

Electron Energy Levels in LaSn_3 . I. A Nonrelativistic Modified Orthogonalized-Plane-Wave Calculation

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Electron energy levels in perfectly ordered LaSn_3 have been 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, is used. The crystal calculation is not self-consistent. $E(\vec{k})$ curves are shown for six directions in \vec{k} space. The nonrelativistic Fermi level has been computed to be -0.47 Ry. Calculations were also carried out for a limited number of points using a potential constructed from the self-consistent relativistic atomic potentials of Liberman. Differences between the levels resulting from this potential and the levels resulting from the Herman-Skillman-based potential are discussed. In a separate paper, perturbation theory is used to determine relativistic corrections to the Herman-Skillman-based levels.

INTRODUCTION

Because of their superconducting properties, there has been a fair amount of interest in the LaX_3 alloys where X is tin, lead, indium, or thallium. All of these alloys have a simple-cubic lattice with the Cu_3Au structure.¹ In particular, LaSn_3 has a superconducting transition temperature of about 6°K ,¹ whereas LaIn_3 has a much lower transition temperature of about 1°K .² There is also considerable interest in determining which LaSn_3 electron energy levels are primarily associated with La and which with Sn. It was thus felt that band-structure calculations for this series of alloys would be useful.

In the present paper we employ the muffin-tin model and a modified orthogonalized-plane-wave (MOPW) method to calculate the nonrelativistic band structure of perfectly ordered LaSn_3 . Although the atomic potentials used in constructing our model potential are self-consistent, the crystal calculation presented here is not self-consistent. In a separate paper we use perturbation theory to determine the relativistic energy corrections, namely, mass-velocity, Darwin, and spin orbit.

CRYSTAL STRUCTURE AND POTENTIAL

The simple-cubic unit cell for LaSn_3 is shown in Fig. 1. A convenient primitive cell contains one La atom and three Sn atoms. The origin is taken at a La atom, \vec{r} vectors describe the position of primitive cells, and \vec{s}_ν vectors describe the position of basis atoms within a primitive cell. A convenient basis consists of one La muffin-tin sphere ($\vec{s}_1 = 0$) and three Sn muffin-tin spheres at $\vec{s}_2 = \frac{1}{2}a(1, 1, 0)$, $\vec{s}_3 = \frac{1}{2}a(1, 0, 1)$, and $\vec{s}_4 = \frac{1}{2}a(0, 1, 1)$. In this and the following paper we will use \vec{r} to denote a vector from the origin (taken at the center of the La sphere)

and $\vec{\rho}$ to denote a vector from the center of the sphere in question. For the La atom, then, $\vec{\rho}$ and \vec{r} coincide but for the Sn atoms $\vec{r} = \vec{s}_\nu + \vec{\rho}$ with $\nu = 2, 3, \text{ or } 4$. Since the unit cell is simple cubic, the Brillouin zone is also simple cubic. This is shown in Fig. 2 with the symmetry points labeled in the Bouckaert, Smoluchowski, and Wigner (BSW) notation.³

A one-electron approach is used. The crystal potential is constructed from the self-consistent nonrelativistic atomic potentials of Herman and Skillman⁴ (HS) using a muffin-tin model. In this model we surround the individual atoms with non-overlapping spheres whose radii are chosen so that the potentials match at the point of contact along the line from La center to Sn center. Inside each of these spheres we take the crystal potential to be the potential of that particular atom as a free ion and outside the spheres we take the potential to be a constant, \bar{V} . The HS potentials were modified slightly near the muffin-tin radii so that the La and

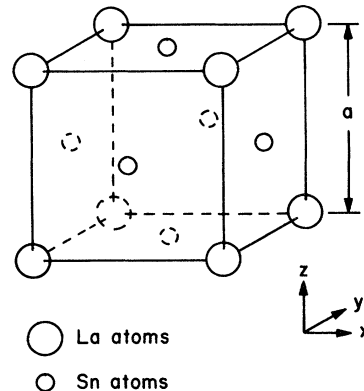


FIG. 1. Unit cell in real space for LaSn_3 .

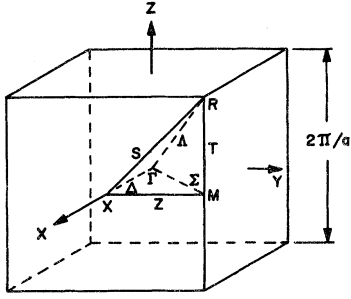


FIG. 2. Unit cell in reciprocal space for LaSn_3 . The symmetry points and lines are labeled in the BSW notation.

Sn potentials join smoothly along the La to Sn line. The value of the potential at the joining point was used for \bar{V} .

MOPW METHOD

We write the Hamiltonian for the system as

$$H = H^0 + H^{re1}, \quad (1)$$

where $H^0 = -\nabla^2 + V(r)$ and H^{re1} represents the relativistic corrections. In this paper we are concerned only with H^0 . We approximate the true (nonrelativistic) electron wave function $\psi_{in}^0(\vec{r})$ by

$$\psi_{an}^0(\vec{r}) = \sum_i c_{ni} \phi_i(\vec{r}), \quad (2)$$

where the ϕ_i are known functions and the coefficients c_{ni} are determined by the variational procedure. In the MOPW method the expansion functions ϕ_i are of two types: (i) higher-lying atomiclike functions which are zero outside the muffin-tin spheres and (ii) orthogonalized plane waves (OPW's) which extend throughout the entire crystal and which are orthogonalized only to the lower-lying atomiclike functions. (Our procedure is very similar to that of Deegan and Twose,⁵ differing mainly in the manner of constructing the atomiclike functions. For a more detailed description of the method than given here, see Ref. 5.) For LaSn_3 we orthogonalized the plane waves to the La 1s, 2s, 3s, 4s, 2p, 3p, 4p, 3d, and 4d atomiclike functions and to the Sn 1s, 2s, 3s, 4s, 2p, 3p, 4p, and 3d atomiclike functions. The La 5s, 5p, and 5d and the Sn 5s, 5p, and 4d atomiclike functions were "kept" as explicit expansion functions. The La 6s atomiclike function was ignored (this point is discussed in more detail below). The variational procedure leads to the set of equations

