vec{k})$ plus mass-velocity, Darwin, and spin-orbit corrections where the $E^0(\vec{k})$ are the nonrelativistic energy levels previously calculated. The mass-velocity and Darwin operators do not affect symmetry and thus involve no mixing between different irreducible single-group representations. These two corrections thus cause only a shift in energy. This shift is calculated by nondegenerate first-order perturbation theory. The spin-orbit operator does affect symmetry so that those nonrelativistic levels associated with two- and three-dimensional single-group representations can split. This splitting is calculated by degenerate first-order perturbation theory. The spin-orbit operator can also mix levels belonging to different irreducible single-group representations providing the nonrelativistic levels are not too widely separated in energy. Perturbation theory has been used to determine this mixing in most of the appropriate cases with particular emphasis given to those levels near the Fermi level. Relativistic $E(\vec{k})$ curves are shown for six directions in \vec{k} space. Using the final $E(\vec{k})$, a Fermi level of -0.50 Ry has been computed. This is about 0.03 Ry lower than the nonrelativistic Fermi level. Comparison with the limited amount of existent LaSn_3 experimental data is discussed briefly.

INTRODUCTION

In the previous paper,¹ hereinafter referred to as GMI, electron energy levels in perfectly ordered LaSn_3 were calculated nonrelativistically for the equivalent of 64 points in the reciprocal-space lattice using a modified orthogonalized-plane-wave method (MOPW). A muffin-tin model potential, constructed from the self-consistent nonrelativistic atomic potentials of Herman and Skillman (see GMI, Ref. 4) was used. As both La and Sn are relatively heavy, with atomic numbers 57 and 50, respectively, relativistic corrections should play an important role. In this paper we calculate these corrections using perturbation theory. Starting with Dirac's theory of the relativistic spinning electron and following the treatment of Slater² we write the final $E(\vec{k})$ as $E^0(\vec{k})$ plus mass-velocity, Darwin, and spin-orbit corrections where the $E^0(\vec{k})$ are the nonrelativistic energy levels calculated in GMI.

There are good arguments for using relativistic atomic potentials as the starting point of such a calculation (see GMI, Ref. 19). However, we did not have such potentials when this calculation was begun and we further thought it would be of interest to see how large the relativistic shifts were for the case in which the unperturbed crystal energy levels were

calculated entirely nonrelativistically. A very few points (Γ , Δ , X) were calculated both with nonrelativistic and with relativistic atomic potentials as starting points and the resulting unperturbed levels were compared in GMI. The fact that the relativistic-potential-based levels lie higher than the nonrelativistic-potential-based levels corroborates the arguments given by Calloway *et al.* (see GMI, Ref. 19). It should thus be clear that the present calculation is of a rather preliminary nature.

In GMI and in the present paper we follow the Bouckaert, Smoluchowski, and Wigner (BSW) notation for the symmetry points (see GMI, Ref. 3). The BSW notation is used in both papers for the single-group representations. For all double-group representations (except those for Λ) we follow Elliott.³ This is consistent as Elliott works from the BSW single-group notation. For the double-group representations for Λ we follow Koster.⁴ For Λ , Koster's single-group notation is identical to that of BSW.

APPLICATION OF PERTURBATION THEORY

Following Slater² we assume that we can start with Dirac's theory of the relativistic spinning electron for a central field and replace the central field by a periodic potential. The resulting equation is

$$\begin{aligned} & \{ -(\hbar^2/2m) \nabla^2 + V(\vec{r}) \\ & - p^4/8m^3 c^2 - (\hbar^2/4m^2 c^2) \nabla V(\vec{r}) \cdot \nabla \\ & + (\hbar/4m^2 c^2) \vec{\sigma} \cdot [\nabla V(\vec{r}) \times \vec{p}] \} \psi = E \psi. \quad (1) \end{aligned}$$

[This is Slater's equation (A9-1) with $\vec{A}=0$, $\vec{B}=0$, i. e., no external magnetic field; with $-e\phi$ replaced by $V(\vec{r})$ and $e\vec{E}$ replaced by $\nabla V(\vec{r})$. We write m for the rest mass.] In this paper, as in GMI, \vec{r} denotes a vector from the origin (taken at the center of the La sphere) and $\vec{\rho}$ denotes a vector from the center of the sphere in question. Equation (1) is not in atomic units. In atomic units Eq. (1) becomes

$$\begin{aligned} & \{ -\nabla^2 + V(\vec{r}) - \frac{1}{4} \bar{\alpha}^2 [E^0 - V(\vec{r})]^2 - \frac{1}{4} \bar{\alpha}^2 \nabla V(\vec{r}) \cdot \nabla \\ & + \frac{1}{4} \bar{\alpha}^2 \vec{\sigma} \cdot [\nabla V(\vec{r}) \times \vec{p}/\hbar] \} \psi = E \psi, \quad (2) \end{aligned}$$

with $\bar{\alpha} = \hbar/mc$, the fine-structure constant. In the p^4 term of Eq. (1) we have used the approximation

$$p^2/2m \approx (E - V) \quad (3)$$

and have further assumed that E may be replaced by E^0 in this term. Equation (2) may be written

$$(H^0 + H^{re1}) \psi = E \psi, \quad (4)$$

with

$$H^0 = -\nabla^2 + V(\vec{r}) \quad (5)$$

as in GMI, and H^{re1} equal to the three remaining terms on the left-hand side of Eq. (2). In applying Eq. (4) to a crystal we note that all the periodicity theorems hold for H^{re1} just as for H^0 so we may again work with one unit cell only. Thus, using perturbation theory, we can solve $H^0 \psi_n^0 = E_n^0 \psi_n^0$ and then add the corrections due to H^{re1} as

$$E_n = E_n^0 + E_n^{re1} \quad (6)$$

with

$$E_n^{re1} = \int \psi_n^{0*} H^{re1} \psi_n^0 d\vec{\tau} \quad (7)$$

for the mass-velocity and Darwin corrections [third and fourth terms, respectively, of Eq. (2)] and with a more involved expression for E^{re1} for the spin-orbit correction [fifth term of Eq. (2)].

Confining the problem to one unit cell, we apply H^{re1} as in Eq. (2). Outside the muffin-tin spheres, $\nabla V(\vec{r}) = 0$ so that only the mass-velocity correction gives a contribution in this region,

$$H_{MV}(\text{outside}) = -\frac{1}{4} \bar{\alpha}^2 (E^0 - \bar{V})^2, \quad (8)$$

where \bar{V} is the constant potential in this intersphere region. Within the muffin-tin spheres we can replace $V(\vec{r})$ with the spherically symmetric $V_\nu(\rho)$, where $\vec{\rho}$ is measured from the center of the ν th sphere. For spherically symmetric V ,

$$\nabla V(\rho) \cdot \nabla = \frac{dV}{d\rho} \frac{\partial}{\partial \rho} \quad (9a)$$

and

$$\nabla V(\rho) = \frac{1}{\rho} \frac{dV}{d\rho} \vec{\rho}. \quad (9b)$$

Thus, inside the ν th sphere, Eq. (2) becomes

$$(H^0 + H_{MV} + H_D + H_{SO}) \psi(\vec{\rho} + \vec{s}_\nu) = E \psi(\vec{\rho} + \vec{s}_\nu), \quad (10)$$

where \vec{s}_ν is a vector from the origin to the center of the ν th sphere as in GMI,

$$H_{MV} = -\frac{1}{4} \bar{\alpha}^2 [E^0 - V_\nu(\rho)]^2, \quad (11)$$

$$H_D = -\frac{1}{4} \bar{\alpha}^2 \frac{dV_\nu(\rho)}{d\rho} \frac{\partial}{\partial \rho}, \quad (12)$$

$$H_{SO} = \frac{1}{4} \bar{\alpha}^2 \frac{1}{\rho} \frac{dV_\nu(\rho)}{d\rho} \vec{\sigma} \cdot \vec{L}, \quad (13)$$

with

$$\vec{L} = \vec{\rho} \times \vec{p}/\hbar. \quad (14)$$

These three operators [plus H_{MV} (outside) given by Eq. (8)] lead, respectively, to energy corrections E_{MV} , E_D , and E_{SO} so that the final energy E is given by

$$E = E^0 + E_{MV} + E_D + E_{SO}. \quad (15)$$

Mass-Velocity and Darwin Corrections

The mass-velocity and Darwin operators are invariant to the single-group operations [as may be seen from their form in Eqs. (11) and (12)] so that symmetry is preserved and these operators involve only a shift in energy for any given E^0 level. From ordinary nondegenerate first-order perturbation theory, then,

$$E_{MV} = \int \psi_n^{0*} H_{MV} \psi_n^0 d\vec{\tau} \quad (16)$$

and

$$E_D = \int \psi_n^{0*} H_D \psi_n^0 d\vec{\tau}. \quad (17)$$

Spin-Orbit Correction

The spin-orbit operator does not satisfy the criterion of invariance above; thus mixing between different irreducible single-group representations (for the same \vec{k} point) must be considered as well as the splitting of the degenerate E^0 levels associated with the two- and three-dimensional irreducible single-group representations.

Spin-Orbit Splitting within a Given Representation

For spin-orbit splitting within a given irreducible single-group representation it can be shown quite generally that the spin-orbit arrays have a rather special form which, for a three-dimensional representation, for example, looks like⁵

$$\begin{array}{cccccc} \psi_{11}^0 \alpha & \psi_{11}^0 \beta & \psi_{21}^0 \alpha & \psi_{21}^0 \beta & \psi_{31}^0 \alpha & \psi_{31}^0 \beta \\ \psi_{11}^{0*} \alpha & a & 0 & c & d & e & f \\ \psi_{11}^{0*} \beta & 0 & a & -d^* & c^* & -f^* & e^* \\ \psi_{21}^{0*} \alpha & c^* & -d & g & 0 & h & k \\ \psi_{21}^{0*} \beta & d^* & c & 0 & g & -k^* & h^* \\ \psi_{31}^{0*} \alpha & e^* & -f & h^* & -k & l & 0 \\ \psi_{31}^{0*} \beta & f^* & e & k^* & h & 0 & l \end{array}, \quad (18)$$

where the elements in the even rows are related to those in odd rows as shown for c and d . The requirement of Hermiticity produces pairs of equal elements on the main diagonal and zeros for some of the off-diagonal elements as shown. In (18), we have

$$d = \int \psi_{11}^{0*} \alpha H_{SO} \psi_{21}^0 \beta d\vec{\tau},$$

where α and β are Pauli spin functions,² α referring to spin up, β to spin down. ψ^0 is the nonrelativistic wave function associated with E^0 obtained in GMI. The subscript 21, e. g., indicates that ψ_{21} was formed using the $D_{21}(R)$ matrix elements. For ψ^0 chosen as ours were, it can be shown that the diagonal elements in (18), i. e., a , g , and l , are imaginary; since Hermiticity requires these to be real then a , g , and l must be zero. The secular equation for E_{SO} is obtained by putting $-E_{SO}$ on the diagonal of (18) and setting the determinant equal to zero.

It then follows that all one-dimensional single-group representations will have spin-orbit determinants of the form

$$\begin{vmatrix} -E_{SO} & 0 \\ 0 & -E_{SO} \end{vmatrix} = 0, \quad (19)$$

from which it follows immediately that E_{SO} for the one-dimensional representations is zero.

