Electronic Structure and Reentrant Magnetism in Superconducting $ErRh_4B_4$

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(Received 3 August 1977)

Results of *ab initio* self-consistent energy-band calculations on the full 18-atom/unit-cell ternary alloys MRh_4B_4 (M = Y, Er and Ho) are reported and used to discuss their superconducting and magnetic properties—including the observation of reentrant magnetism in the normal state at $T < 0.9$ K in $ErRh_4B_4$.

The recent discovery[1] of reentrant magnetism (at $T = 0.9$ K) accompanying a transition to a normal metallic state in $ErRh_4B_4$, a ternary rare-earth superconductor with $T_c^s = 8.7$ K, has generated considerable interest in the origin of this new phenomenon. It has also raised important questions regarding our understanding of magnetism and superconductivity and the nature of their possible coexistence. This Letter reports results of *ab initio* self-consistent (SC) energy-band calculations carried out on three of these MRh_4B_4 systems, with M = Er, Y (an 11.3-K superconductor), and Ho (a ferromagnet below 6.6 K), in their paramagnetic states. Very similar total and orbital (l) angular momentum decomposed atomic densities of states (DOS) are found for the three systems investigated. The peak in the total DOS at the Fermi energy arises from the 4d states at the Rh site and appears to be responsible for the superconductivity of the Y and Er systems. The lower 5d DOS at the rare-earth site could give rise to magnetic ordering via the 4f-5d (on the rare-earth site) Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction in $HoRh_4B_4$ (at a temperature above its otherwise possible superconducting-transition temperature T_c^s) and at a temperature well below the observed T_c^s in $ErRh_4B_4$.

In this new group of ternary borides, MRh_4B_4, Matthias *et al.*[2] originally reported the existence of either ferromagnetism (M = Gd, Tb, Dy, and Ho) or superconductivity (M = Y, Nd, Sm, Th, Er, Tm, and Lu), with transition temperatures ranging from ~2.5 to ~12 K and noted the unexplained switchover from magnetism to superconductivity in going from Ho to Er. The later discovery of a transition from superconductivity to magnetism[1] in the same system upon lowering the temperature of the sample was surprising. For our studies we therefore chose M = Ho and Er, and also Y (which has no 4f electrons), and a T_c^s which is almost exactly equal to that of the Lu alloy (which has a full 4f shell).

The band calculations for the full 18-atom/unit-cell structures were performed self-consistently using the linear muffin-tin orbital (LMTO) method and other related methods.[3] The calculational scheme is essentially the same as the one used earlier for a number of A-15 compounds[4] but extended to cover also ternary systems. The LMTO method[3] is a computationally rapid and efficient method for obtaining insight into the major physical aspects of energy-band structure. By using the logarithmic derivative as a parameter, the usual energy dependence of the elements in the eigenvalue matrices can be neglected to a good approximation. Moreover, by replacing the Wigner-Seitz–cell integrations by integration over overlapping Wigner-Seitz spheres, the matrix elements are very easily set up. All this makes the LMTO method much more rapid than the augmented-plane-wave and Kohn-Korringa-Rostoker methods, without much sacrifice of accuracy.

The potential contained the Hedin-Lundqvist

treatment for the exchange and correlation, and for the heavier elements (Ho and Er) the relativistic Dirac equation without spin-orbit splitting was used.[5] The potential was defined to be spherically symmetric around each site out to the overlapping-sphere radii. In the derivation of the Madelung contribution to the potential, however, a nonoverlapping-sphere model was used. The energies were calculated at 18 $\vec{k}$ points in the irreducible wedge of the Brillouin zone (BZ) and l_{max} was 1 for boron atoms and 2 for the other atoms, resulting in 122×122 eigenvalue matrixes. The l convergence was improved by setting the maximum l in the internal summations equal to $l_{max}+1$. The self-consistency convergence is estimated to be better than 3 mRy for energy states below the Fermi level. The matrix elements included the corrections to the overlapping spheres. At first the relative sizes of the atoms were deduced entirely from given atomic-radii data, but preliminary canonical calculations showed a poor potential at the M sites; the most repulsive potential was reached about 15% inside the spheres. Therefore, the size of the M volumes was decreased and that of the Rh and B volumes was increased.

Figure 1 shows the resultant total DOS for one spin for $ErRh_4B_4$, and the l-decomposed contributions to the DOS for the two Er and eight Rh atoms in a unit cell. (The DOS for the B atoms, not shown, shows a moderate p contribution of ~11.7 states/Rydberg·cell-spin at E_F, but a negligible s contribution.) This figure provides us with a qualitative understanding of the properties of the alloys. We focus on the fact that the Fermi energy, E_F, falls at a peak in the DOS and that this peak structure arises from the structure in the Rh $4d$ contribution. Since E_F did not occur at a peak in the DOS in the non-self-consistent calculations, this indicates the importance of the charge-transfer effects which are taken into account in the self-consistent calculations. The large transition-metal DOS from the Rh contribution indicates that a crucial requirement for the occurrence of superconductivity is satisfied. Further, a crude estimate of the electron-phonon coupling parameter, λ, obtained using our calculated bare total DOS and the measured electronic specific heat[2] yields $\lambda=0.96$ and indicates that in strong-coupling theory a large $T_c{}^s$ value would result.