$$\sum_j c_{nj} \int \phi_i^*(\vec{r}) (H^0 - E_n^0) \phi_j(\vec{r}) d\vec{r} = 0, \quad (3)$$

where E_n^0 is the n th nonrelativistic energy eigenvalue. (We arbitrarily order the E_n^0 's from lowest to highest.) These equations are to be solved for

each reciprocal-space \vec{k} value used. This set is equivalent to the matrix equation

$$H^0 \vec{c}_n = E_n^0 S \vec{c}_n, \quad (4)$$

where

$$H_{ij}^0 = \int \phi_i^*(\vec{r}) H^0 \phi_j(\vec{r}) d\vec{r} \quad (5)$$

and

$$S_{ij} = \int \phi_i^*(\vec{r}) \phi_j(\vec{r}) d\vec{r}. \quad (6)$$

Since the ϕ_i are not necessarily orthogonal, S is not the identity matrix. However, if we define a (lower-triangular) matrix L by $S = LL^\dagger$, we can write⁶ Eq. (4) as

$$H^{0'} \vec{c}'_n = E_n^0 \vec{c}'_n, \quad (7)$$

where $H^{0'}$ is the Hermitian matrix $L^{-1} H^0 L^{-\dagger}$ and $\vec{c}'_n = L^\dagger \vec{c}_n$.

The atomiclike functions are Bloch sums of atomic orbitals, namely, $\sum_j \exp[i\vec{k} \cdot (\vec{r}_j + \vec{s}_v)] F_{nlm}(\vec{r} - \vec{r}_j - \vec{s}_v)$, where F_{nlm} is an atomic orbital.⁷ These atomic orbitals are free-atom solutions of the Schrödinger equation with the modification that they are zero outside the muffin-tin spheres. These functions were calculated in a separate program⁸ by solving the Schrödinger equation numerically using the appropriate HS potential for each atom. The OPW's are of the form⁷

$$P(\vec{K}_j) - \sum_i a_{jt} C_t(\vec{r}),$$

where \vec{K}_j is a reciprocal-lattice vector, $P(\vec{K}_j) = e^{i(\vec{k} + \vec{K}_j) \cdot \vec{r}}$, the ordinary plane-wave term, and $C_t(\vec{r})$ is a lower-lying atomiclike function. For C_t satisfying

$$\langle C_t | C_{t'} \rangle = \langle C_t | C_t \rangle \delta_{tt'}, \quad (8)$$

the orthogonalization coefficients a are given by

$$a_{jt} = \langle C_t | P(\vec{K}_j) \rangle / \langle C_t | C_t \rangle. \quad (9)$$

For each symmetry point, group theory is used to reduce the number of expansion functions for each representation.

$E(\vec{k})$ has been evaluated for the equivalent of 64 uniformly spaced points in \vec{k} space. Because of the high degree of symmetry involved, it is sufficient to take 10 points in the portion of \vec{k} space bounded by $\Gamma\Delta X$, $\Gamma\Sigma M$, $\Gamma\Delta R$, XSR , MTR , and XZM , as indicated in Fig. 2.

For a number of symmetry points we also calculated energy levels using the modified-plane-wave (MPW) method.⁹ In the MPW method the expansion functions ϕ_i of Eq. (2) are either atomiclike functions or plane waves. Since there is no orthogonalization in the MPW method, convergence from above is guaranteed. The MPW method has been quite adequately established by Butler *et al.*¹⁰ in a calculation for copper. Their calculation gave excellent agreement with that of Burdick,¹¹ who

used the augmented-plane-wave (APW) method. Both of these copper calculations used the Chodorow¹² potential. For the 11 irreducible representations for which we calculated energy levels using both the MPW and MOPW methods, the biggest discrepancy (for a given number of plane waves) was 0.0004 Ry.¹³

Calculation of Matrix Elements and Diagonalization

In calculating the S_{ij} and H_{ij}^0 matrix elements, it is sufficient to symmetrize just one of the ϕ_i , ϕ_j functions. An unsymmetrized plane wave (before orthogonalization) has the form

$$\phi_j^u(\vec{r}) = e^{i(\vec{k} \cdot \vec{r} + \vec{s}_j \cdot \vec{r})} \quad (10)$$

An unsymmetrized atomiclike function has the form

$$\phi_i^u(r) = \sum_j e^{i\vec{k} \cdot (\vec{r}_j + \vec{s}_j)} F_{nm}(\vec{r} - \vec{r}_j - \vec{s}_j) \quad (11)$$

Symmetrization, as used here, is defined by

$$f^s(\vec{r}) = (h/g) \sum_R D_{11}^*(R) f^u(R^{-1}\vec{r}), \quad (12)$$

where the R are members of the "group of \vec{k} ," a subgroup of the full 48-member cubic group. The R of this subgroup must satisfy $R\vec{k} = \vec{k}$ or $R\vec{k} = \vec{k} + \vec{K}$. $D_{11}(R)$ is the "one-one" element of the matrix representing R , h is the dimensionality of the representation, and g is the number of members in the group. The function $f^s(\vec{r})$ is the "symmetrized function" generated from the "unsymmetrized function" $f^u(\vec{r})$.

Symmetrized expressions¹⁴ for the atomiclike functions and the unorthogonalized plane waves along with the resulting (MPW) S_{ij} and H_{ij}^0 matrix elements are given in an Appendix. For the MOPW formulation, rather than directly evaluating those matrix elements which involve OPW's, we have instead evaluated these elements from the appropriate MPW elements. The necessary relationships were given in an earlier paper.¹⁵ Once the (MOPW) S_{ij} and H_{ij}^0 elements have been evaluated, Eq. (4) is put into the form of Eq. (7), as discussed above. H^0 of Eq. (7) is then diagonalized using a Jacobi routine, giving both eigenvalues and eigenfunctions.¹⁶

Computational Difficulties

(i) La 6s. When this atomiclike function was included as an expansion function, negative values occurred on the S-matrix diagonal for some representations. There are computational reasons why this can happen which need not concern us here. It is conceivable that this is due to over-completeness of the expansion set. At any rate, we have simply ignored this atomiclike function; the five other La s-type functions plus plane waves should easily make up for the missing La 6s function. Some representations were calculated both

with and without this function (for a limited number of plane waves) with essentially identical results.