From an array similar to (18), the two-dimensional single-group representations⁶ must have determinants of the form

$$\begin{vmatrix} -E_{SO} & 0 & A+iB & C+iD \\ 0 & -E_{SO} & -C+iD & A-iB \\ A-iB & -C-iD & -E_{SO} & 0 \\ C-iD & A+iB & 0 & -E_{SO} \end{vmatrix} = 0, \quad (20)$$

where A , B , C , and D are real. This leads to

$$E_{SO} = \pm G, \quad (21)$$

with

$$G^2 = A^2 + B^2 + C^2 + D^2. \quad (22)$$

With the exception of Γ_{12} , Γ_{12}' , R_{12} , R_{12}' , and Λ_3 , all two-dimensional representations of the simple cubic group have $A = C = D = 0$, $B = S \neq 0$ in Eq. (20). For this case

$$E_{SO} = \pm S. \quad (23)$$

[As Eq. (20) is a 4×4 determinant, there are actually four roots, two equal to $+S$ and two equal to $-S$.] The representations Γ_{12} , Γ_{12}' , R_{12} , and R_{12}' have no spin-orbit splitting [i. e., for these four representations $A = B = C = D = 0$ in Eq. (20)]. For the Λ_3 representation $A = 0$, $B = C = D = S \neq 0$. Thus, for Λ_3

$$E_{SO} = \pm \sqrt{3}S. \quad (24)$$

All three-dimensional representations⁶ of the simple cubic group have spin-orbit arrays of the form given in (18) with the additional restriction $c = k = iS$, $f = -S$, and $d = e = h = 0$ (with $a = g = l = 0$ as discussed above). This gives a determinant

$$\begin{vmatrix} -E_{SO} & 0 & iS & 0 & 0 & -S \\ 0 & -E_{SO} & 0 & -iS & S & 0 \\ -iS & 0 & -E_{SO} & 0 & 0 & iS \\ 0 & iS & 0 & -E_{SO} & iS & 0 \\ 0 & S & 0 & -iS & -E_{SO} & 0 \\ -S & 0 & -iS & 0 & 0 & -E_{SO} \end{vmatrix} = 0. \quad (25)$$

This results in a cubic equation

$$E_{SO}^3 - 3S^2 E_{SO} - 2S^3 = 0 \quad (26)$$

with the solution

$$E_{SO} = -S, -S, +2S. \quad (27)$$

(Again, as in the two-dimensional case, there is an inherent two-fold degeneracy here so that there are actually six roots, four equal to $-S$, two equal to $+2S$.) Thus, for the three-dimensional single-group representations the amount of splitting is not "even" as it was in the two-dimensional case but rather in a 1-down, 2-up or 2-down, 1-up ratio depending on whether S is positive or negative, respectively. The smaller magnitude shift has a four-fold degeneracy while the larger magnitude shift has a two-fold degeneracy.

One could also tell *a priori* which single-group representations will split under spin orbit by an inspection of single- to double-group compatibility.³ Those single-group representations which are compatible with more than one⁷ double-group representation can split under spin orbit. (See Tables I and II.)

Identification as to which split single-group level is associated with which of the compatible double-group representations may be done as follows: For the three-dimensional single-groups the smaller shifted level is always four-fold degenerate and must be associated with $\Gamma_{8\pm}$ or $R_{8\pm}$ as the case may be. The larger shifted level is two-fold degenerate

TABLE I. Complete list of single-group two- and three-dimensional irreducible representations for the simple cubic lattice. The notation is that of BSW (Ref. 3 of GMI).

Two-dimensional representations	
Γ_{12}	Γ_{12}' , R_{12} , R_{12}' , Δ_5 , T_5 , X_5 , X_5' , M_5 , M_5' , Λ_3
Three-dimensional representations	
Γ_{15}	Γ_{25} , Γ_{15} , Γ_{25} , R_{15} , R_{25}' , R_{15} , R_{25}

TABLE II. Single-group to double-group compatibility for the simple cubic lattice. Except for Λ the notation is that of Elliott (Ref. 3). Elliott works from the single-group notation of BSW (Ref. 3 of GM I). For Λ the notation of Koster (Ref. 4) is followed. In general, those single-group representations which are compatible with two or more double-group representations will split under spin orbit.

Single	Double
(a) Γ point (valid for R also)	
Γ_1	Γ_{6^+}
Γ_2	Γ_{7^+}
Γ_{12}	Γ_{8^+}
$\Gamma_{15'}$	$\Gamma_{6^+} + \Gamma_{8^+}$
$\Gamma_{25'}$	$\Gamma_{7^+} + \Gamma_{8^+}$
Γ_1'	Γ_6^-
Γ_2'	Γ_7^-
\vdots	\vdots
(b) Δ point (valid for T also)	
Δ_1 or Δ_1'	Δ_6
Δ_2 or Δ_2'	Δ_7
Δ_5	$\Delta_6 + \Delta_7$
(c) X point (valid for M also)	
X_1 or X_4	X_{6^+}
X_2 or X_3	X_{7^+}
X_5	$X_{6^+} + X_{7^+}$
X_1' or X_4'	X_{6^-}
\vdots	\vdots
(d) Λ point	
Λ_1 or Λ_2	Λ_6
Λ_3	$\Lambda_4 + \Lambda_5 + \Lambda_6^a$

^a Λ_4 and Λ_5 are degenerate by time reversal.

and is associated with the appropriate $\Gamma_{6\pm}$, $\Gamma_{7\pm}$, etc. For the two-dimensional representations one could determine how the resultant functions transform but it is probably easier to first identify the function which goes with $E_{SO} = +S$ and then to show that this function has nonzero elements with $\Delta_1(\Delta_6)$ and no nonzero elements with $\Delta_2(\Delta_7)$ if we are investigating the splitting of Δ_5 , for example. In this way one finds that the $E_{SO} = +S$ solution goes with Δ_6 , $X_{6\pm}$, $M_{6\pm}$, or T_6 as appropriate and that the $E_{SO} = -S$ solution goes with Δ_7 , $X_{7\pm}$, $M_{7\pm}$, or T_7 . For Λ_3 one finds $E_{SO} = +\sqrt{3}S$ goes with $\Lambda_4 + \Lambda_5$ (Λ_4 and Λ_5 are degenerate by time reversal) and $E_{SO} = -\sqrt{3}S$ goes with Λ_6 .

Spin-Orbit Mixing between Representations

When the E^0 (or, more precisely, the $E_P = E^0 + E_{MV} + E_D$) energy levels of different irreducible single-group representations for the same \vec{k} point lie close to one another in energy one must also

consider mixing between representations. This involves a number of different types of determinantal solutions, most of which can be reduced to quadratic equations. We give two examples. The general form for the mixed representation arrays also obeys the requirements associated with (18) but now there will be different E_P values for the different representations. Thus, in forming these mixed representation arrays we take the operator as the total Hamiltonian H . As H^0 , H_{MV} , and H_D have zero values between ψ^0 's associated with different representations or between ψ^0 's associated with different rows of the same representation, adding H^0 , H_{MV} , and H_D to the operator associated with (18) results only in producing E_P values on the diagonal.

For all mixed representation arrays which can be reduced to a 4×4 (either from two one-dimensional single-group representations or from the reduction of larger arrays), the determinant analogous to Eq. (20) is

$$\begin{vmatrix} E_P^1 - E & 0 & A + iB & C + iD \\ 0 & E_P^1 - E & -C + iD & A - iB \\ A - iB & -C - iD & E_P^2 - E & 0 \\ C - iD & A + iB & 0 & E_P^2 - E \end{vmatrix} = 0, \quad (28)$$

with A , B , C , and D real and with E_P^1 and E_P^2 being the E_P values from two different single-group representations here labeled 1 and 2 for convenience. Equation (28) leads to

$$(E)^2 - (E_P^1 + E_P^2)E + E_P^1 E_P^2 - G^2 = 0, \quad (29)$$

with

$$G^2 = A^2 + B^2 + C^2 + D^2,$$

as before. Then

$$E = \frac{1}{2}(E_P^1 + E_P^2) \pm \frac{1}{2}[(E_P^1 - E_P^2)^2 + 4G^2]^{1/2}. \quad (30)$$

For the case $4G^2 \ll \Delta^2$, where $\Delta = E_P^1 - E_P^2$, Eq. (30) can be approximated by

$$E = E_P^1 + G^2/\Delta, \quad E = E_P^2 - G^2/\Delta. \quad (31)$$

As a first example of spin-orbit mixing we consider the M_5, E^0 level at -0.4001 Ry and the M_2, E^0 level at -0.4670 Ry.⁸ As M_5 is compatible with M_6^- and M_7^- , and M_2 is compatible with M_7^- we know there can be a mixing here (between the two M_7^- levels). M_5 is a two-dimensional representation with mass-velocity and Darwin shifts such that $E_P = -0.4573$ Ry. For M_5 , the S of Eq. (23) is $+0.0069$ Ry so that M_5 splits into two levels at -0.4504 and -0.4643 Ry. As S is positive the lower M_5 level is associated with M_7^- and the upper M_5 level is associated with M_6^- . The E_P value for M_2 is -0.4948 Ry. The 6×6 M_5, M_2 array can be written as

	ψ_2^0, α	ψ_2^0, β	ϕ_{7-}^1	ϕ_{7-}^2	ϕ_{6-}^1	ϕ_{6-}^2	
ψ_2^{0*}, α	$E_P^{2'} - E$	0	0	$-i\sqrt{2}P$	0	0	
ψ_2^{0*}, β	0	$E_P^{2'} - E$	$-i\sqrt{2}P$	0	0	0	
ϕ_{7-}^{1*}	0	$i\sqrt{2}P$	$E_{7-} - E$	0	0	0	(32)
ϕ_{7-}^{2*}	$i\sqrt{2}P$	0	0	$E_{7-} - E$	0	0	
ϕ_{6-}^{1*}	0	0	0	0	$E_{6-} - E$	0	
ϕ_{6-}^{2*}	0	0	0	0	0	$E_{6-} - E$	

where E_{7-} and E_{6-} are the lower and upper M_5 , levels, respectively, ϕ_{7-}^1 and ϕ_{7-}^2 are the two functions associated with E_{7-} , ϕ_{6-}^1 and ϕ_{6-}^2 are the two functions associated with E_{6-} , and $P = -\int \psi_2^{0*} \alpha H_{SO} \psi_{5',11}^0 \beta d\tau$. (Here the first subscript on ψ^0 indicates the representation. The second subscript on $\psi_{5',11}^0$ indicates that $\psi_{5',11}^0$ was formed using the $D_{11}(R)$ matrix elements. ψ_2^0 does not require a second subscript as M_2 , is one dimensional.) From (32) it is clear that there is no further shift associated with the M_6 -solution and that the solution of the ψ_2 , ϕ_{7-} 4×4 is given by [see Eqs. (28)–(30)]

$$E = \frac{1}{2}(E_P^{2'} + E_{7-}) \pm \frac{1}{2}[(E_P^{2'} - E_{7-})^2 + 8P^2]^{1/2}. \quad (33)$$

A measure of the size of this mixing effect is given by the ratio of $8(P/\Delta)^2$ to 1 (with $\Delta = E_P^{2'} - E_{7-}$). Here $P = 0.0107$ Ry giving $8(P/\Delta)^2 = 0.985$ so that one expects an appreciable effect due to the mixing. Final E values for this example are -0.4504 Ry for the M_6 -level and -0.4580 and -0.5011 Ry for the M_7 -levels. From Fig. 1 we see that the "mixing" shift is 0.0063 Ry or almost as large as the spin-orbit shift for M_5 , alone (0.0069 Ry).

As a second example we consider the Γ_{12} E^0 level at -0.4266 Ry and the Γ_{25} , E^0 level at -0.4748 Ry. The E_P value for Γ_{12} is -0.4892 Ry (there is no spin-orbit splitting for Γ_{12}). For the three-dimensional Γ_{25} , representation E_P is -0.4932 Ry with the S of Eq. (27) equal to $+0.0029$ Ry so that Γ_{25} , splits into a four-fold Γ_{8^+} level at -0.4962 Ry (E_{8^+}) and a two-fold Γ_{7^+} level at -0.4874 Ry (E_{7^+}). As Γ_{12} is compatible with Γ_{8^+} there will be mixing between the Γ_{12} level and the lower Γ_{25} , level. Making use of the functions associated with E_{8^+} and E_{7^+} the 10×10 Γ_{12} , Γ_{25} , array may be written as two separate determinants, one 8×8 involving the four Γ_{12} functions and the four Γ_{8^+} functions associated with E_{8^+} , and one 2×2 involving the two Γ_{7^+} functions associated with E_{7^+} . The 2×2 determinant is diagonal and immediately gives a final $E = E_{7^+}$. The 8×8 determinant reduces to a quadratic equation with solution

$$E = \frac{1}{2}(E_P^{12} + E_{8^+}) \pm \frac{1}{2}[(E_P^{12} - E_{8^+})^2 + 8P^2]^{1/2}, \quad (34)$$

where

$$P = -\int \psi_{12,11}^{0*} \alpha H_{SO} \psi_{25',21}^0 \beta d\tau = 0.0043 \text{ Ry}.$$

The further shift associated with Eq. (34) is 0.0036 Ry or slightly larger than the $S = 0.0029$ Ry determining the splitting of Γ_{25} , alone. In this particular case the "mixing" correction actually changes the ordering of the levels as shown in Fig. 2. (It must be remembered that the Γ_{7^+} level in Fig. 2 is two-fold degenerate and that the Γ_{8^+} levels are each four-fold degenerate.)

