Band structure and superconductivity in Bi_3Sr and Bi_3Eu

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Band-structure calculations of Bi_3Sr and Bi_3Eu with the use of the augmented-plane-wave method are presented. The results show a discrepancy with the measured value of the electronic specific-heat coefficient for Bi_3Sr, and suggest that the measured value is inaccurate. Also for Bi_3Sr, an evaluation of the superconducting properties with the use of a recently proposed correction to the rigid-muffin-tin approximation for free-electron-like metals gives satisfactory agreement with experiment.

I. INTRODUCTION

The subject of the possible coexistence of superconductivity and magnetism has received much attention recently.[1] The system $Bi_3Sr_{1-x}Eu_x$ has been investigated by Kempf *et al.*[2] who confirmed the previous measurements of Matthias and Hulm[3] showing a superconducting temperature $T_c = 5.6$ K for Bi_3Sr. Kempf *et al.*[2] also found that Bi_3Eu orders antiferromagnetically at 7.8 K. In the solid solution of the two binaries Kempf *et al.*[2] suggested a region around $x = 0.35$ where coexistence of superconductivity and a spin-glass-type magnetism may occur.

We have performed band-structure calculations for paramagnetic Bi_3Sr and Bi_3Eu and used the results to calculate the superconducting properties of these compounds. For Bi_3Sr our calculations are in accord with the above experiments regarding T_c, but in disagreement with the specific-heat measurements.[2] For Bi_3Eu any quantitative study of the magnetic properties depends upon the completion of a spin-polarized band-structure calculation. We also present Fermi-surface calculations for Bi_3Sr, although there are as yet no measurements with which to compare. Planned future work will deal with the magnetic and pseudobinary properties of these materials.

II. COMPUTATIONAL PROCEDURE

The band-structure calculations reported here were performed in the muffin-tin approximation with the use of a symmetrized semirelativistic (no spin-orbit coupling) augmented-plane-wave (APW) method[4] adapted for the Cu_3Au structure. Exchange and correlation were incorporated in the crystal potentials with the use of the form of the local density theory suggested by Hedin and Lundqvist.[5] The lattice constants were taken equal to 9.524 and 9.429 a.u. for Bi_3Sr and Bi_3Eu, respectively.[6,2] The muffin-tin sphere radii were chosen equal to one-half the nearest-neighbor distances.

The calculations were carried out to self-consistency with the use of the assumed core, semicore, and valence state configurations shown in Table I. The core states have essentially no interatomic overlap, and were therefore treated in an atomiclike manner with the use of a suitably modified version of the relativistic atomic structure computer code of Liberman *et al.*[7] The narrow-band semicore states were calculated on a mesh of four $\vec{k}$ points (Γ, X, M, and R) in each self-consistency cycle, while the relatively wide-band valence-conduction states were calculated on a ten $\vec{k}$-point mesh ($\Gamma, X, M, R, \Delta, Z, \Lambda, \Sigma, S, T$). Note that the seven $4f$ electrons of Eu were included as core states, as it is well known that it is improper to treat

TABLE I. Assumed core, semicore, and valence electron configurations for Bi, Sr, and Eu.

	Core	Semicore	Valence
Bi	$[Xe] + 4f^{14}$	$5d^{10}$	$6s^2 6p^3$
Sr	$[Ar] + 3d^{10}$	$4s^2 4p^6$	$5s^2$
Eu	$[Kr] + 4d^{10} + 4f^7$	$5s^2 5p^6$	$6s^2$

the rare-earth f-shell electrons as itinerant.[8] If the f electrons were to be treated as band states, then the unfilled f band would be pinned at the Fermi level in disagreement with the photoemission experiments in rare-earth metals.[9] However, treating these states as localized gives reasonable agreement with the experimental data.[10] In each iteration fractions of the input (75%) and output (25%) total charge densities were mixed to form the potentials for the following cycles. The energy eigenvalues for Bi_3Sr converged to ± 2 mRy in three cycles, while similar convergence for Bi_3Eu required eight iterations. In addition, to avoid large oscillations for Bi_3Eu, only a few percent of the new charge density could be mixed for the first few cycles. These difficulties in converging the Bi_3Eu calculation are probably related to the partially occupied f states.