(ii) La 4f. There is still considerable confusion about possible f-type levels. When the HS potentials are used in our program⁸ to generate atomiclike functions, we get a 4f level in La which seems quite low (about -1.14 Ry). When this function is included in the crystal calculation as one of the expansion functions (for a representation allowing La f symmetry), we get a resultant crystal level at about -1.14 Ry. Since convergence of our levels is somewhat better¹⁷ with this La f function included, we have included it (where allowed by symmetry) as an expansion function. We feel that this -1.14-Ry crystal level is, however, a spurious level, and indicative of a possible inappropriateness of the HS potentials for LaSn₃; therefore, although the La 4f function is included as an expansion function in obtaining the energy levels given in Table II, the "La 4f" levels themselves are not given in Table II nor were they counted in computing the Fermi level. The ignoring of these La 4f levels is supported by the calculation of a few symmetry points with a second potential (see below).

SENSITIVITY OF ENERGY LEVELS TO THE POTENTIAL CHOSEN

To obtain an idea of the sensitivity of energy levels to the potential, we calculated some Γ , Δ , and X representations using a second muffin-tin potential constructed from the self-consistent relativistic atomic potentials of Liberman.¹⁸ For those levels whose eigenfunctions do not contain La d, the Liberman levels are about 0.1 Ry higher than the corresponding HS levels. For the levels whose eigenfunctions do contain La d, the Liberman levels are about 0.2 Ry higher than the HS levels. The fact that these relativistic-potential-based levels are higher than the nonrelativistic-potential-based levels corroborates the arguments given by Callaway *et al.*¹⁹ Figure 3 shows both Liberman and HS levels for some selected representations in the $\Gamma\Delta X$ direction. (The Liberman levels as plotted in Fig. 3 are all 0.1 Ry below the actual calculated level.)

When the Liberman potentials are used in our program⁸ to generate atomiclike functions, we get a 4f level in La at about -0.30 Ry (the corresponding HS value is -1.14 Ry). When this function is included in the crystal calculation for the appropriate Γ , Δ , or X representations, we get La 4f levels between about -0.33 and -0.40 Ry (the corresponding HS value is about -1.14 Ry). The fact that the La f level shifts by about 0.8 Ry in going from the HS to the Liberman potentials, whereas d-like levels shift by about 0.2 Ry and non-d-levels by only about 0.1 Ry, corroborates

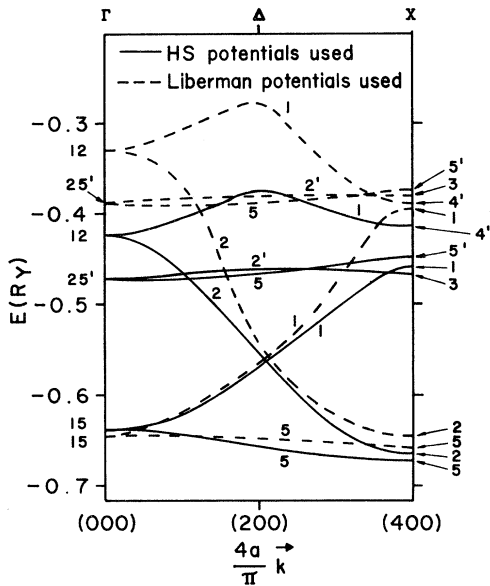


FIG. 3. Comparison of the HS-based and Liberman-based energy levels for some $\Gamma\Delta X$ representations. The HS atomic potentials are nonrelativistic whereas the Liberman atomic potentials are relativistic. To facilitate the comparison, all the Liberman-based levels shown here have been shifted downward 0.1 Ry from the actual calculated values. Some of the HS-based levels in Fig. 3 lie slightly above the corresponding Fig. 4 levels, as fewer plane waves were used for these comparison values. It should be noted that only the middle and end points of Figs. 3-9 have actually been calculated and that the vertical scale of Fig. 3 differs from that of Figs. 4-9.

our having considered the HS $4f$ crystal levels as spurious levels. This statement does not imply that the actual location of any possible f levels in LaSn_3 has been settled but only that the $\text{La } f$ levels are far more sensitive to changes in potentials than the other levels are.

CONVERGENCE

In the following discussion k_g represents $(a/2\pi)|\vec{k} + \vec{K}|$ and k_{max} denotes the largest value of k_g used for any particular irreducible representation. For any given representation all symmetrized \vec{K} 's were taken in increasing order of k_g up to some value k_{max} . Computer time and storage space requirements restrict the number of plane waves used. For LaSn_3 the atomlike functions which contribute strongly to the crystal energy levels of interest (energy levels lying roughly between -0.2 and -1.2 Ry) are $\text{La } 5d$ and $\text{Sn } 5s$ and $5p$. In plotting the energy of a given level vs k_{max} , we have noted that those levels whose eigenfunctions are composed mainly of p functions (or of s and p) show a large drop in energy at a k_{max} of about 2.0 and level off at k_{max} about 4.0. For levels whose eigenfunctions include large contributions from $\text{La } d$ functions, the corresponding k_{max} values are 3.6 and 5.4, respec-

tively. Thus, for the eigenfunctions containing $\text{La } d$, convergence cannot be obtained until one has k_{max} at least as large as 5.4. For the high-symmetry points (Γ, R, X, M) it was generally possible to go beyond a k_{max} of 5.4 without exceeding time and storage limits. Thus most levels for these points are probably converged to about 0.004 Ry. For the lower-symmetry points it was frequently not possible to get to a k_{max} of either 4.0 or 5.4 and convergence for many levels for these points is only good to about 0.02 Ry. In Table II these poorly converged levels are given to two decimal places only. The lower levels of Table II (roughly -0.8 to about -1.2 Ry) are generally s -type levels and are quite well converged for all symmetry points considered.