Proceeding as indicated in the two examples just given, spin-orbit mixing between different representations has been considered for most of the

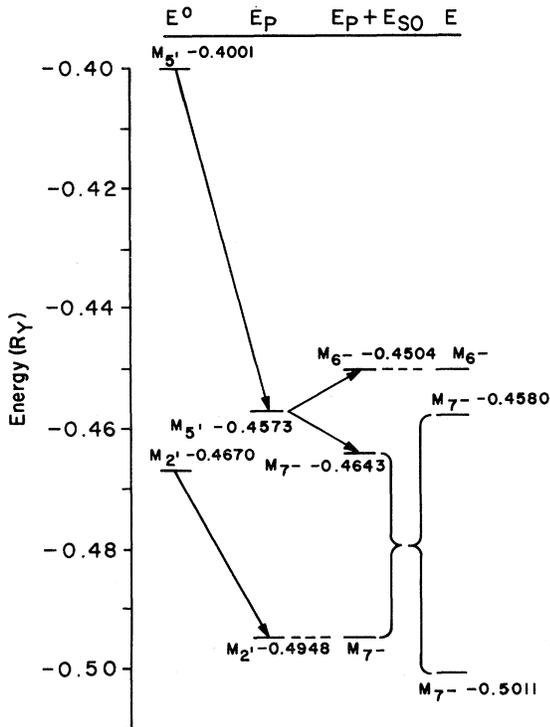


FIG. 1. Example of spin-orbit mixing between representations. The two-dimensional M_5 , splits into M_6 - and M_7 -; this M_7 - interacts with the M_7 - associated with the one-dimensional M_2 ,. M_6 - and the two M_7 - levels are each two-fold degenerate. $E_P = E^0 + E_{MV} + E_D$. All levels are given to four decimal places for comparison.

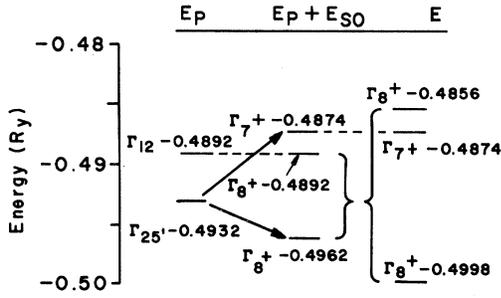


FIG. 2. Example of spin-orbit mixing between representations. The three-dimensional $\Gamma_{25'}$ splits into Γ_{7+} and Γ_{8+} ; this Γ_{8+} interacts with the Γ_{8+} associated with the two-dimensional Γ_{12} (Γ_{12} does not split). The Γ_{8+} levels are four-fold degenerate while Γ_{7+} is two-fold degenerate. $E_P = E^0 + E_{MV} + E_D$ (E^0 is not shown in Fig. 2). Note that in this case the mixing changes the level ordering. All levels are given to four decimal places for comparison.

cases where we felt that the E_P levels were sufficiently close and where the double-group representations associated with the levels indicated mixing could occur. In some cases this mixing effect was ignored as it was felt the correction involved would not affect levels near the Fermi level. (The actual computation of this mixing effect involves a rather tedious procedure as our original computer program was basically designed to handle one single-group representation at a time. For this reason one Λ_1 , Λ_3 case quite near the Fermi level was ignored; Λ_1 , Λ_3 mixing being a particularly involved computation.) In the tabulation of our final relativistic results (Table IV) the notation indicates whether such mixing was included.

EVALUATION OF THE RELATIVISTIC CORRECTION INTEGRALS

The explicit integrals to be evaluated to obtain the mass-velocity and Darwin corrections arise from substituting

$$\psi_n^{0*}(\vec{r}) = \sum_i c_{ni} \phi_i(\vec{r}) \quad (35)$$

into Eqs. (16) and (17), respectively. The spin-orbit correction involves the substitution of Eq. (35) into integrals of the form

$$H^{SO}(m, n : 1, 2) = \int \psi_m^{0*}(\vec{r}) \vec{\eta}_1 H_{SO} \psi_n^0(\vec{r}) \vec{\eta}_2 d\vec{\tau}, \quad (36)$$

where ψ_m^0 and ψ_n^0 can belong to different single-group representations or to different rows of the same representation and $\vec{\eta}_1$, $\vec{\eta}_2$ can be either α or β (spin up or spin down). In the modified plane wave (MPW) formulation the ϕ_i of Eq. (35) are either symmetrized atomiclike functions or symmetrized plane waves; in the MOPW formulation the ϕ_i are either symmetrized higher-lying atomiclike functions or symmetrized orthogonalized plane waves (OPW's).

(See GMI for details.) We first discuss the evaluation of Eqs. (16), (17), and (36) for the MPW formulation and then outline how one uses these MPW expressions to obtain the appropriate MOPW evaluations.

MPW Integrals

A number of types of integrals are needed, namely, the three combinations plane wave-plane wave, atomic term-plane wave, and atomic term-atomic term for each of the three operators H_{MV} , H_D , and H_{SO} .⁹ For the mass-velocity and Darwin integrals it is only necessary to symmetrize one of the two ϕ functions comprising these integrals when Eq. (35) is substituted into Eqs. (16) or (17). For the spin-orbit integrals one needs symmetrized ϕ functions on both sides of the integral in Eq. (36) since the spin-orbit operator H_{SO} can break the single-group symmetry. However, when ψ_m^0 and ψ_n^0 belong to different rows of the same single-group representation and are associated with the same E^0 , we show in Appendix A that H_{SO} can be modified enabling one to replace

$$H_{ij}^{SO}(m, n : 1, 2) = \int \phi_i^{s*}(\vec{r}) \vec{\eta}_1 H_{SO} \phi_j^n(\vec{r}) \vec{\eta}_2 d\vec{\tau}, \quad (37)$$

with

$$H_{ij}^{SO}(m, n : 1, 2) = \int \phi_i^{u*}(\vec{r}) \vec{\eta}_1 \sum_{t=1}^{h-1} H'_{SO}(t) \phi_j^{st}(\vec{r}) \vec{\eta}_2 d\vec{\tau}, \quad (38)$$

where the superscripts s and u mean symmetrized and unsymmetrized, respectively, $H'_{SO}(t)$ is a modified H_{SO} operator and h is the dimensionality of the representation in question.¹⁰ The spin-orbit integrals involving two different single-group representations have been evaluated in the form of Eq. (37) where ϕ_i and ϕ_j now belong to different representations.

For completeness, mass-velocity and Darwin mixing between different but close-lying E^0 energy levels belonging to the same single-group representation should be calculated in the same manner as the spin-orbit mixing between representations. This has not been done here as it was felt that the accuracy of our E^0 levels did not warrant the rather tedious calculations involved. (Typically, such situations occur for the lower symmetry k points where convergence is particularly poor.)

The derivation of the individual expansion integrals for the various combinations is quite involved; in Appendix B the resultant MPW expressions for the necessary combinations for E_{MV} , E_D , and E_{SO} ¹¹ are given without derivation.

MOPW Integrals

For the MOPW formulation the MPW expressions of Appendix B must be assembled properly. Schematically, we write

$$\psi_n^0(\vec{r}) = \sum_i c_{ni} A_i(\vec{r}) + \sum_j c_{nj} \phi_j(\vec{r}), \quad (39)$$

where the $A_i(\vec{r})$ are the higher-lying atomiclike functions (we do not orthogonalize to these functions) and the $\phi_j(\vec{r})$ are OPW's. All functions are symmetrized. We have

$$\phi_j = P(\vec{K}_j) - \sum_b a_{jb} C_b(\vec{r}), \quad (40)$$

where $P(\vec{K}_j)$ is the ordinary plane-wave term and the $C_b(\vec{r})$ are the lower-lying atomiclike functions. We assume here that

$$\langle C_b | C_t \rangle = \delta_{bt}, \quad (41)$$

so that

$$a_{jb} = \langle C_b | P(\vec{K}_j) \rangle. \quad (42)$$

The relativistic corrections E_{MV} , E_D , and E_{SO} will then each involve integrals of the following types:

$\langle A | O | A \rangle$, $\langle A | O | \phi \rangle$, and $\langle \phi | O | \phi \rangle$, where O stands for any of the operators H_{MV} , H_D , or H_{SO} . (For H_D one also needs $\langle \phi | O | A \rangle$. See Ref. 9.)

$\langle A_i | O | A_j \rangle$: These are just the atomic-term-atomic-term integrals given in Appendix B.

$\langle A_i | O | \phi_j \rangle$: We have

$$\langle A_i | O | \phi_j \rangle = \langle A_i | O | P(\vec{K}_j) \rangle - \sum_b a_{jb} \langle A_i | O | C_b \rangle, \quad (43)$$

where the first term is just the appropriate atomic-term-plane-wave integral of Appendix B and the second term sums the appropriate atomic-term-atomic-term integrals of Appendix B.

$\langle \phi_j | O | A_i \rangle$: We have

$$\langle \phi_j | O | A_i \rangle = \langle P(\vec{K}_j) | O | A_i \rangle - \sum_b a_{jb} \langle C_b | O | A_i \rangle. \quad (44)$$

This expression is needed only in those cases for which the operator is not Hermitian term by term.

$\langle \phi_i | O | \phi_j \rangle$: This becomes

$$\langle \phi_i | O | \phi_j \rangle = \langle P(\vec{K}_i) | O | P(\vec{K}_j) \rangle - F - B + D, \quad (45)$$

with

$$F = \sum_t a_{it} \langle C_t | O | P(\vec{K}_j) \rangle,$$

$$B = \sum_b a_{jb} \langle P(\vec{K}_i) | O | C_b \rangle,$$

$$D = \sum_{t,b} a_{it} a_{jb} \langle C_t | O | C_b \rangle,$$

where the appropriate plane-wave-plane-wave, atomic-term-plane-wave, and atomic-term-atomic-term integrals are taken from Appendix B. (The a_{jb} are real.)

Following Chow and Liu¹² one expects the relativistic corrections to be large near the nucleus so that most of the contribution to the above expressions comes from the atomic-term-atomic-term integrals; this would mean keeping all the $\langle A_i | O | A_j \rangle$ integrals above but only the last terms of Eqs. (43) and (44) and only D of Eq. (45). Although this approximation is borne out by an inspection of the various contributions, we have actually kept all the

terms for all the mass-velocity, Darwin, and *single-representation* spin-orbit splittings listed (with the exception of the Λ_3 spin-orbit case). For Λ_3 spin-orbit and for all the spin-orbit mixing *between* representations we have used only the atomic-term-atomic-term integrals.

CALCULATIONAL CHECKS

Radial integrals. As a check on our differentiation¹³ of the potential $V(\rho)$ and of the radial function $u_{n\ell}(\rho)$ we note that our Darwin radial integrals [associated with Eq. (B29), Appendix B] and our spin-orbit radial integrals [Eq. (B51), Appendix B] agree with those of HS (see GMI, Ref. 4) to about four significant figures for the lower-lying atomic-atomic integrals (with $n=n'$ in our equations).

TABLE III. Comparison of relativistic corrections with atomic values for selected lower-lying crystal levels. In the three tables below column 2 gives the Herman-Skillman (HS) value (Chap. 2 of Ref. 4 of GMI), column 3 is our value, and column 4 gives the representation(s) from which our value was obtained. All energies are in rydbergs.

Atomic function	HS ^a	Present paper	Rep. used
(a) Mass-velocity correction (E_{MV})			
La 5s	-0.830	-0.8307	X_1
La 3p	-4.10	-4.288	Γ_{15}
La 4d	-0.236	-0.2406	$R_{25'}$
Sn 4s	-2.2990	-2.3086	$R_{25'}$
Sn 4p	-0.4256	-0.4266	Γ_{15}
Sn 3d	-0.5514	-0.5512	$R_{25'}$
(b) Darwin correction (E_D)			
La 5s	0.461	0.4678	X_1
La 3p	-0.042	-0.0423	Γ_{15}
La 4d	-0.0045	-0.0046	$R_{25'}$
Sn 4s	1.3409	1.3478	$R_{25'}$
Sn 4p	-0.0046	-0.0045	R_{15}
Sn 3d	-0.0154	-0.0154	$R_{25'}$
(c) Spin-orbit correction ^b			
La 4p	0.383	0.3869	Γ_{15}
La 5p	0.0557	0.0549	Γ_{15}
La 4d	0.0457	0.0466	R_{12} and $R_{25'}$ ^c
Sn 3p	0.9689	0.9687	Γ_{15} and $\Gamma_{25'}$ ^c

^aThe relativistic corrections given by HS are for even atomic numbers (Z) only. To obtain the HS values listed here for La ($Z=57$) we have interpolated linearly between the values given by HS for Ba ($Z=56$) and Ce ($Z=58$). The values for Sn ($Z=50$) are taken directly from HS.