The Er $5d$ DOS at E_F, ~8.9 states/Rydberg·cell-spin, is quite a bit smaller ($\sim\frac{1}{3}$) than it is in the heavy pure rare-earth metals. Thus, through the exchange interaction between the localized $4f$ and rare-earth $5d$ electrons (hybridized with the Rh $4d$'s), the magnetic- (RKKY-) type coupling between the $4f$ local moments may lead to a still sizable magnetic ordering at a temperature, $T_c{}^m$. (Note that there is a substantial bandwidth associated with the Er $5d$ electrons in Fig. 1.) For the alloys from Gd to Ho, the large effective spin moment leads to a magnetic interaction which dominates over the superconducting interaction and $T_c{}^m > T_c{}^s$. In the Er and Tm alloys—with their smaller spin moments, reduced $4f$-$5d$ exchange integrals (caused by the lanthanide contraction), and somewhat lower $5d$ DOS than in Ho—the "effective" magnetic-ordering temperature the system would have in the absence of the

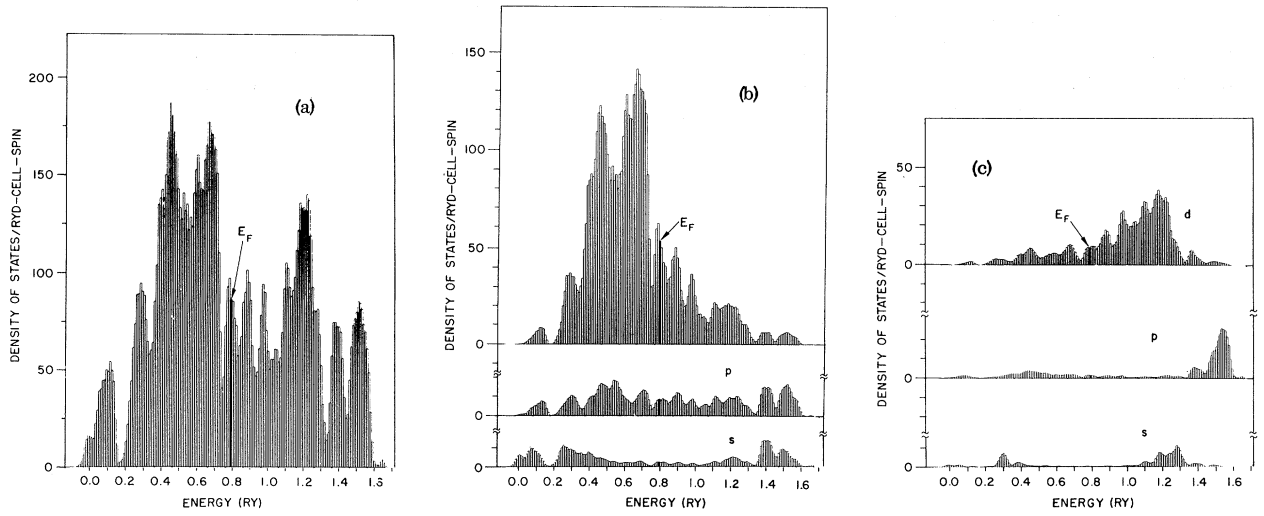

FIG. 1. The calculated (a) total DOS and l-decomposed partial DOS for (b) Rh and (c) Er sites in $ErRh_4B_4$.

onset of the superconducting state is reduced, and so $T_c^s > T_c^m$. The *observed* value of T_c^m in Er is smaller than this effective ordering temperature because once the superconducting state has been achieved the conduction-electron susceptibility is zero in principle—at least for the Rh electrons. Hence, for this compound, the RKKY interaction is largely ineffective compared to that in Ho (and earlier elements in the series); of course, dipole-dipole coupling may also contribute to the magnetic ordering. However, at lower temperatures, the RKKY interaction is still sufficiently strong to order magnetically the localized Er $4f$ moments which produces a sufficiently large exchange field to destroy then the superconducting state.

Above the effective magnetic ordering temperature, the effect of the $4f$ localized electrons —which are quite well separated from the Rh $4d$ "superconducting" carriers because of the distances involved—is to lower T_c^s in the way expected of *dilute impurities*. This is confirmed by the experimental observations: The *change* in superconducting temperature expected in the Er and Tm alloys, ΔT_c^s, due to dilute impurities should be proportional to $(g-1)^2 J(J+1)$, where g is the gyromagnetic ratio and J is the total angular momentum of the $4f$ shell of the trivalent rare-earth ion. Referring to the data of Fertig *et al.*[1] and using the Lu alloy's T_c^s as base, one sees indeed that the measured ΔT_c^s for Er and Tm are proportional to $(g-1)^2 J(J+1)$. Furthermore, this simple estimate—assuming all other factors equal—shows that in the absence of magnetic ordering the $4f$ local moments in the Ho alloy would result in a ΔT_c^s of ~5 K and a T_c^s of ~6.5 K (compared with an observed[1] magnetic-ordering temperature, $T_c^m \sim 6.6$ K). Strong confirmation to this view of weak interaction between the Er $4f$ and Rh $4d$ electrons is given by the very recent Mössbauer experiments of Shenoy *et al.*[6] They find from relaxation measurements that the spin-flip scattering in $ErRh_4B_4$ is weaker than in the superconducting ternaries[7] $ErMo_6(S, Se)_8$ (which exhibit similar properties and are similarly describable).

The self-consistent calculations reported here for these complex ternary systems have provided a first level of interpretation to the complex phenomena already reported.[1,2] Additional experiments are needed in order to test these *ab initio* results (and speculations) further—as are additional theoretical calculations (such as detailed estimates of both T_c^s and T_c^m which we are currently undertaking). Hopefully, these combined efforts may lead to a unified treatment of magnetism and superconductivity in the same system.

We are grateful to Merwyn Brodsky for enthusiastic support and encouragement and to Frank Y. Fradin and Dale D. Koelling for enlightening and fruitful discussions and suggestions. This work was supported in part by the U. S. Air Force Office of Scientific Research, the National Science Foundation, and the U. S. Energy Research and Development Administration.

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