Our final self-consistent potentials were used to calculate the energy eigenvalues $E_n(\vec{k})$ and the electronic charges inside the APW spheres, $Q_{n,l}(\vec{k})$, on a mesh of 35 $\vec{k}$ points in the irreducible zone (or equivalently, 512 $\vec{k}$ points in the full Brillouin zone). The charges $Q_{n,l}(\vec{k})$ are needed for obtaining the wave-function character of each state $(n,\vec{k})$, and hence are used as weights to decompose the density of states (DOS) per site and per angular momentum l. Our DOS calculations proceed in two steps. First, the symmetrized Fourier method[11] is used to interpolate $E_n(\vec{k})$ and $Q_{n,l}(\vec{k})$ onto a 969 $\vec{k}$-point mesh in the irreducible zone. This method[11] consists of a sequence of Fourier-series expansions that have built in the compatibility relations between symmetry points and lines, and also between symmetry lines and planes for the space group considered. In the second step the 969 $\vec{k}$-point interpolated results are utilized to calculate the DOS by the tetrahedron method.[12]

III. ENERGY BANDS AND DENSITIES OF STATES

The results of the present calculations are illustrated in Figs. 1 and 2 where the energy bands and the DOS are shown. Both Bi_3Sr and Bi_3Eu are characterized by a low-lying set of bands that have strong Bi s-like contributions. Centered at Γ_{15} we have a complex of states which are dominated by Bi p-like character. Near E_F the states continue to be predominantly Bi p-like. In the high-energy region (Γ_{15} and $\Gamma_{25'}$) the d-like components of both Bi and Sr have very significant contributions. The only qualitative difference between Figs. 1 and 2 is the appearance of unoccupied Eu $4f$ levels approximately 0.15 Ry above E_F. The reader should note here that these $4f$ bands correspond to 14 electrons instead of seven f states per atom which are actually unoccupied in Eu. This demonstrates that nonspin-polarized band theory fails in treating f electrons properly.[8] Therefore, the f bands shown in Fig. 2 should not be considered as an accurate representation of the unoccupied $4f$ levels of Eu. Since the f states hybridize very little with the other bands, they should not have a large effect on E_F.

Our results for Bi_3Sr are in serious disagreement with the specific-heat measurements of Kempf *et al.*[2] Our calculated bare DOS at the Fermi level is $N(E_F)=0.22$ states/(eV atom spin) while the value deduced from the measured electronic specific-heat coefficient γ is only 0.08 states/(eV atom spin). Considering that the calculated $N(E_F)$ must be multiplied by an enhancement $(1+\lambda)$ before comparing with experiment, the disagreement is even worse than the above numbers indicate. It is probable, since γ is small and the lattice contribution is large, that the measured value cannot be extracted with sufficient accuracy.[13] According to Fischer,[13] in order to resolve this discrepancy precise low-temperature measurements in a magnetic field (to quench superconductivity) are needed. The question of the accuracy of our $N(E_F)$ value could have been answered if the Pauli susceptibility χ_P was available from experiment. However, according to Kempf *et al.*,[2] Bi_3Sr remains diamagnetic in the entire temperature range and therefore it was not possible to determine χ_P. We have calculated the Stoner enhancement factor S to be 1.15 and hence we present here a prediction for $\chi_p/\mu_B^2=2SN(E_F)=7.06$ Ry/atom.

IV. FERMI SURFACE OF Bi_3Sr

Figure 3 shows planar sections of our calculated Fermi surface of Bi_3Sr. These were determined with the use of energy values interpolated onto the 969-point mesh as described in Sec. II. The seventh- and eighth-band hole surfaces around Γ resemble closed spheres, with the eighth-band surface having "dimples" along the [111] direction. The eighth-band hole surface centered at R resembles a closed octahedron. The closed ninth-band hole surfaces around Γ and R are of a complicated structure. Tenth-band closed electron surfaces around X and M are boxlike and ellipsoidal, respectively. No Fermi-surface measurements are avail-