^bThe spin-orbit values listed here are for Q where Q is always positive. For the p cases the energy shifts are $+Q$ and $-2Q$. For the d case the energy shifts are $+2Q$ and $-3Q$.

^cTo obtain the spin-orbit corrections for La 4d and for Sn 3p from our crystal calculation it is necessary to combine two representations in each case because of degeneracies.

large hole around R . In the $R\Gamma$ direction (long-diagonal) this hole extends about three-fourths of the way toward Γ ; in the RSX (short-diagonal) direction it extends about half-way to X ; and in the RTM direction the hole extends all the way to M , just touching E_F at M . The ninth band is completely empty.

COMPARISON WITH EXPERIMENT

Using the McMillan strong-coupling model¹⁸ and measured values of the superconducting critical temperature (T_c), the Debye temperature, and the electronic specific heat coefficient (see GMI Ref. 2), Toxen and Gambino¹⁹ have calculated $N(0)$, the bare density of states at E_F . They obtain an $N(0)$ of 0.644 states/eV atom, whereas we find $N(0)$ equal to 1.4 states/eV atom for our relativistic density of states (based on 0.02-Ry ΔE increments). Thus, our value is about twice as large as that of Toxen and Gambino. Curiously, our nonrelativistic $N(0)$ value is 0.87 states/eV atom, considerably closer to their value. We emphasize that our density-of-states value is based on an extremely limited number of points and is, therefore, not very accurate.

Havinga *et al.*²⁰ have performed an extensive series of measurements of T_c , the magnetic sus-

ceptibility (χ), and the thermoelectric power of a number of alloys with the Cu_3Au structure. Their results show the oscillatory dependence of these three properties on the average number of valence electrons per atom. They conclude that such behavior can be explained on the basis of a nearly-free-electron model. While the free-electron theory does lead to an E_F at about the same height above the bottom of the valence bands as we find it to be, our Fermi surface is not what one would expect from a free-electron picture.²¹ It may be that properties like T_c and χ are not very sensitive to departures from the free-electron picture. Havinga's arguments depend on the Fermi surface hitting zone boundaries; for LaSn_3 with 15 valence electrons this could occur at about the same energy even with considerable departure of the Fermi surface from the free-electron sphere.

SUMMARY AND CONCLUSIONS

In GMI the MOPW method has been used to calculate $E^0(\vec{k})$ for the equivalent of 64 points in the Brillouin zone. In the present paper $E(\vec{k})$ for the same 64 points has been computed using

$$E = E^0 + E_{MV} + E_D + E_{SO},$$

including spin-orbit mixing between representations

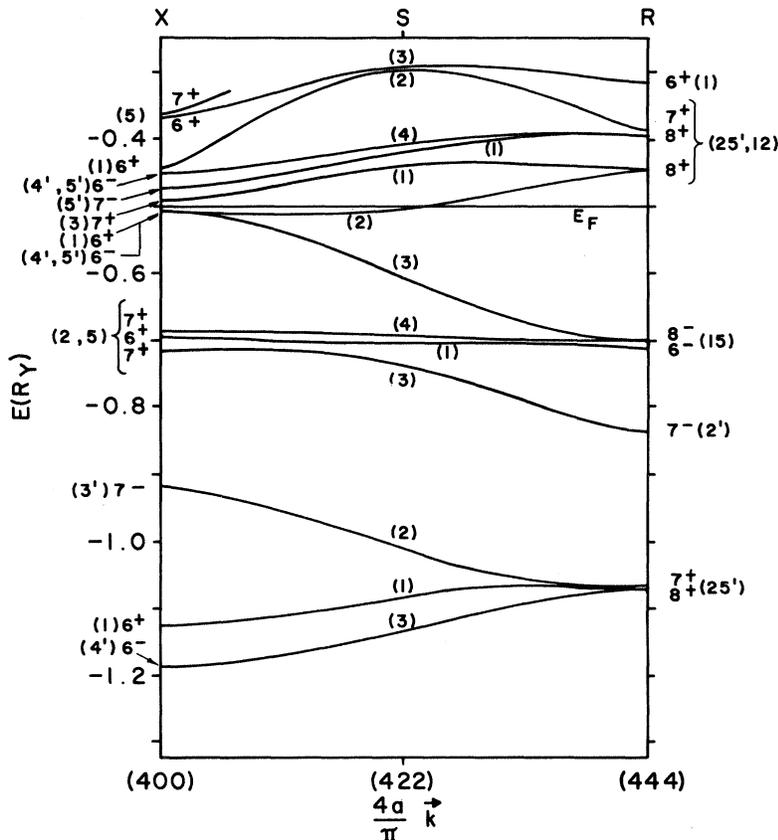


FIG. 6. Relativistic E vs k for the XSR direction.

$$I \equiv \langle P_{\mu 1} f(\vec{r}) | \vec{\sigma} \cdot \vec{L} | P_{\nu 1} g(\vec{r}) \rangle \quad (\text{A1a})$$

$$= \langle f(\vec{r}) | \sum_{\gamma=1}^h \vec{\sigma} \cdot \vec{L}(1\mu : \gamma\nu) P_{\gamma 1} g(\vec{r}) \rangle, \quad (\text{A1b})$$

where

$$P_{\nu n} f(\vec{r}) = (h/g) \sum_R D_{\nu n}^*(R) f(R^{-1} \vec{r}), \quad (\text{A2})$$

and $\vec{L}(1\mu : \gamma\nu)$ is a modified form of \vec{L} . h and g are as in Eq. (12) of GMI. Substituting Eq. (A2) into Eq. (A1a) we have

$$I = (h^2/g^2) \int U_R [\vec{\sigma} \cdot \vec{L}(\vec{r}')] V_S d\vec{r}',$$

with

$$U_R = \sum_R D_{\mu 1}(R) f^*(R^{-1} \vec{r}')$$

and

$$V_S = \sum_S D_{\nu 1}^*(S) g(S^{-1} \vec{r}').$$

Let $R^{-1} \vec{r}' = \vec{r}$ and $S = RT$, then

$$I = (h^2/g^2) \int f^*(\vec{r}) \sum_R D_{\mu 1}(R) [\vec{\sigma} \cdot \vec{L}(R \vec{r})] W_T d\vec{r},$$

with

$$W_T = \sum_T D_{\nu 1}^*(RT) g(T^{-1} \vec{r}).$$

Now substitute

$$D_{\nu 1}^*(RT) = \sum_{\gamma} D_{\nu \gamma}^*(R) D_{\nu 1}^*(T),$$

with γ running over the dimensionality. Replace R with Q^{-1} , use

$$D_{\mu 1}(Q^{-1}) = D_{\mu 1}^*(Q), \quad D_{\nu \gamma}^*(Q^{-1}) = D_{\nu \gamma}(Q),$$

and sum on Q . This gives

$$I = \langle f(\vec{r}) | \sum_{\gamma} \vec{\sigma} \cdot \vec{L}(1\mu : \gamma\nu) P_{\gamma 1} g(\vec{r}) \rangle, \quad (\text{A3})$$

with

$$\vec{L}(1\mu : \gamma\nu) \equiv (h/g) \sum_Q D_{1\mu}^*(Q) D_{\nu \gamma}(Q) \vec{L}(Q^{-1} \vec{r}), \quad (\text{A4})$$

which proves Eq. (A1b). The effect of Eq. (A1b) is to replace $\vec{\sigma} \cdot \vec{L}$ integrals which have symmetrized functions on both sides by integrals containing an unsymmetrized function on the left-hand side and a sum over modified \vec{L} operators and symmetrized functions on the right-hand side.

Since the $P_{\nu n}$ and \vec{L} operate on the space coordinates only, we may write $f(\vec{r})$ and $g(\vec{r})$ above as $f(\vec{r})\alpha$, $g(\vec{r})\beta$, etc., without affecting the proof of Eq. (A1b). (The α and β are Pauli spin functions as in the main text.) Values for S of Eqs. (23) and (27) of the main text may be obtained from

$$iS = \int \psi_{11}^{0*} \alpha H_{SO} \psi_{21}^0 \alpha d\vec{r}.$$

Thus, we are primarily interested in the " $\alpha\alpha$ " combination of Eq. (A1b) with $\mu=1$ and $\nu=2$, i. e.,

$$I = \langle P_{11} f(\vec{r}) \alpha | \vec{\sigma} \cdot \vec{L} | P_{21} g(\vec{r}) \alpha \rangle \\ = \langle f(\vec{r}) \alpha | \sum_{\gamma=1}^h \vec{\sigma} \cdot \vec{L}(11 : \gamma 2) P_{\gamma 1} g(\vec{r}) \alpha \rangle.$$

For all two-dimensional simple cubic representations except Λ_3 it can be shown²² that $\vec{L}(11 : 12) = 0$, $\vec{L}(11 : 22) = \hat{k}L_z$. Since

$$\alpha \vec{\sigma} \alpha = \hat{k}, \quad (\text{A5})$$

Eq. (A1b) for this case becomes

$$\langle P_{11} f(\vec{r}) \alpha | \vec{\sigma} \cdot \vec{L} | P_{21} g(\vec{r}) \alpha \rangle = \langle f(\vec{r}) | L_z P_{21} g(\vec{r}) \rangle. \quad (\text{A6})$$

[Equation (A6) is valid for all two-dimensional representations except Λ_3 , Γ_{12} , $\Gamma_{12'}$, R_{12} , and $R_{12'}$.] Using Eq. (A5) in the left-hand side of Eq. (A6) would lead directly to

$$\langle P_{11} f(\vec{r}) \alpha | \vec{\sigma} \cdot \vec{L} | P_{21} g(\vec{r}) \alpha \rangle = \langle P_{11} f(\vec{r}) | L_z P_{21} g(\vec{r}) \rangle. \quad (\text{A7})$$

Thus, for the $D_{11} - D_{21}$ $\alpha\alpha$ case for these two-dimensional representations an unsymmetrized or symmetrized function may be used on the left-hand side of the integral in Eq. (37) of the main text.

For the Λ_3 representation $\vec{L}(1\mu : \gamma\nu)$ is considerably more involved so that we form the Λ_3 spin-orbit integrals using Eq. (A7).

For all three-dimensional simple-cubic representations it can be shown that $\vec{L}(11 : 12) = 0$, $\vec{L}(11 : 22) = \hat{k}(\frac{1}{2}L_z)$, and $L(11 : 32) = -\hat{k}(\frac{1}{2}L_y)$. Thus Eq. (A1b) becomes

$$\langle P_{11} f(\vec{r}) \alpha | \vec{\sigma} \cdot \vec{L} | P_{21} g(\vec{r}) \alpha \rangle = \frac{1}{2} \langle f(\vec{r}) | L_z P_{21} g(\vec{r}) \rangle \\ - \frac{1}{2} \langle f(\vec{r}) | L_y P_{31} g(\vec{r}) \rangle. \quad (\text{A8})$$

[Equation (A8) is valid for all three-dimensional representations.]

APPENDIX B: MPW RELATIVISTIC CORRECTION INTEGRALS

In this appendix we give the resultant MPW integral expressions (without derivation) for the relativistic corrections. The MOPW expressions are obtained by assembling these MPW integrals as indicated in the main text. In the expressions below j_l is the l th-order spherical Bessel function; $u_{nl}(\rho)$ and $X_{li}(\vec{\rho}/\rho)$ are as defined in the Appendix to GM I. In deriving these integral expressions we have multiplied by $(g/h)(1/4\pi)$ so that all the relativistic corrections will be normalized properly. h and g are as in Eq. (12) of GM I. The relation between \vec{r} and $\vec{\rho}$ is as in GM I.