$E^0(\vec{k})$ CURVES AND DETERMINATION OF THE FERMI LEVEL

With the energy levels determined to the precision indicated above, curves of energy vs \vec{k} were plotted in six principal directions in \vec{k} space for energies in the range from -0.2 to -1.2 Ry. These are shown in Figs. 4-9.

Coordinates for all \vec{k} used along with the number of equivalent points for each are given in Table I. Table II lists nonrelativistic $E^0(\vec{k})$ for the ten symmetry points considered for energies between

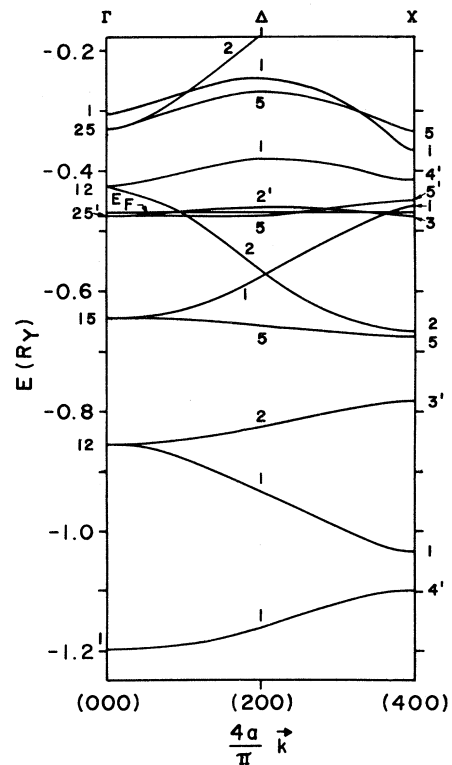
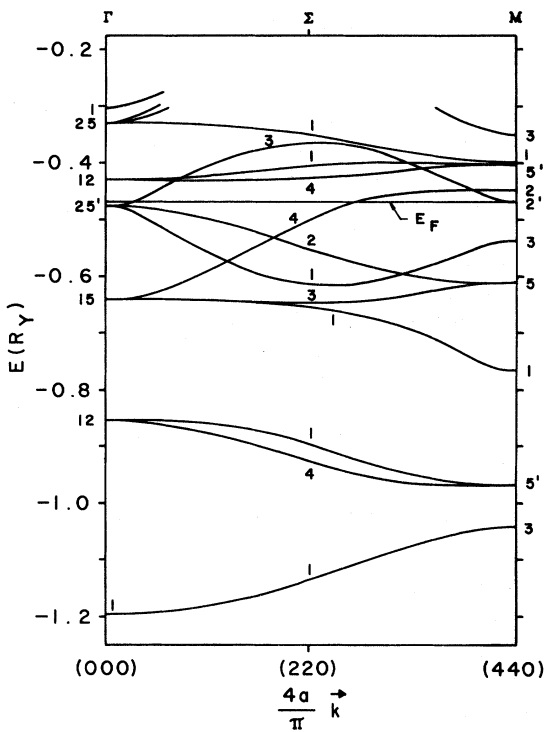
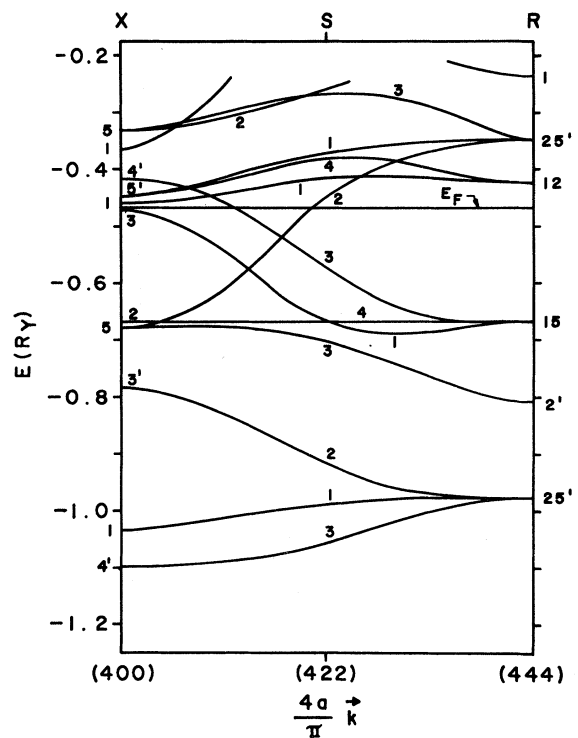
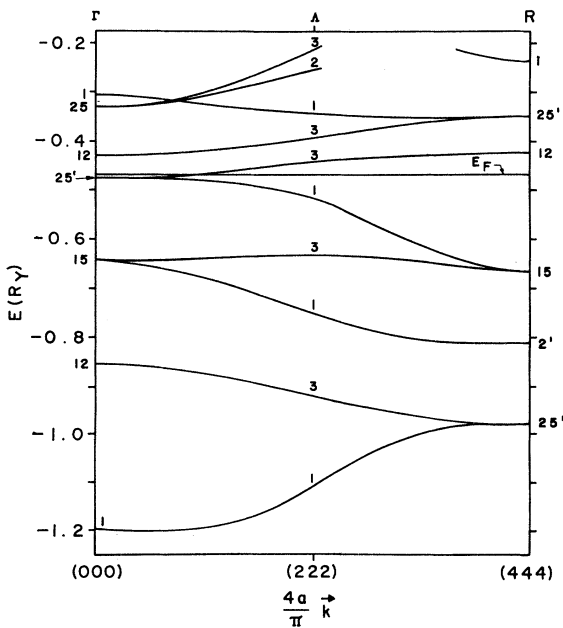
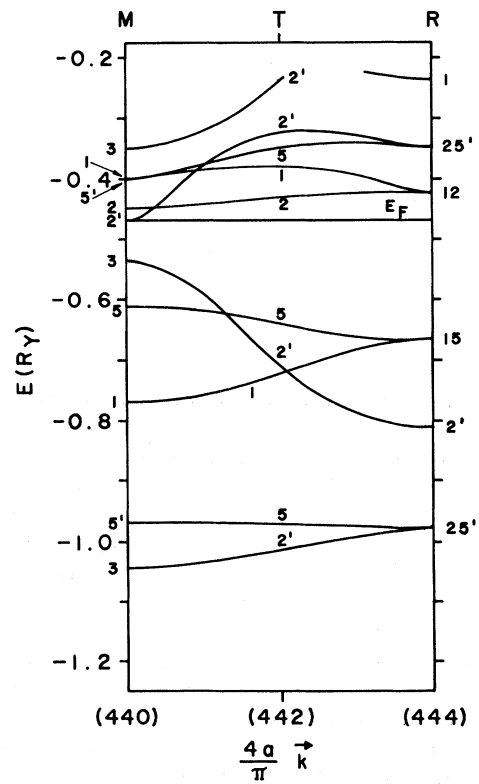