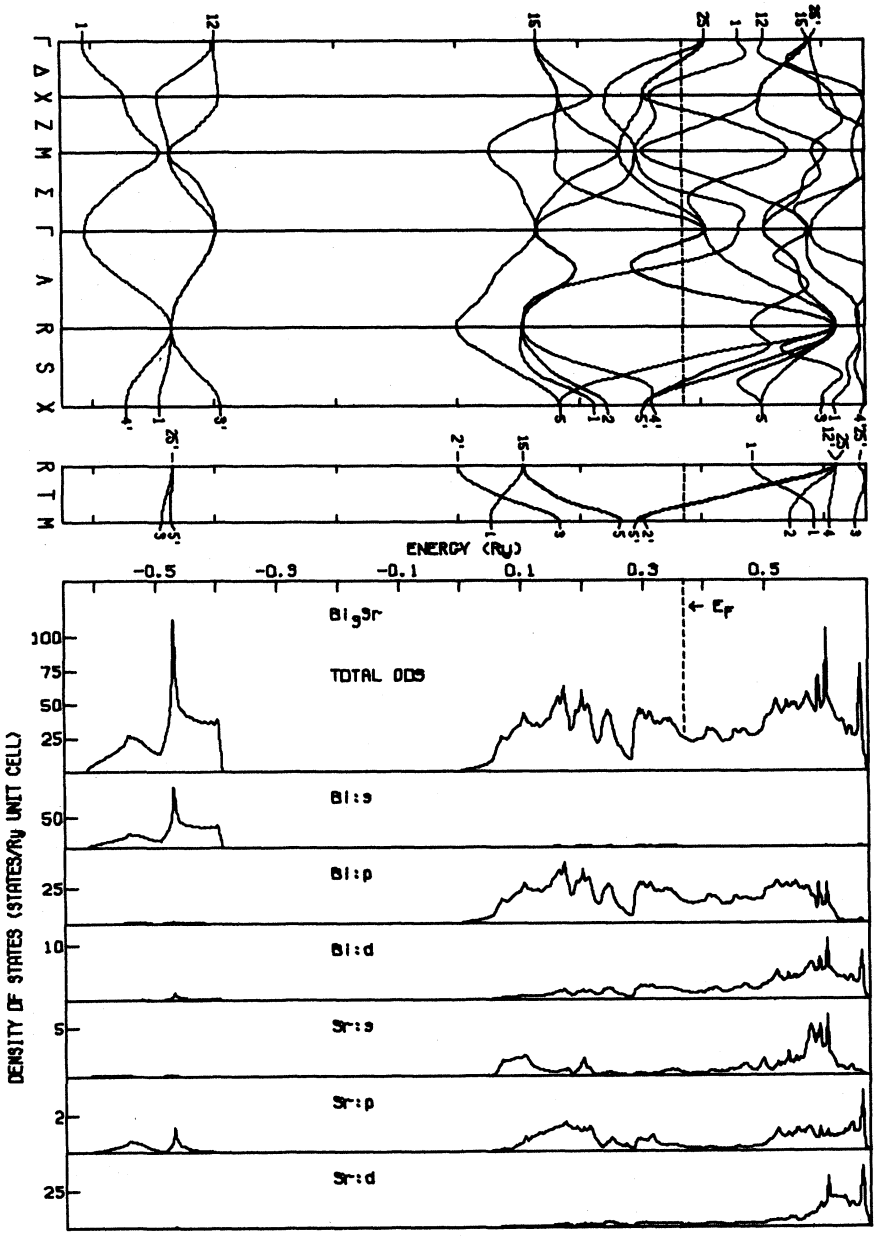

FIG. 1. Energy bands and densities of states for Bi_3Sr. The angular-momentum components of the densities of states are given within the muffin-tin spheres.

able in the literature at the present time for comparison

V. SUPERCONDUCTING PROPERTIES

We have used our band-structure results in a McMillan-type[14] approach and the rigid-muffin-tin-approximation (RMTA) of Gaspari and Gyorffy[15] to calculate the electron-phonon coupling constant λ and the superconducting temperature T_c. As is now well known[16] the above theory for determining λ and T_c utilizes first-principles calculated values of the electronic factors $\eta_s = N(E_F)\langle I^2\rangle_s$ where s labels the atom, together with estimates from the experiment of the moments of the phonon DOS. The Debye-temperature measurements of Kempf *et al.*[2] suggest that the phononic data are very similar to those of Pb and hence we have used the Pb data[14] in our calculations. In Table II we