Mass-Velocity Integrals

From Eqs. (8), (11), and (16) of the main text we have

$$E_{MV} = -\frac{1}{4}\bar{\alpha}^2 \int \psi_n^{0*}(\vec{r}) [E_n^0 - V(\vec{r})]^2 \psi_n^0(\vec{r}) d\vec{r}, \quad (\text{B1})$$

with

$$\psi_n^0(\vec{r}) = \sum_i c_{ni} \phi_i(\vec{r}) \quad (\text{B2})$$

and $\bar{\alpha} = \hbar/mc$, as in the main text. (As the mass-velocity correction involves only one E^0 level we will suppress the subscript n .) E_{MV} is conveniently broken into three terms:

$$E_{MV} = -\frac{1}{4}\bar{\alpha}^2 (E_{MV1} + E_{MV2} + E_{MV3}), \quad (\text{B3})$$

TABLE IV. LaSn_3 energy levels for the ten symmetry points of GMI including the relativistic corrections. The symmetry point labels and the single-group representation labels are in the BSW notation (Ref. 3 of GMI). Except for Λ the double-group representation labels are those of Elliott (Ref. 3). For Λ we follow the notation of Koster (Ref. 4). The third and alternate columns of Table IV give the double-group representation (no parentheses) followed by the single-group representation(s) (in parentheses) which labels the associated E^0 level. [For three symmetry points (Σ , S , Z) there is only one extra double-group representation and all final levels belong to the same representation; no double-group label is given for these points. Spin-orbit mixing between different single-group representations is indicated by the presence of two or more single-group labels within the parentheses.] The fourth and alternate columns give the final energy levels E for the respective bands. The method of counting bands is described in the text. Here $E = E^0 + E_{\text{MV}} + E_D + E_{\text{SO}}$, where E^0 is the nonrelativistic level given in GMI and the other terms are the relativistic corrections (see text). All energies are in rydbergs and must be multiplied by -1.0 to obtain the actual value. Energy values given to only two decimal places indicate that either the underlying E^0 value is poorly converged or that spin-orbit mixing between close-lying levels was ignored.

Label	$4a\vec{k}/\pi$	Rep.	Band 1	Rep.	Band 2	Rep.	Band 3	Rep.	Band 4
Γ	000	$6^*(1)$	1.272	$8^*(12)$	0.951	$8^*(12)$	0.951	$8^-(15)$	0.675
Δ	200	$6(1)$	1.246	$6(1)$	1.022	$7(2)$	0.934	$7(2, 5)$	0.687
X	400	$6^-(4')$	1.185	$6^*(1)$	1.122	$7^-(3')$	0.915	$7^-(2, 5)$	0.713
Σ	220	(1)	1.213	(1, 4)	1.024	(1, 4)	0.980	(1, 3, 1)	0.68
M	440	$7^+(3)$	1.115	$6^-(5')$	1.070	$7^-(5')$	1.067	$6^*(1)$	0.802
Λ	222	$6(1)$	1.191	$6(3)$	1.017	$4, 5(3)^a$	1.016	$6(1)$	0.775
R	444	$8^+(25')$	1.068	$8^+(25')$	1.068	$7^+(25')$	1.067	$7^-(2')$	0.84
S	422	(3)	1.133	(1)	1.080	(2)	1.007	(3)	0.74
T	442	$7(2')$	1.09	$6(5)$	1.069	$7(5)$	1.06	$6(1)$	0.755
Z	420	(3)	1.159	(1)	1.092	(3)	0.975	(1)	0.72
Label	$4a\vec{k}/\pi$	Rep.	Band 5	Rep.	Band 6	Rep.	Band 7	Rep.	Band 8
Γ	000	$8^-(15)$	0.675	$6^-(15)$	0.668	$8^+(12, 25')$	0.500	$8^+(12, 25')$	0.500
Δ	200	$6(1, 5)$	0.678	$6(1, 5)$	0.61	$7(2, 5)$	0.61	$6(1, 5)$	0.51
X	400	$6^+(5)$	0.697	$7^+(2, 5)$	0.684	$6^-(4', 5')$	0.51	$6^*(1)$	0.506
Σ	220	(1, 3, 1)	0.67	(1, 3, 1)	0.66	(2)	0.58	(4)	0.52
M	440	$6^+(5)$	0.633	$7^+(3, 5)$	0.632	$7^+(3, 5)$	0.584	$7^-(5', 2')$	0.501
Λ	222	$4, 5(3)^a$	0.66	$6(3)$	0.66	$6(1)$	0.55	$4, 5(3)^a$	0.49
R	444	$6^-(15)$	0.703	$8^-(15)$	0.701	$8^-(15)$	0.701	$8^+(25', 12)$	0.445
S	422	(1)	0.70	(4)	0.69	(3)	0.61	(2)	0.50
T	442	$7(2')$	0.744	$6(5)$	0.669	$7(5)$	0.668	$7(2)$	0.45
Z	420	(2)	0.67	(3)	0.63	(4)	0.59	(1)	0.55
Label	$4a\vec{k}/\pi$	Rep.	Band 9	Rep.	Band 10	Rep.	Band 11	Rep.	Band 12
Γ	000	$7^+(25')$	0.487	$8^+(12, 25')$	0.486	$8^+(12, 25')$	0.486	$8^-(25)$	0.37
Δ	200	$7(2', 5)$	0.49	$7(2', 5)$	0.48	$6(1, 5)$	0.44	$6(1, 5)$	0.31
X	400	$7^+(3)$	0.490	$7^-(5')$	0.47	$6^-(4', 5')$	0.452	$6^+(5, 1)$	0.442
Σ	220	(4)	0.49	(1, 3, 1)	0.44	(1, 3, 1)	0.40	(1, 3, 1)	0.39
M	440	$7^+(2)$	0.470	$7^-(5', 2')$	0.46	$6^-(5')$	0.45	$6^*(1)$	0.43
Λ	222	$6(3)$	0.49	$4, 5(3)^a$	0.44	$6(3)$	0.43	$6(1)$	0.39
R	444	$8^+(25', 12)$	0.445	$8^+(25', 12)$	0.40	$8^+(25', 12)$	0.40	$7^+(25')$	0.39
S	422	(1)	0.44	(1)	0.42	(4)	0.41	(2)	0.30
T	442	$6(1)$	0.41	$7(5)$	0.40	$6(5)$	0.39	$7(2')$	0.37
Z	420	(2, 1, 3)	0.48	(2, 1, 3)	0.45	(2, 1, 3)	0.42	(1)	0.31
Label	$4a\vec{k}/\pi$	Rep.	Band 13	Rep.	Band 14	Rep.	Band 15		
Γ	000	$8^-(25)$	0.37	$7^-(25)$	0.35	$6^*(1)$	0.337		
Δ	200	$7(5)$	0.30	$6(1, 5)$	0.28				
X	400	$6^+(5, 1)$	0.37	$7^+(5)$	0.36				
Σ	220	(3)	0.28	(4)	0.24	(2)	0.23		
M	440	$7^+(3)$	0.40						
Λ	222	$6(2)$	0.29	$6(3)$	0.26	$4, 5(3)^a$	0.25		
R	444	$6^*(1)$	0.315						
S	422	(3)	0.29	(3)	0.24				
T	442	$7(2')$	0.29						
Z	420	(4)	0.30	(3)	0.26	(3)	0.25		

^a Λ_4 and Λ_5 are degenerate by time reversal.

with

$$E_{MV1} = (E^0)^2 \int \psi^{0*}(\vec{r}) \psi^0(\vec{r}) d\vec{r}, \quad (B4)$$

$$E_{MV2} = -2E^0 \int \psi^{0*}(\vec{r}) V(\vec{r}) \psi^0(\vec{r}) d\vec{r}, \quad (B5)$$

and

$$E_{MV3} = \int \psi^{0*}(\vec{r}) [V(\vec{r})]^2 \psi^0(\vec{r}) d\vec{r}. \quad (B6)$$

(We break E_{MV} up in this fashion so that these relativistic correction integrals can be evaluated in the same part of the program in which the H_{ij}^0 and S_{ij} integrals are computed. E^0 is, of course, not available until the nonrelativistic part of the program has finished.) Substituting $\psi^0(\vec{r})$ from Eq. (B2) we obtain the expressions given below.

$$E_{MV1} = (E^0)^2 \sum_{i,j} c_i c_j S_{ij}, \quad (B7)$$

where the S_{ij} expressions are given in the Appendix to GM I. [Equation (B7) is valid as it stands for MOPW also.]

E_{MV2} . This is derived exactly as the $V(\vec{r})$ part of the original H^0 matrix. Let

$$E_{MV2} = -2E^0 \left[\sum_{i,j}^{\xi} c_i c_j E_{MV2}(\vec{K}_i, \vec{K}_j) + 2 \sum_{b,j}^{\eta} c_b c_j E_{MV2}(A_b, \vec{K}_j) + \sum_{b,t}^{\xi} c_b c_t E_{MV2}(A_b, A_t) \right]. \quad (B8)$$

The ξ sum is over plane waves, the η sum is over atomiclike functions and plane waves, and the ζ sum is over atomiclike functions. [The factor 2 in the

second sum comes from combining the (A_b, \vec{K}_j) and (\vec{K}_j, A_b) terms.]

Plane wave-plane wave. We have

$$E_{MV2}(\vec{K}_i, \vec{K}_j) = \bar{V} S_{ij} + \sum_R D_{11}(R) [I(\text{La}) + F(\vec{K}) I(\text{Sn})], \quad (B9)$$

with

$$\vec{K} = R^{-1}(\vec{k} + \vec{K}_j) - (\vec{k} + \vec{K}_i),$$

$$I(\nu) = \int_V (\rho V_\nu(\rho) - \rho \bar{V}) j_0(K\rho) \rho d\rho,$$

and

$$F(\vec{K}) = \sum_{\nu}^{\bar{s}_n} e^{i\vec{K} \cdot \bar{s}_\nu} \quad (B10)$$

as in GM I. \bar{V} is the constant potential in the region between the muffin-tin spheres, \bar{s}_ν is a site vector as defined in GM I, and the sum on ν in Eq. (B10) runs over the three Sn basis sites. $D_{11}(R)$ is the "one-one" element in the matrix representing the operation R . The sum on R runs over the group of \vec{k} .

Atomic term-plane wave. We have

$$E_{MV2}(A_b, \vec{K}_j) = s \int_V u_{n1}(\rho) j_1(K\rho) \rho V_\nu(\rho) d\rho, \quad (B11)$$

where

$$s = \sum_R D_{11}(R) X_{1b}(\vec{B}) e^{i\vec{K}' \cdot \bar{s}_\nu}, \quad (B12)$$

with $\vec{K}' = \vec{k} + \vec{K}_j$, $\vec{K}' = R^{-1}\vec{K} - \vec{k}$, and $\vec{B} = R^{-1}\vec{K}/K$.

Atomic term-atomic term. We have

$$E_{MV2}(A_b, A_t) = \frac{1}{4\pi} \int_V u_{n1}(\rho) V_\nu(\rho) u_{n't}(\rho) d\rho \times \int X_{1b} \frac{\vec{\rho}}{\rho} X_{1t}^* \frac{\vec{\rho}}{\rho} d\Omega, \quad (B13)$$

TABLE V. Breakdown of relativistic corrections for the Γ point. E^0 is the nonrelativistic energy level. E_{MV} and E_D are the mass-velocity and Darwin corrections, respectively. $E_P = E^0 + E_{MV} + E_D$, i. e., the energy level before the spin-orbit correction (E_{SO}) is added. The next to last column gives $E = E_P + E_{SO}$ with no mixing between different single-group representations. The last column gives the final energy level including spin-orbit mixing between close-lying levels where appropriate. The number in parentheses following the E^0 value is the single-group representation; the numbers in parentheses in the last two columns are the double-group representations. The representation labels used here follow Elliott (Ref. 3). For comparison all values are given to three decimal places even though the third decimal place is not significant in some cases. All energies are in rydbergs and must be multiplied by -1.0 to give the actual value.