FIG. 4. Nonrelativistic E^0 vs k for the $\Gamma\Delta X$ direction.

FIG. 5. Nonrelativistic E^0 vs k for the $\Gamma\Sigma M$ direction.FIG. 7. Nonrelativistic E^0 vs k for the XSR direction.

-0.2 and -1.2 Ry (about 15 bands). The band numbering starts with the first energy level (for the \vec{k} point in question) above the nonvalence atomic levels as band 1, next lowest as band 2, etc. The two- and three-dimensional representations

FIG. 6. Nonrelativistic E^0 vs k for the ΓAR direction.FIG. 8. Nonrelativistic E^0 vs k for the MTR direction.

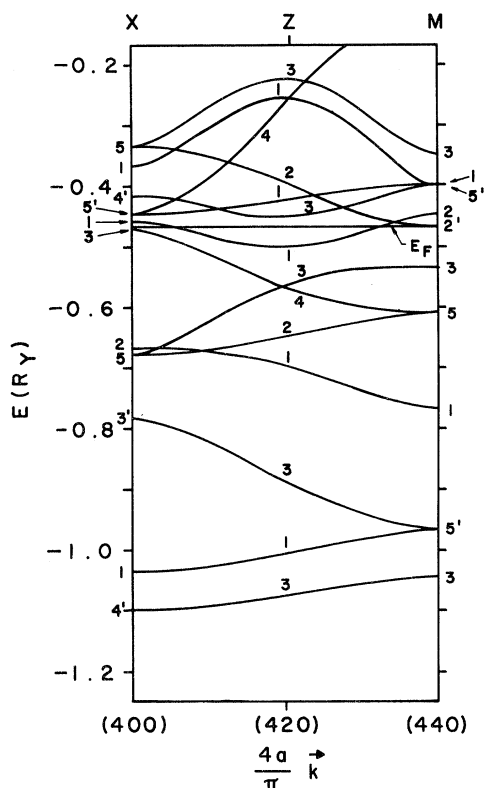


FIG. 9. Nonrelativistic E^0 vs k for the XZM direction.

such as Γ_{12} and $\Gamma_{25'}$, always have identical levels in each of two and three bands, respectively. It should be remembered that all levels listed in Table II are at least doubly degenerate due to spin.

Fermi level. Since the equivalent of 64 uniformly spaced points in \vec{k} space was used, there are electrons from 64 unit cells to be placed into the available states. We consider the lower-lying atomic electrons to have "flat" $E^0(\vec{k})$ curves and count only the two 6s and one 5d electron of La and the two 5s and two 5p electrons of Sn. As there are three Sn sites per unit cell, there are then 3 La plus 3×4 Sn or 15 electrons per unit cell or $64 \times 15 = 960$ electrons in all. Dividing by 2 (for spin) gives 480 levels to be filled with electrons. We then count up from the bottom of our "levels of interest" to the 480th level. In counting levels, one counts a Γ_1 level as 1 (one-dimensional representation, 1 equivalent point), a Δ_5 level as 12 (two-dimensional representation, 6 equivalent points), and so on. Continuing, we find the nonrelativistic Fermi level to be at $-0.46(8)$ Ry where the digit in parenthesis is probably not significant.

Identification of atomiclike functions contributing to the various crystal energy levels. For some irreducible representations one can tell immediately which atomiclike functions must be the main contributors to levels in the region of interest. For

example, $\Gamma_{25'}$ allows only La d and Sn d atomiclike functions. As there is no Sn d valence function, the main atomic contribution to the $\Gamma_{25'}$ level at -0.475 must come from La $5d$. In more complicated cases one must analyze the resultant crystal wave function to determine these atomic contributions.

Table III lists the major atomic contributions to levels near the Fermi level for the ten symmetry points studied. When more than one atomiclike function contributes, the ratios given are the squares of the appropriate²⁰ coefficients c_{ni} of Eq. (2). It must be remembered that the plane waves also make substantial contributions to the eigenfunctions associated with each energy level.

CONCLUSION

On comparing energy levels for different potentials for a few selected symmetry points we find the La $4f$ levels to have shifted upward by about 0.8 Ry on going from the nonrelativistic HS potentials to the relativistic Liberman potentials. The d -like levels and the non- d -like levels shift upward by about 0.2 and 0.1 Ry, respectively, under the same potential change. This does not locate any possible f -like levels in LaSn_3 but merely indicates that these levels are far more sensitive than other levels to changes in the potential.

For the high-symmetry points (Γ, R, X, M), our nonrelativistic energy levels are generally converged to within about 0.004 Ry. Some of the low-symmetry points, however, are quite poorly converged—probably to within about 0.02 Ry in the worst cases. The nonrelativistic Fermi level has been computed to be -0.47 Ry.

As both La and Sn have fairly high atomic numbers (57 and 50, respectively), relativistic effects should be quite important in the electronic band structure of LaSn_3 . In the second, and concluding, paper²¹ in this series we use perturbation theory to compute relativistic corrections to the

TABLE I. Values of \vec{k} and the number of equivalent points for each \vec{k} .