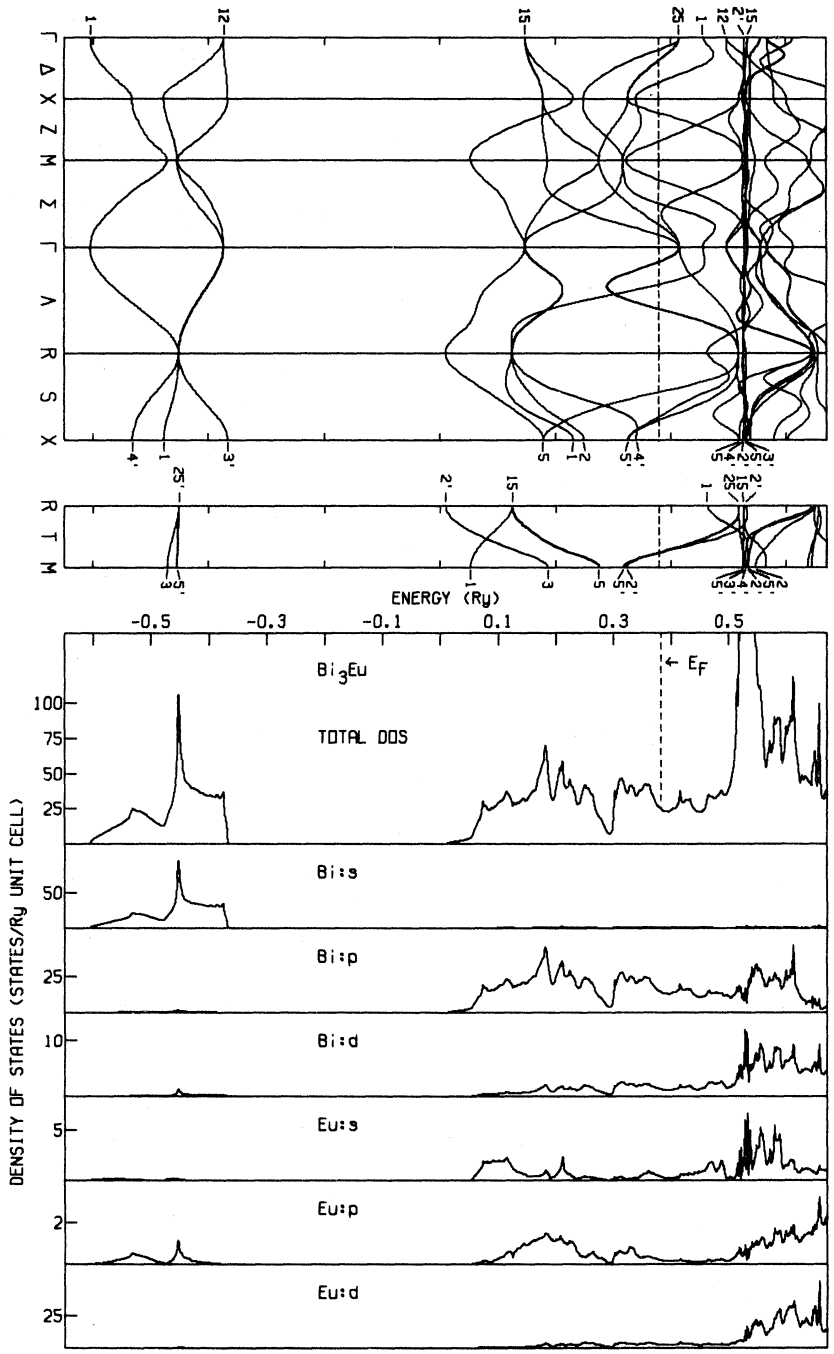

FIG. 2. Energy bands and densities of states for Bi_3Eu. The angular-momentum components of the densities of states are given within the muffin-tin spheres.

show our results for Bi_3Sr and Bi_3Eu and compare them with previous calculations[17] for Pb. From Table II we note first that the Bi contribution to the electron-phonon interaction is the dominant factor while Sr and Eu contribute very little. The second observation is the close similarity between the Bi compounds and Pb. The third point is that since both Bi_3Sr and Bi_3Eu have very similar values of

TABLE II. Rigid-muffin-tin results for the superconducting properties of Bi_3Sr, Bi_3Eu, and Pb.