E^0	E_{MV}	E_D	E_P	E (no mixing)	E (with mixing) ^a
0.304 (1)	0.074	-0.041	0.337	0.337 (6 ⁺)	0.337 (6 ⁺)
0.329 (25)	0.035	0.000	0.364	{ 0.350 (7 ⁻) 0.372 (8 ⁻)	{ 0.350 (7 ⁻) 0.372 (8 ⁻)
0.427 (12)	0.123	-0.061	0.489	0.489 (8 ⁺)	0.486 (8 ⁺)
0.475 (25')	0.018	0.000	0.493	{ 0.487 (7 ⁺) 0.496 (8 ⁺)	{ 0.487 (7 ⁺) 0.500 (8 ⁺)
0.642 (15)	0.030	0.000	0.672	{ 0.668 (6 ⁻) 0.675 (8 ⁻)	{ 0.668 (6 ⁻) 0.675 (8 ⁻)
0.854 (12)	0.220	-0.122	0.951	0.951 (8 ⁺)	0.951 (8 ⁺)
1.196 (1)	0.177	-0.101	1.272	1.272 (6 ⁺)	1.272 (6 ⁺)

^aFor the Γ point, symmetry and/or large differences in E_P levels eliminate the consideration of mixing for all cases except the close-lying Γ_{12} , Γ_{25} levels; thus, with these exceptions, the entries in the last two columns are identical.

TABLE VI. Breakdown of relativistic corrections for the Δ point. The format is identical to that of Table V. For comparison all values are given to three decimal places even though the third place is not significant in some cases. All energies are in rydbergs and must be multiplied by -1.0 to give the actual value.

E^0	E_{MV}	E_D	E_P	E (no mixing)	E (with mixing) ^a
0.244 (1)	0.061	-0.017	0.288	0.288 (6)	0.282 (6)
0.266 (5)	0.033	0.000	0.299	$\left. \begin{matrix} 0.296 (7) \\ 0.302 (6) \end{matrix} \right\}$	$\left. \begin{matrix} 0.296 (7) \\ 0.308 (6) \end{matrix} \right\}$
0.381 (1)	0.119	-0.058	0.441	0.441 (6)	0.441 (6)
0.463 (2')	0.018	0.000	0.482	0.482 (7)	0.480 (7)
0.468 (5)	0.027	0.000	0.496	$\left. \begin{matrix} 0.487 (7) \\ 0.505 (6) \end{matrix} \right\}$	$\left. \begin{matrix} 0.488 (7) \\ 0.505 (6) \end{matrix} \right\}$
0.562 (2)	0.079	-0.034	0.607	0.607 (7)	0.606 (7)
0.576 (1)	0.058	-0.021	0.613	0.613 (6)	0.613 (6)
0.656 (5)	0.026	0.000	0.682	$\left. \begin{matrix} 0.678 (6) \\ 0.686 (7) \end{matrix} \right\}$	$\left. \begin{matrix} 0.678 (6) \\ 0.687 (7) \end{matrix} \right\}$
0.826 (2)	0.243	-0.135	0.934	0.934 (7)	0.934 (7)
0.933 (1)	0.194	-0.106	1.022	1.022 (6)	1.022 (6)
1.164 (1)	0.186	-0.104	1.246	1.246 (6)	1.246 (6)

^aFor the Δ point, mixing between levels is appreciable only for the highest-lying Δ_1 , Δ_5 levels. Symmetry prohibits mixing between the three lowest levels of this table.

with

$$X_{it}^s(\vec{\rho}/\rho) = \sum_R' D_{11}(R) \exp[i\vec{k} \cdot (R^{-1}\vec{s}_\nu - \vec{s}_\nu)] \times X_{it}(R^{-1}\vec{\rho}/\rho), \quad (\text{B14})$$

where we have combined an unsymmetrized function (index b) on site \vec{s}_ν and a symmetrized function (index t) generated from an unsymmetrized function

on site \vec{s}'_ν . The prime on the R sum indicates that only those R for which some $\vec{\tau}$ satisfies $R^{-1}\vec{s}_\nu = \vec{s}'_\nu + \vec{\tau}$ are allowed.

E_{MV3} . Let

$$E_{MV3} = \sum_{i,j} c_i c_j E_{MV3}(\vec{K}_i, \vec{K}_j)$$

TABLE VII. Breakdown of relativistic corrections for the X point. The format is identical to that of Table V. For comparison all values are given to three decimal places even though the third place is not significant in some cases. All energies are in rydbergs and must be multiplied by -1.0 to give the actual value.

E^0	E_{MV}	E_D	E_P	E (no mixing)	E (with mixing) ^a
0.334 (5)	0.034	0.000	0.369	$\left. \begin{matrix} 0.364 (7^+) \\ 0.373 (6^+) \end{matrix} \right\}$	$\left. \begin{matrix} 0.364 (7^+) \\ 0.373 (6^+) \end{matrix} \right\}$
0.366 (1)	0.150	-0.075	0.442	0.442 (6 ⁺)	0.442 (6 ⁺)
0.416 (4')	0.058	-0.017	0.457	0.457 (6 ⁻)	0.452 (6 ⁻)
0.447 (5')	0.038	0.000	0.486	$\left. \begin{matrix} 0.471 (7^-) \\ 0.501 (6^-) \end{matrix} \right\}$	$\left. \begin{matrix} 0.471 (7^-) \\ 0.506 (6^-) \end{matrix} \right\}$
0.459 (1)	0.078	-0.031	0.506	0.506 (6 ⁺)	0.506 (6 ⁺)
0.470 (3)	0.019	0.000	0.490	0.490 (7 ⁺)	0.490 (7 ⁺)
0.667 (2)	0.019	0.000	0.686	0.686 (7 ⁺)	0.684 (7 ⁺)
0.678 (5)	0.025	0.000	0.704	$\left. \begin{matrix} 0.697 (6^+) \\ 0.711 (7^+) \end{matrix} \right\}$	$\left. \begin{matrix} 0.697 (6^+) \\ 0.713 (7^+) \end{matrix} \right\}$
0.782 (3')	0.303	-0.170	0.915	0.915 (7 ⁻)	0.915 (7 ⁻)
1.037 (1)	0.192	-0.106	1.122	1.122 (6 ⁺)	1.122 (6 ⁺)
1.099 (4')	0.184	-0.099	1.185	1.185 (6 ⁻)	1.185 (6 ⁻)

^aDue to symmetry restrictions and/or large energy differences we considered mixing for three "sets" of levels only. The mixing effect for the X_5 , X_1 set is negligible.

$$+ 2 \sum_{b,j}^{\eta} c_b c_j E_{MV3}(A_b, \vec{K}_j) + \sum_{b,t}^{\xi} c_b c_t E_{MV3}(A_b, A_t), \quad (\text{B15})$$

where the ξ , η , ζ sums run as in E_{MV2} . The $E_{MV3}(\vec{K}_i, \vec{K}_j)$, etc., expressions will be identical to the $E_{MV2}(\vec{K}_i, \vec{K}_j)$, etc., expressions given in Eqs. (B9), (B11), and (B13) with $V_\nu(\rho)$ replaced by $[V_\nu(\rho)]^2$ and \bar{V} replaced by $(\bar{V})^2$.

Darwin Integrals

From Eqs. (12) and (17) of the main text we have

$$E_D = -\frac{\bar{\alpha}^2}{4} \int \psi_n^{0*}(\vec{r}) \frac{dV}{d\rho} \frac{\partial \psi_n^0(\vec{r})}{\partial \rho} d\vec{\tau}, \quad (\text{B16})$$

where, in each ν sphere,

$$\vec{r} = \vec{\rho} + \vec{s}_\nu \quad (\text{B17})$$

and \vec{r} is measured from the origin (taken at the center of the La atom as in GM I). (We again suppress the subscript n .)

Let

$$E_D = -\frac{1}{4} \bar{\alpha}^2 \left[\sum_{i,j}^{\xi} c_i c_j E_D(\vec{K}_i, \vec{K}_j) + \sum_{b,j}^{\eta} c_b c_j E_D(A_b, \vec{K}_j) + \sum_{j,b}^{\eta} c_j c_b E_D(\vec{K}_j, A_b) + \sum_{b,t}^{\xi} c_b c_t E_D(A_b, A_t) \right], \quad (\text{B18})$$

where the ξ , η , ζ sums run as in the mass-velocity expressions. As the Darwin expressions are not Hermitian term by term in the expansion functions both $E_D(A_b, \vec{K}_j)$ and $E_D(\vec{K}_j, A_b)$ are needed.

Plane wave-plane wave. Substituting a symmetrized plane wave into the left-hand side of the integral in Eq. (B16) and an unsymmetrized plane wave on the right-hand side we have

$$E_D(\vec{K}_i, \vec{K}_j) = (1/4\pi) \sum_R D_{11}(R) \sum_\nu e^{-i\vec{K} \cdot \vec{s}_\nu} \int \exp[-iR^{-1}(\vec{k} + \vec{K}_i) \cdot \vec{\rho}] \frac{dV_\nu}{d\rho} \frac{\partial e^{i(\vec{k} + \vec{K}_j) \cdot \vec{\rho}}}{\partial \rho} d\vec{\tau}, \quad (\text{B19})$$

with

$$\vec{K} = R^{-1}(\vec{k} + \vec{K}_i) - (\vec{k} + \vec{K}_j). \quad (\text{B20})$$

After considerable manipulation, Eq. (B19) becomes

$$E_D(\vec{K}_i, \vec{K}_j) = \sum_R D_{11}(R) \vec{K} \cdot (\vec{k} + \vec{K}_j) (1/K) \times [I(\text{La}) + F(\vec{K})I(\text{Sn})], \quad (\text{B21})$$

with

$$I(\nu) = \int_\nu j_1(K\rho) \frac{dV_\nu}{d\rho} \rho^2 d\rho$$

and $F(\vec{K})$ as defined in Eq. (B10).

Atomic term-plane wave. Substituting an unsymmetrized atomiclike function (on site \vec{s}_ν) into the left-hand side of the integral in Eq. (B16) and a symmetrized plane wave into the right-hand side we have

$$E_D(A_b, \vec{K}_j) = (1/4\pi) \sum_R D_{11}(R) e^{i\vec{K}' \cdot \vec{s}_\nu} \times \int_\nu F_{nlm}^*(\vec{\rho}) \frac{dV_\nu}{d\rho} \frac{\partial e^{iR^{-1}(\vec{k} + \vec{K}_j) \cdot \vec{\rho}}}{\partial \rho} d\vec{\tau}, \quad (\text{B22})$$

with

$$\vec{K}' = R^{-1}(\vec{k} + \vec{K}_j) - \vec{k}. \quad (\text{B23})$$

After considerable manipulation we have

$$E_D(A_b, \vec{K}_j) = [K/(2l+1)] [I_1 - (l+1)I_2] s, \quad (\text{B24})$$

with

$$I_1 = \int_\nu u_{nl}(\rho) \frac{dV_\nu}{d\rho} j_{l-1}(K\rho) \rho d\rho,$$

$$I_2 = \int_\nu u_{n1}(\rho) \frac{dV_\nu}{d\rho} j_{l+1}(K\rho) \rho d\rho, \quad (\text{B25})$$

$$s = \sum_R D_{11}(R) X_{l0}(\vec{B}) e^{i\vec{K}' \cdot \vec{s}_\nu},$$

and $\vec{K} = \vec{k} + \vec{K}_j$, $\vec{B} = R^{-1}\vec{K}/K$.

Plane wave-atomic term. Substituting a symmetrized plane wave into the left of the integral in Eq. (B16) and an unsymmetrized atomiclike function (on site \vec{s}_ν) into the right-hand side we have

$$E_D(\vec{K}_j, A_b) = (1/4\pi) \sum_R D_{11}(R) e^{-i\vec{K}' \cdot \vec{s}_\nu} \times \int_\nu e^{-iR^{-1}\vec{K} \cdot \vec{\rho}} \frac{dV_\nu}{d\rho} \frac{\partial F_{nlm}(\vec{\rho})}{\partial \rho} d\vec{\tau}, \quad (\text{B26})$$

where \vec{K} and \vec{K}' are as defined in the section above. After some manipulation this becomes

$$E_D(\vec{K}_j, A_b) = s \int_\nu \frac{dV_\nu}{d\rho} j_l(K\rho) \left[\rho \frac{du_{nl}}{d\rho} - u_{nl}(\rho) \right] d\rho, \quad (\text{B27})$$

with s as in Eq. (B25). (It can easily be shown that $e^{-i\vec{K}' \cdot \vec{s}_\nu} = e^{i\vec{K}' \cdot \vec{s}_\nu}$ for any reciprocal-lattice vector, \vec{K}' .)