BSW label	Order of group of \vec{k}	Number of like vectors	Wave vector $4a\vec{k}/\pi$
Γ	48	1	(0, 0, 0)
Δ	8	6	(2, 0, 0)
X	16	3	(4, 0, 0)
Σ	4	12	(2, 2, 0)
M	16	3	(4, 4, 0)
Λ	6	8	(2, 2, 2)
R	48	1	(4, 4, 4)
S	4	12	(4, 2, 2)
T	8	6	(4, 4, 2)
Z	4	12	(4, 2, 0)

TABLE II. LaSn_3 nonrelativistic energy levels. The labels are the BSW symbols. The third and alternate columns give the BSW irreducible representation. The fourth and alternate columns give the energy eigenvalues for the respective bands. All energies are in rydbergs and must be multiplied by -1.0 to obtain the actual value. Energy values given to two decimal places only represent poorly converged levels (see text).

Label	$4a\vec{k}/\pi$	Rep	Band 1	Rep	Band 2	Rep	Band 3	Rep	Band 4
Γ	(0, 0, 0)	1	1.196	12	0.854	12	0.854	15	0.642
Δ	(2, 0, 0)	1	1.164	1	0.933	2	0.826	5	0.656
X	(4, 0, 0)	4'	1.099	1	1.037	3'	0.782	5	0.678
Σ	(2, 2, 0)	1	1.133	4	0.926	1	0.897	1	0.65
M	(4, 4, 0)	3	1.042	5'	0.968	5'	0.968	1	0.768
Λ	(2, 2, 2)	1	1.108	3	0.921	3	0.921	1	0.745
R	(4, 4, 4)	25'	0.978	25'	0.978	25'	0.978	2'	0.81
S	(4, 2, 2)	3	1.057	1	0.990	2	0.917	3	0.70
T	(4, 4, 2)	2'	1.016	5	0.971	5	0.971	1	0.721
Z	(4, 2, 0)	3	1.077	1	1.006	3	0.886	1	0.70
Label	$4a\vec{k}/\pi$	Rep	Band 5	Rep	Band 6	Rep	Band 7	Rep	Band 8
Γ	(0, 0, 0)	15	0.642	15	0.642	25'	0.475	25'	0.475
Δ	(2, 0, 0)	5	0.656	1	0.58	2	0.56	5	0.47
X	(4, 0, 0)	5	0.678	2	0.667	3	0.470	1	0.459
Σ	(2, 2, 0)	3	0.65	1	0.62	2	0.56	4	0.50
M	(4, 4, 0)	5	0.610	5	0.610	3	0.536	2'	0.467
Λ	(2, 2, 2)	3	0.63	3	0.63	1	0.51	3	0.44
R	(4, 4, 4)	15	0.665	15	0.665	15	0.665	12	0.423
S	(4, 2, 2)	1	0.668	4	0.667	3	0.58	2	0.45
T	(4, 4, 2)	2'	0.707	5	0.639	5	0.639	2	0.43
Z	(4, 2, 0)	2	0.65	4	0.57	3	0.57	1	0.51
Label	$4a\vec{k}/\pi$	Rep	Band 9	Rep	Band 10	Rep	Band 11	Rep	Band 12
Γ	(0, 0, 0)	25'	0.475	12	0.427	12	0.427	25	0.33
Δ	(2, 0, 0)	5	0.47	2'	0.46	1	0.38	5	0.27
X	(4, 0, 0)	5'	0.45	5'	0.45	4'	0.416	1	0.366
Σ	(2, 2, 0)	4	0.43	1	0.41	3	0.37	1	0.35
M	(4, 4, 0)	2	0.448	5'	0.40	5'	0.40	1	0.40
Λ	(2, 2, 2)	3	0.44	3	0.40	3	0.40	1	0.35
R	(4, 4, 4)	12	0.423	25'	0.35	25'	0.35	25'	0.35
S	(4, 2, 2)	1	0.42	4	0.38	1	0.37	3	0.27
T	(4, 4, 2)	1	0.38	5	0.35	5	0.35	2'	0.33
Z	(4, 2, 0)	3	0.45	1	0.43	2	0.39	4	0.27
Label	$4a\vec{k}/\pi$	Rep	Band 13	Rep	Band 14	Rep	Band 15		
Γ	(0, 0, 0)	25	0.33	25	0.33	1	0.304		
Δ	(2, 0, 0)	5	0.27	1	0.25				
X	(4, 0, 0)	5	0.33	5	0.33				
Σ	(2, 2, 0)	3	0.25	4	0.20	2	0.20		
M	(4, 4, 0)	3	0.35						
Λ	(2, 2, 2)	2	0.26	3	0.22	3	0.22		
R	(4, 4, 4)	1	0.236						
S	(4, 2, 2)	2	0.27	3	0.19				
T	(4, 4, 2)	2'	0.24						
Z	(4, 2, 0)	1	0.26	3	0.23	3	0.20		

$E^0(\vec{k})$ values given here. Comparison with experimental results and further concluding remarks will be given at the end of that paper.

APPENDIX Symmetrization

For a given irreducible representation the symmetrization procedure used here [see Eq. (12) of

main text] is

$$f_i^s(\vec{r}) = (h/g) \sum_R D_{11}^*(R) f_i^u(R^{-1}\vec{r}) \quad (\text{A1})$$

$[f_i^u(R^{-1}\vec{r}) = v_i(\vec{r})]$ is the function obtained by operating on $f_i^u(\vec{r})$ with R .] As the D 's used here are real, we drop the asterisk on D_{11} of Eq. (A1). By using the unitary property of the D 's we may transform Eq. (A1) by letting $T = R^{-1}$, summing over

TABLE III. Atomic contributions to crystal energy levels near the Fermi level. The third column gives the major contributing atomiclike function(s). The fourth column gives the ratio of the squares of the appropriate coefficients (see text) when more than one function contributes. The ratios are given in the same order as the labels in column three. It must be remembered that the plane waves also make substantial contributions to the eigenfunctions associated with each energy level.