	Bi_3Sr	Bi_3Eu	Pb[a]
$N(E_F)$/(Ry atom spin)	3.07	3.20	3.48
η_A (eV/Å^2)	0.93	0.88	1.20
η_B (eV/Å^2)	0.10	0.17	
λ_A	0.59	0.56	0.84
λ_B	0.06	0.11	
λ_{tot}	0.65	0.67	0.84
μ^*	0.09	0.30[b]	0.09
T_c^{calc}	1.8	0.0	3.3
T_c^{expt}	5.68[c]	0.0	7.2

[a]Reference 17.
[b]In order to suppress superconductivity in Bi_3Eu we use $\mu^* \approx 0.3$.
[c]Reference 2.

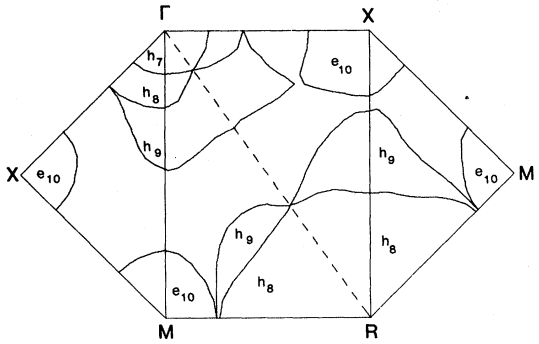

FIG. 3. Planar sections of the Fermi surface of Bi_3Sr.

η's and λ's, the way to account for the absence of superconductivity in Bi_3Eu is either to assume much different phonon spectra or to invoke a value larger than 0.3 for the Coulomb pseudopotential μ^*.

Finally, we note that the T_c of Bi_3Sr is underestimated by the RMTA. This is a common occurence in the simple metals where the RMTA omits the screened potential tail. This problem has recently been addressed by Zdetsis *et al.*[18] who have introduced a correction to the RMTA for all free-electron-like metals, which should be applicable to the present system. Their theory is based on the idea of constructing a potential that has the correct asymptotic behavior at large distances and reduces to essentially a uniform potential well inside the muffin-tin sphere. This theory gives results that are a substantial improvement over the RMTA.[18]

We have applied the method of Zdetsis *et al.*[18] to the case of Bi_3Sr by restricting our calculation to the Bi site only, since the Sr-site contribution is very small. The results shown in Table III are in reasonable agreement with experiment.

TABLE III. Non-rigid-muffin-tin results for the superconducting properties of Bi_3Sr and Pb using the theory of Zdetsis *et al.* (Ref. 18).

	Bi_3Sr	Pb[a]
η_A (eV/Å^2)	2.52	2.46
η_B (eV/Å^2)	0.10	
λ_A	1.61	1.59
λ_B	0.06	
λ_{tot}	1.67	1.59
μ^*	0.09	0.09
T_c^{calc}	6.9	6.8
T_c^{expt}	5.68[b]	7.2

[a]Reference 18.
[b]Reference 2.

VI. CONCLUSIONS

We have presented band-structure calculations of the compounds Bi_3Sr and Bi_3Eu. The results are used to extract the value of the electronic specific-heat coefficient and the electron-phonon coupling constant. The present calculations offer a good account of the superconducting properties of Bi_3Sr, but they point to a disagreement with the measured specific-heat data. The question of the spin-glass-type of magnetism suggested by experiments in $Bi_3Sr_{1-x}Eu_x$ cannot be settled by the present study and needs to be addressed via spin-polarized band-structure calculations. A prediction of Fermi-surface cross sections in Bi_3Sr is also presented.

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