Atomic term-atomic term. Since $(dV/d\rho)(\partial/\partial\rho)$ does not affect angles these integrals are still orthogonal in l ; orthogonality in n is no longer a good approximation. Starting with an unsymmetrized atomiclike function (index b) on site \vec{s}_ν and a symmetrized atomiclike function (index t) generated from an unsymmetrized function on site \vec{s}_ν , we substitute into Eq. (B16) and eventually obtain

$$E_D(A_b, A_t) = (1/4\pi) I_{bt} \int X_{ib} \frac{\vec{\rho}}{\rho} X_{it}^s \frac{\vec{\rho}}{\rho} d\Omega, \quad (\text{B28})$$

with

$$I_{bt} = \int_{\nu} u_{n_t}(\rho) \frac{dV_{\nu}}{d\rho} \left(\frac{du_{n_t}}{d\rho} - \frac{u_{n_t}}{\rho} \right) d\rho. \quad (\text{B29})$$

Index n is associated with $A_b(\vec{r})$, index n' with $A_t(\vec{r})$ and X_{it}^s is as in Eq. (B14).

Spin-Orbit Integrals

The "regular form" for spin-orbit integrals is obtained by substituting H_{SO} as given by Eq. (13) of the main text into

$$I_{SO} = \int \psi^{0*} H_{SO} \psi^0 d\vec{\tau}, \quad (\text{B30})$$

where the wave function ψ^0 is now expanded to include a spin function. This gives

$$I_{SO} = \frac{\bar{\alpha}^2}{4} \int \psi_s^{0*}(\vec{r}) \vec{\eta}_1 \frac{1}{\rho} \frac{dV}{d\rho} [\vec{\sigma} \cdot \vec{L}(\vec{\rho}) \psi_s^0(\vec{r}) \vec{\eta}_2] d\vec{\tau}, \quad (\text{B31})$$

where the subscript s on ψ^0 implies that ψ^0 is a symmetrized function; $\vec{\eta}_1$ and $\vec{\eta}_2$ can be either of the Pauli spin functions, α or β , as in the main text and $\vec{r} = \vec{\rho} + \vec{s}_{\nu}$ as before.

Two-Dimensional Representations

For all two-dimensional single-group representation only the $\int \psi_{11}^* \alpha H_{SO} \psi_{21} \alpha d\tau$ form of I_{SO} is needed [see Eqs. (20)–(23) of the main text]. For this $\alpha\alpha$ combination we have shown in Appendix A [see Eq. (A6)] that Eq. (B31) can be written as

$$I_{SO}^{2d}(\alpha, \alpha) = \frac{1}{4} \bar{\alpha}^2 \int \psi_u^{0*}(\vec{r}) \frac{1}{\rho} \frac{dV}{d\rho} [L_z \psi_{21}^0(\vec{r})] d\vec{\tau}. \quad (\text{B32})$$

In Eq. (B32) the subscript u implies that ψ_u^{0*} is an unsymmetrized function whereas the subscript 21 implies that ψ_{21}^0 is symmetrized using D_{21} . In Eq. (B32) we have

$$L_z = -i \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right), \quad (\text{B33})$$

where (x, y, z) are the components of $\vec{\rho}$. Equation (B32) is valid for all two-dimensional representations except Λ_3 . We write

$$\begin{aligned} I_{SO}^{2d}(\alpha, \alpha) = & \frac{\bar{\alpha}^2}{4} \left(\sum_{i,j} c_i c_j I_{SO}^{2d}(\alpha\alpha; \vec{K}_i, \vec{K}_j) \right. \\ & + 2 \sum_{j,b} c_j c_b I_{SO}^{2d}(\alpha\alpha; \vec{K}_j, A_b) \\ & \left. + \sum_{b,t} c_b c_t I_{SO}^{2d}(\alpha\alpha; A_b, A_t) \right), \quad (\text{B34}) \end{aligned}$$

where $\xi, \eta,$ and ζ have the same meaning as in Eq. (B8). [It can be shown that $I_{SO}^{2d}(\alpha\alpha; A_b, \vec{K}_j) = I_{SO}^{2d}(\alpha\alpha; \vec{K}_j, A_b)$.] Since all the c_i are real and as

all I_{SO}^{2d} expressions can be shown to be i (real number) we may write

$$I_{SO}^{2d}(\alpha, \alpha) = iS, \quad (\text{B35})$$

where S is real and is the S of Eqs. (20)–(23) of the main text.

Plane wave–plane wave. Substituting an unsymmetrized plane wave for ψ_u^{0*} in Eq. (B32) and a symmetrized plane wave for ψ_{21}^0 , we have

$$\begin{aligned} I_{SO}^{2d}(\vec{K}_i, \vec{K}_j) = & \frac{1}{4\pi} \sum_R D_{21}(R) e^{i\vec{K} \cdot \vec{s}_{\nu}} \\ & \times \int_{\nu} e^{-i(\vec{k} + \vec{K}_i) \cdot \vec{\rho}} \frac{1}{\rho} \frac{dV_{\nu}}{d\rho} (L_z e^{iR(\vec{k} + \vec{K}_j) \cdot \vec{\rho}}) d\vec{\tau} \end{aligned} \quad (\text{B36})$$

in each of the four atomic spheres. In Eq. (B36) $\vec{K} = R(\vec{k} + \vec{K}_j) - (\vec{k} + \vec{K}_i)$. (We suppress the $\alpha\alpha$ notation in I_{SO}^{2d} .) Eq. (B36) eventually becomes

$$I_{SO}^{2d}(\vec{K}_i, \vec{K}_j) = i \sum_R D_{12}(R) [I(La) + F(\vec{K})I(Sn)] Z(R), \quad (\text{B37})$$

with

$$I(\nu) = \int j_1(K\rho) \frac{dV_{\nu}}{d\rho} \rho^2 d\rho, \quad (\text{B38})$$

$$Z(R) = [(\vec{k} + \vec{K}_j)_y (\vec{k} + \vec{K}_i)_x - (\vec{k} + \vec{K}_j)_x (\vec{k} + \vec{K}_i)_y] / K, \quad (\text{B39})$$

where $(\vec{k} + \vec{K}_i)_y$ is the y component of $(\vec{k} + \vec{K}_i)$ and $(\vec{k} + \vec{K}_i)_x$ is the x component of $R^{-1}(\vec{k} + \vec{K}_i)$, etc. \vec{K} is as in Eq. (B9) and $F(\vec{K})$ is as in Eq. (B10).

Plane wave–atomic term. Substituting an unsymmetrized plane wave for ψ_u^{0*} in Eq. (B32) and a symmetrized atomiclike function $A_b^s(\vec{r})$ for ψ_{21}^0 we have

$$\begin{aligned} I_{SO}^{2d}(\vec{K}_j, A_b) = & \frac{1}{4\pi} \frac{g}{h} \int e^{-i(\vec{k} + \vec{K}_j) \cdot \vec{r}} \frac{1}{\rho} \frac{dV}{d\rho} \\ & \times [L_z A_b^s(\vec{r})] d\vec{\tau}, \quad (\text{B40}) \end{aligned}$$

with A_b^s as defined in GM I (but with no sum over cells here). Starting with an unsymmetrized function on site \vec{s}_{ν} , $A_b^s(\vec{r})$ may be written schematically as

$$A_b^s(\vec{r}) = \frac{u_{n_t}(\rho)}{\rho} \sum_{\nu, p} a(21, b, \nu, p) X_{ip} \frac{\vec{\rho}}{\rho}, \quad (\text{B41})$$

where the 21 label reminds us the symmetrization is with D_{21} , $\nu = 1$ for an unsymmetrized function on La, while ν runs over the three Sn basis atoms for an unsymmetrized function on any Sn atom. (Usually there will be only one or two terms in the sum above.) L_z operating on any X_{ip} of Eq. (B41) will produce some $X_{ip'}$. We represent this as

$$L_z X_{ip}(\vec{\rho}/\rho) = ig(L_z, p, p') X_{ip'}(\vec{\rho}/\rho) \quad (\text{B42})$$

and eventually obtain

$$I_{\text{SO}}^{2d}(\vec{K}_j, A_b) = iI \sum_{\nu} e^{-i\vec{K}_j \cdot \vec{s}_{\nu}} P_Z(b, \nu), \quad (\text{B43})$$

where

$$I = \int j_l(K\rho) \frac{dV}{d\rho} u_{nl}(\rho) d\rho, \quad (\text{B44})$$

$$P_Z(b, \nu) = \sum_{\rho} a(21, b, \nu, \rho) g(L_z, \rho, \rho') X_{l\rho'}(\vec{B}), \quad (\text{B45})$$

with $\vec{K} = \vec{k} + \vec{K}_j$ and $\vec{B} = \vec{K}/K$. For an unsymmetrized function on La, I is an integral over the La sphere, ν in Eq. (B43) is 1, and $\vec{s}_{\nu} = 0$; for an unsymmetrized function on a Sn sphere, I is a Sn integral and ν runs over the three Sn sites. The pertinent cubic harmonics are listed in Table VIII. The $g(L_z, \rho, \rho')$ are given in Table IX (a).

Atomic term-atomic term. Substituting an unsymmetrized atomiclike function for ψ_u^{0*} in Eq. (B32) and a symmetrized atomiclike function for ψ_{21}^0 we have

$$I_{\text{SO}}^{2d}(A_b, A_t) = \frac{1}{4\pi} \frac{g}{h} \int A_b^{u*}(\vec{r}) \frac{1}{\rho} \frac{dV}{d\rho} [L_z A_t^s(\vec{r})] d\vec{r}, \quad (\text{B46})$$

with A_b^u and A_t^s defined as in GMI (but with no sum over cells). Schematically, we write

$$A_b^{u*}(\vec{r}) = \frac{u_{nl}(\rho)}{\rho} X_{lb} \frac{\vec{\rho}}{\rho}, \quad (\text{B47})$$

$$A_t^s(\vec{r}) = \frac{u_{nl}(\rho)}{\rho} \sum_{\mu', q} a(21, t, \mu', q) X_{tq} \frac{\vec{\rho}}{\rho}, \quad (\text{B48})$$

as in the preceding section. L_z operating on the X_{tq} produces various $X_{lq'}$, as defined in Eq. (B42). Tabulating this (see Table X) as

$$i4\pi G_{bq} = \int X_{lb} \frac{\vec{\rho}}{\rho} \left(L_z X_{tq} \frac{\vec{\rho}}{\rho} \right) d\Omega, \quad (\text{B49})$$

we obtain

$$I_{\text{SO}}^{2d}(A_b, A_t) = iI S_Z(b, t, \nu), \quad (\text{B50})$$

TABLE VIII. The nine s , p , d types of cubic harmonics, X_q , and their integrals. Here the single index, q , replaces the two indices of X_{lb} of the text. The last column gives the integral $I_{qq} = (1/4\pi) \int [X_q(\vec{\rho}/\rho)]^2 d\Omega$. I_{qq} equals zero for $q \neq q'$. x , y , and z are the components of $\vec{\rho}$.

l	q	X_q	I_{qq}
0	1	1	1
1	2	x/ρ	$\frac{1}{3}$
1	3	y/ρ	$\frac{1}{3}$
1	4	z/ρ	$\frac{1}{3}$
2	5	$(2z^2 - x^2 - y^2)/\rho^2$	$\frac{12}{15}$
2	6	$(x^2 - y^2)/\rho^2$	$\frac{4}{15}$
2	7	yz/ρ^2	$\frac{4}{15}$
2	8	xz/ρ^2	$\frac{4}{15}$
2	9	xy/ρ^2	$\frac{4}{15}$

TABLE IX. Values of $g(L_z, q, q')$ and $g(L_y, q, q')$ for Eqs. (B42) and (B62), respectively. The indices q and q' have the same meaning as in Table VIII. The third column gives $g(L_z, q, q')$ and $g(L_y, q, q')$ for the L_z and L_y operations, respectively.

q	q'	g
(a) L_z operation, Eq. (B42)		
1	...	0
2	3	1
3	2	-1
4	...	0
5	...	0
6	9	4
7	8	-1
8	7	1
9	6	-1
(b) L_y operation, Eq. (B62)		
1	...	0
2	4	-1
3	...	0
4	2	1
5	8	6
6	8	-2
7	9	1
8 ^a	{ 5 6	{ - $\frac{1}{2}$ $\frac{1}{2}$
9	7	-1

^a L_y operating on X_8 produces both X_5 and X_6 .

where

$$I = \int u_{nl}(\rho) u_{n'l'}(\rho) \frac{1}{\rho} \frac{dV}{d\rho} d\rho, \quad (\text{B51})$$

$$S_Z(b, t, \nu) = \sum_q a(21, t, \nu, q) G_{bq}. \quad (\text{B52})$$

We have taken the unsymmetrized function A_b^{u*} to be on site \vec{s}_{ν} . The integral I is over the La or a Sn sphere depending on whether \vec{s}_{ν} refers to La or Sn.