BSW label	Energy	Predominant function(s)	Ratio
Γ_{12}	-0.427	La <i>d</i> /Sn <i>s</i>	2/1
$\Gamma_{25'}$	-0.475	La <i>d</i>	
Γ_{15}	-0.642	Sn <i>p</i>	
Δ_1	-0.38	La <i>d</i> /Sn <i>s</i>	5/2
$\Delta_{2'}$	-0.46	La <i>d</i>	
Δ_5	-0.47	Sn <i>p</i> /La <i>d</i>	6/5
Δ_2	-0.56	La <i>d</i> /Sn <i>s</i> /Sn <i>p</i>	2/1/1
Δ_1	-0.58	Sn <i>p</i> /La <i>d</i> /Sn <i>s</i>	10/3/2
$X_{4'}$	-0.416	Sn <i>p</i> /Sn <i>s</i>	4/1
$X_{5'}$	-0.45	Sn <i>p</i>	
X_1	-0.459	La <i>d</i> /Sn <i>p</i>	2/1
X_3	-0.470	La <i>d</i>	
X_2	-0.667	La <i>d</i> /Sn <i>p</i>	2/1
X_5	-0.678	Sn <i>p</i> /La <i>d</i>	3/2
Σ_1	-0.35	La <i>d</i> /Sn <i>p</i> /Sn <i>s</i>	3/2/1
Σ_3	-0.37	La <i>d</i> /Sn <i>p</i>	5/2
Σ_1	-0.41	La <i>d</i> /Sn <i>p</i>	3/1
Σ_4	-0.43	Sn <i>p</i> /Sn <i>s</i>	2/1
Σ_4	-0.50	La <i>d</i> /Sn <i>p</i>	2/1
Σ_2	-0.56	La <i>d</i> /Sn <i>p</i>	2/1
M_1	-0.40	La <i>d</i>	
$M_{5'}$	-0.40	Sn <i>p</i> /Sn <i>s</i>	3/1
M_2	-0.448	La <i>d</i>	
$M_{2'}$	-0.467	Sn <i>p</i>	
M_3	-0.536	Sn <i>p</i> /Sn <i>s</i> /La <i>d</i>	5/2/1
M_5	-0.610	La <i>d</i> /Sn <i>p</i>	3/2
Λ_1	-0.35	La <i>d</i> /La <i>s</i>	5/1
Λ_3	-0.40	La <i>d</i> /Sn <i>s</i>	6/1
Λ_3	-0.44	Sn <i>p</i> /La <i>d</i> /Sn <i>s</i>	8/4/3
Λ_1	-0.51	Sn <i>p</i> /La <i>d</i> /Sn <i>s</i>	5/2/1
Λ_3	-0.63	Sn <i>p</i> /La <i>d</i>	2/1
$R_{25'}$	-0.35	La <i>d</i>	
R_{12}	-0.423	La <i>d</i>	
R_{15}	-0.665	Sn <i>p</i>	
S_1	-0.37	La <i>d</i> /Sn <i>s</i>	6/1
S_4	-0.38	La <i>d</i> /Sn <i>p</i>	2/1
S_1	-0.42	La <i>d</i> /Sn <i>p</i>	3/1
S_2	-0.45	La <i>d</i> /Sn <i>p</i> /Sn <i>s</i>	3/2/2
S_3	-0.58	Sn <i>p</i> /La <i>d</i>	3/2
$T_{2'}$	-0.33	La <i>d</i>	
T_5	-0.35	La <i>d</i> /Sn <i>p</i> /Sn <i>s</i>	7/3/2
T_1	-0.38	La <i>d</i>	
T_2	-0.43	La <i>d</i>	
T_5	-0.639	Sn <i>p</i> /La <i>d</i>	3/1
Z_2	-0.39	Sn <i>p</i> /La <i>d</i>	9/4
Z_1	-0.43	La <i>d</i> /Sn <i>p</i>	4/1
Z_3	-0.45	La <i>d</i> /Sn <i>p</i> /Sn <i>s</i>	5/4/1
Z_1	-0.51	Sn <i>p</i> /La <i>d</i> /Sn <i>s</i>	2/1/1

TABLE III. (Continued)

BSW label	Energy	Predominant function(s)	Ratio
Z_3	-0.57	Sn <i>p</i> /Sn <i>s</i>	3/2
Z_4	-0.57	La <i>d</i> /Sn <i>p</i>	4/3

T instead of T^{-1} , and, finally, replacing T by R obtaining

$$f_i^s(\vec{r}) = (h/g) \sum_R D_{11}(R) f_i^u(R\vec{r}) . \quad (A2)$$

In the following we use whichever of Eq. (A1) or (A2) is most convenient in each case.

An unsymmetrized plane wave has the form

$$P_i^u(\vec{r}) = e^{i(\vec{k} + \vec{k}_i) \cdot \vec{r}} . \quad (A3)$$

Symmetrized using Eq. (A2), this becomes

$$P_i^s(\vec{r}) = (h/g) \sum_R D_{11}(R) e^{iR^{-1}(\vec{k} + \vec{k}_i) \cdot \vec{r}} .$$

An unsymmetrized atomiclike function has the form²²

$$A_i^u(\vec{r}) = \sum_j e^{i\vec{k} \cdot (\vec{r}_j + \vec{s}_j)} F_{nlm}(\vec{r} - \vec{r}_j - \vec{s}_j) , \quad (A4)$$

where j runs over all the unit cells and F_{nlm} is an atomiclike orbital which can be written as

$$F_{nlm}(\vec{\rho}) = i^l [u_{nl}(\rho)/\rho] X_{lq}(\vec{\rho}/\rho) , \quad (A5)$$

where X_{lq} is a cubic harmonic which can be expanded as a linear combination of spherical harmonics. The i^l factor was added to make the S matrix real. Using Eq. (A1), the symmetrized atomiclike function becomes

$$A_i^s(\vec{r}) = (h/g) \sum_R D_{11}(R) \sum_j e^{i\vec{k} \cdot (\vec{r}_j + \vec{s}_j)} F_{nlm}(R^{-1}\vec{r} - \vec{r}_j - \vec{s}_j) .$$

Matrix Elements

The H_{ij}^0 and S_{ij} matrix elements [see Eqs. (5) and (6) of main text] will be of three types: plane wave-plane wave, plane wave-atomic, and atomic-atomic. As the Hamiltonian operator is invariant to the group it is only necessary to symmetrize one of the two functions in the H_{ij}^0 and S_{ij} integrals. As the derivation of the final form of these integrals is quite lengthy,¹⁴ we simply list the final expressions below. In these expressions j_l is the l th spherical Bessel function; the subscript ν runs over the one La and three Sn basis atoms. All integrals have been multiplied by $(g/h)1/4\pi$ for convenience.