Λ_3 Representation

For the Λ_3 representation, while we still need to evaluate only the $\alpha\alpha$ combination (see the discussion associated with Eq. (24) of the main text), the modification on going from a "symmetrized-symmetrized" integral to an "unsymmetrized-symmetrized" integral leads to a much more involved

TABLE X. The factor $G_{qq'}$, as defined by Eq. (B49). The q, q' subscripts have the same meaning as in Table VIII. All combinations not listed are equal to zero.

Label	Value
$G_{2,3}$	$-\frac{1}{3}$
$G_{3,2}$	$+\frac{1}{3}$
$G_{6,9}$	$-\frac{4}{15}$
$G_{9,6}$	$+\frac{4}{15}$
$G_{7,8}$	$+\frac{4}{15}$
$G_{8,7}$	$-\frac{4}{15}$

expression than that in Eq. (B32) above. For this reason we evaluated I_{SO} for Λ_3 using the form of Eq. (B31) directly but using only the atomiclike-atomiclike terms (this is probably a quite good approximation; see discussion of this point in the main text). The procedure is essentially the same as in obtaining $I_{SO}^{2d}(\alpha\alpha: A_b, A_t)$ of the preceding section but now both functions are symmetrized. We write

$$iS = \frac{1}{4}\bar{\alpha}^2 \sum_{b,t} c_b c_t I_{SO}^{3d}(\alpha\alpha: A_b, A_t), \quad (\text{B53})$$

where S is real and is the S of Eq. (24) of the main text. The sum in Eq. (B53) is over atomiclike functions only.

Three-Dimensional Representations

For all three-dimensional single-group representations only the $\int \psi_{11}^* \alpha H_{SO} \psi_{21} \alpha d\vec{\tau}$ form of I_{SO} of Eq. (B31) is needed [see Eqs. (25)–(27) of the main text]. For this case we have shown in Appendix A [see Eq. (A8)] that Eq. (B31) can be rewritten as

$$I_{SO}^{3d}(\alpha, \alpha) = \frac{\bar{\alpha}^2}{4} \int \psi_u^{0*}(\vec{r}) \frac{1}{\rho} \frac{dV}{d\rho} [\mathcal{L}\psi^0(\vec{r})] d\vec{\tau}, \quad (\text{B54})$$

with

$$\mathcal{L}\psi^0(\vec{r}) \equiv \frac{1}{2}[L_x \psi_{21}^0(\vec{r}) - L_y \psi_{31}^0(\vec{r})]. \quad (\text{B55})$$

L_z is defined in Eq. (B33) and

$$L_y = -i \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right). \quad (\text{B56})$$

As in the two-dimensional case we write

$$I_{SO}^{3d}(\alpha, \alpha) = \frac{\bar{\alpha}^2}{4} \left(\sum_{i,j} c_i c_j I_{SO}^{3d}(\vec{K}_i, \vec{K}_j) + 2 \sum_{j,b} c_j c_b I_{SO}^{3d}(\vec{K}_j, A_b) + \sum_{b,t} c_b c_t I_{SO}^{3d}(A_b, A_t) \right), \quad (\text{B57})$$

where we have suppressed the $\alpha\alpha$ notation in $I_{SO}^{3d}(K_i, K_j)$, etc., and with ξ , η , and ζ having the same meaning as in Eq. (B8). As in the two-dimensional case we may write

$$I_{SO}^{3d}(\alpha, \alpha) = iS, \quad (\text{B58})$$

where S is real and is the S involved in Eqs. (25)–(27) of the main text.

Plane wave–plane wave. Proceeding as in the two-dimensional case we obtain

$$I_{SO}^{3d}(\vec{K}_i, \vec{K}_j) = \frac{1}{2}i \left[\sum_R D_{12}(R) Q(R) Z(R) - \sum_T D_{13}(T) Q(T) Y(T) \right], \quad (\text{B59})$$

where

$$Q(P) = I(La, K_P) + F(\vec{K}_P) I(Sn, K_P), \quad (\text{B60})$$

with the I integrals having the same form as in Eq. (B38), $\vec{K}_P = P^{-1}(\vec{k} + \vec{K}_j) - (\vec{k} + \vec{K}_i)$, and $F(\vec{K}_P)$ is as defined in Eq. (B10). $Z(R)$ is given by Eq. (B39) and

$$Y(T) = [(\vec{k} + \vec{K}_j)_{z'} (\vec{k} + \vec{K}_i)_x - (\vec{k} + \vec{K}_j)_{x'} (\vec{k} + \vec{K}_i)_z] / K_T, \quad (\text{B61})$$

with the primed and nonprimed components having the same meaning as in Eq. (B39) (the primes here being associated with operation T).²³

Plane wave–atomic term. Proceeding as in the two-dimensional case and writing²⁴

$$L_y X_{I_q}(\vec{\rho}/\rho) = i \sum_{q'} g(L_y, q, q') X_{I_q'}(\vec{\rho}/\rho) \quad (\text{B62})$$

analogously to Eq. (B42), we obtain

$$I_{SO}^{3d}(\vec{K}_j, A_b) = iI \sum_{\nu} e^{-i\vec{K}_j \cdot \vec{s}_{\nu}} \frac{1}{2} [P_Z(b, \nu) - P_Y(b, \nu)], \quad (\text{B63})$$

with $P_Z(b, \nu)$ as in the two-dimensional case [Eq. (B45)] and

$$P_Y(b, \nu) = \sum_q a(31, b, \nu, q) \sum_{q'} g(L_y, q, q') X_{I_q'}(\vec{B}). \quad (\text{B64})$$

The radial integral I is defined in Eq. (B44). The comments following Eq. (B45), including the definitions of \vec{K} and \vec{B} , apply here also.

Atomic term–atomic term. For these integrals it is most convenient to determine I_{SO} in the form given in Eq. (B31) directly with symmetrized functions on both sides of the integral.²⁵ The procedure is like that for the two-dimensional case except that the function on the left-hand side is now represented schematically as

$$A_b^{s*}(\vec{r}) = \frac{u_{nl}(\rho)}{\rho} \sum_{\mu,p} a(11, b, \mu, p) X_{I_p} \frac{\vec{\rho}}{\rho} \quad (\text{B65})$$

in place of Eq. (B47). For the right-hand function Eq. (B48) may be used as is.

Since

$$\alpha \vec{\sigma} \cdot \vec{L}(\vec{\rho}) \alpha = L_x, \quad (\text{B66})$$

we may use the same tabulation (Table X) as in the two-dimensional case and write

$$I_{SO}^{3d}(A_b, A_t) = iI \sum_{\mu,p} a(11, b, \mu, p) S_Z(p, t, \mu), \quad (\text{B67})$$

with the radial integral I as in Eq. (B51) and S_Z as in Eq. (B52). I is an integral over either the La or a Sn sphere depending on whether the original unsymmetrized functions are on the La atom or on a Sn atom. (There can be no mixing between La and Sn atomiclike functions in our model.)

¹D. M. Gray and L. V. Meisel, preceding paper, Phys. Rev. B **5**, 1299 (1972).

²J. C. Slater, *Quantum Theory of Molecules and Solids*

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³R. J. Elliott, Phys. Rev. **96**, 280 (1954). Elliott's comments regarding Λ for the simple cubic lattice are

in error as pointed out by R. H. Parmenter, Phys. Rev. 100, 573 (1955).

⁴G. F. Koster, in *Solid State Physics*, Vol. 5, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), pp. 173–256. For the X and M points Koster's single-group representation labeling differs somewhat from that of BSW (GMI Ref. 3).

⁵T. L. Loucks, *The Augmented Plane Wave Method* (Benjamin, New York, 1967).

⁶For a complete list of two- and three-dimensional single-group representations for the simple cubic lattice see Table I.

⁷These compatibility relations are given in Table II (a)–(d). For the Λ point the representations Λ_4 and Λ_5 are degenerate by time reversal and must be considered as one representation in determining splitting.

⁸In these two examples all energy levels are given to four decimal places for comparison.

⁹For the Darwin correction one needs both atomic-term–plane-wave and plane-wave–atomic-term types of integrals since this operator is not term-by-term Hermitian in the expansion functions.

¹⁰We are grateful to Professor E. Brown for suggesting this modification. For our MOPW method the modified spin-orbit operator is particularly useful in evaluating plane-wave–plane-wave terms.

¹¹For spin-orbit we give the expressions for S . S is related to E_{SO} through Eqs. (23), (24), and (27).

¹²L. Liu, Phys. Rev. 126, 1317 (1962); P. C. Chow and L. Liu, *ibid.* 140, A1817 (1965).

¹³The derivative routines were developed by Ray Scanlon. These routines involve fitting a spline function to the tabulated points and then differentiating this function.

¹⁴This assumption is the justification for orthogonalizing to these lower-lying atomiclike functions in either the OPW or MOPW method.

¹⁵For these test comparisons we do not, of course, orthogonalize to these atomiclike functions.

¹⁶It should be emphasized that the excellent agreement

obtained here merely indicates that the atomic-term–atomic-term integrals are being handled properly. Less direct tests, however, indicate that the atomic-term–plane-wave and the plane-wave–plane-wave integrals are also correctly treated. At any rate, the major contributions to the relativistic corrections come from the atomic-term–atomic-term integrals (see Ref. 12).

¹⁷As described in GMI, there are 960 electrons to account for; we count a Γ_6 level as 2 (two-dimensional representation, one equivalent point), a Δ_3 level as 12 (two-dimensional representation, six equivalent points), and so on.

¹⁸W. L. McMillan, Phys. Rev. 167, 331 (1968).

¹⁹A. M. Toxen and R. J. Gambino, in Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto, Japan, 1970, p. 351 (unpublished).

²⁰E. E. Havinga, H. Damsma, and M. H. van Maaren, J. Phys. Chem. Solids, 31, 2653 (1970).

²¹Although we have not worked out the geometry, the free-electron sphere for 15 valence electrons would cut pieces of zones 7, 8, 9, etc. Folding the, say, 8th zone back into the simple cube should give a much more complicated Fermi surface than we get.

²²For the two-dimensional representations Γ_{12} , Γ_{12}' , R_{12} , and R_{12}' , both $\bar{L}(11:12)$ and $\bar{L}(11:22)$ equal zero. This is consistent with these representations not splitting under spin orbit.

²³Since the same group is involved in both the R and T sums, Eq. (B59) could be organized somewhat differently; since, however, $D_{12}(P)$ may be zero when $D_{13}(P)$ is non-zero and vice versa, the present form of Eq. (B59) is most convenient for our procedure.

²⁴For the L_y operator there is one case where two different $X_{1q'}$ are produced from one X_{1q} [see Table IX(b)]; thus, a sum on q' appears in Eq. (B62).

²⁵One could also do the plane-wave–plane-wave and the plane-wave–atomic terms directly [i.e., using Eq. (B31)]; for our program, however, it is more convenient to use Eq. (B54) for these integrals.

Magnetoelastic Anomaly in Gadolinium

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Magnetoelastic energy considerations are used to explain the occurrence of anomalous dips in the velocity of sound in gadolinium below T_C . A molecular-field treatment gives reasonable quantitative agreement with the elastic-constant experiments of Long, Wazzan, and Stern and the magnetization curve as determined from neutron diffraction.

I. INTRODUCTION

During the past several years many of the physical and magnetic properties of the hexagonal rare-earth metal gadolinium have been studied. Magnetization measurements by Nigh, Legvold, and Spedding¹ showed that Gd was a ferromagnet with a Curie temperature (T_C) of 293°K. Measure-

ments of the angle between the magnetization and the crystallographic c axis of Gd were made by neutron diffraction techniques.^{2,3} These showed that the magnetization vector rotated from the c axis into an easy cone and that there did not exist a spiral structure as is common in many other rare earths. By measuring the torque required to pre-