Plane Wave-Plane Wave

$$S_{ij} = (W/4\pi) \sum_R D_{11}(R) \delta[\vec{k} + \vec{K}_i, R^{-1}(\vec{k} + \vec{K}_j)] ,$$

where W is volume of the unit cell,

$$\delta(x, y) = 0, \quad x \neq y$$

$$= 1, \quad x=y$$

$$H_{ij}^0 = [(\vec{k} + \vec{K}_j)^2 + \bar{V}] S_{ij} + \sum_R D_{11}(R) \left[\int_0^{\rho_s} (\rho V_{La}(\rho) - \rho \bar{V}) j_0(K\rho) \rho d\rho + \sum_{S_n} e^{i\vec{K} \cdot \vec{S}_n} \int_0^{\rho_s} (\rho V_{Sn}(\rho) - \rho \bar{V}) j_0(K\rho) \rho d\rho \right],$$

where $\vec{K} = R^{-1}(\vec{k} + \vec{K}_j)$ and ρ_s is the radius of the appropriate muffin-tin sphere. The sum on the Sn term above may be written

$$F(\vec{K}) \int_0^{\rho_s} (\rho V_{Sn}(\rho) - \rho \bar{V}) j_0(K\rho) \rho d\rho,$$

with

$$F(\vec{K}) = \sum_{S_n} e^{i\vec{K} \cdot \vec{S}_n} = (-1)^{n_1 + n_2} + (-1)^{n_1 + n_3} + (-1)^{n_2 + n_3},$$

where $\vec{K} = (2\pi/a)(n_1, n_2, n_3)$ and the n_i are integers.

Atomic Term-Plane Wave

$$S_{ij} = s \int_0^{\rho_s} u_{ni}(\rho) j_i(K\rho) \rho d\rho,$$

$$H_{ij}^0 = K^2 S_{ij} + s \int_0^{\rho_s} u_{ni}(\rho) j_i(K\rho) \rho V_\nu(\rho) d\rho,$$

where $\vec{K} = \vec{k} + \vec{K}_j$ and

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

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

Atomic Term-Atomic Term

For an unsymmetrized function (index i) on site \vec{S}_ν and a symmetrized function (index j) generated

from an unsymmetrized function on site $\vec{S}_{\nu'}$, we have

$$S_{ij} = (1/4\pi) \int_0^{\rho_s} u_{ni}(\rho) u_{n'i}(\rho) d\rho \times \int X_{i1}(\vec{\rho}/\rho) X_{i'j}^s(\vec{\rho}/\rho) d\Omega, \quad (A6)$$

$$H_{ij}^0 = (1/4\pi) \int_0^{\rho_s} u_{ni}(\rho) H_\tau u_{n'i}(\rho) d\rho \times \int X_{i1}(\vec{\rho}/\rho) X_{i'j}^s(\vec{\rho}/\rho) d\Omega, \quad (A7)$$

where

$$H_\tau = \frac{-d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2} + V_\nu(\rho)$$

and

$$X_{i'j}^s(\vec{\rho}/\rho) = \sum_R' D_{11}(R) e^{i\vec{k} \cdot (R^{-1}\vec{S}_\nu - \vec{S}_{\nu'})} X_{ij}(R^{-1}\vec{\rho}/\rho).$$

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. If the $u_{ni}(\rho)$ satisfy

$$H_\tau u_{ni}(\rho) = E_{ni} u_{ni}(\rho), \quad (A8)$$

then

$$H_{ij}^0 = E_{ni} S_{ij} \quad (A9)$$

and S_{ij} of Eq. (A6) is zero for $n \neq n'$. In our application some of our atomiclike functions do not satisfy Eq. (A8) exactly throughout the entire range of ρ because of fitting a cubic function onto them near ρ_s so that they go to zero with zero slope. For these functions Eq. (A7) must be used and not Eq. (A9). Calculation of actual values indicated that taking H_{ij}^0 and S_{ij} equal to zero for $n \neq n'$ was still a good approximation.

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⁶The program to determine L and L^{-1} was written by Dr. D. G. Shankland. This procedure avoids the Jacobi diagonalization of the S matrix and cuts computer time per problem by a factor of about 2. We are grateful to Dr. R. N. Euwema for bringing this procedure to our attention.

⁷For simplicity, the symmetrization notation has been suppressed in these expressions.

⁸We are indebted to Dr. F. K. Bloom, Jr., for this program.

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¹⁴D. M. Gray, Watervliet Arsenal Technical Report No. WVT-7005, 1970 (unpublished). This report gives details of the symmetrization and integration procedures for a crystal such as LaSn₃ with more than one atom per primitive cell.

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¹⁶This program was written by Dr. F. W. Quelle.

¹⁷As a test of the effect on other levels we calculated energy levels for a number of representations both with and without the La $4f$ function included in the basis set. The biggest shift for levels near the Fermi level (i.e., in the range from -0.4 to -0.6 Ry) was 0.006 Ry and in most cases considerably less.

¹⁸D. A. Liberman (private communication).

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$$\int \psi_n^0(\vec{r}) \psi_n^0(\vec{r}) d\tau = 1.0, \quad \tilde{c}_{ni}^2 = c_{ni}^2 \int \phi_i^*(\vec{r}) \phi_i(\vec{r}) d\vec{r}.$$

²¹D. M. Gray and L. V. Meisel, following paper, Phys.

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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 $C_{\frac{1}{2}}$.

PHYSICAL REVIEW B

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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