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Abstract

Superconductivity and magnetism in the new group of rare-earth ternary borides, MRh_4B_4, has been reported recently by Matthias et al. Particularly striking has been their observation of re-entrant magnetism accompanying the return to a normal state at low temperatures (T=0.9 K) in the superconductor $ErRh_4B_4$ which has a superconducting transition temperature of 8.5 K. We discuss the origin of superconductivity and magnetism in these systems using results of ab initio self-consistent LMTO energy [illegible] calculations for the alloys M = Y, Er and Ho.

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EAB

I. INTRODUCTION

There has developed, in recent years, great interest in the electronic structure and properties of ternary compounds. A key motivation has been the hope that higher superconducting transition temperatures, T_c, and higher critical field materials could be obtained. For the Chevrel phases, with general formula $M_xMo_6S_8$ (where M is a metal and x a number near 1), there are a number of metallic elements which cause the compound to be superconducting. Surprisingly, Fischer and collaborators[1] at Geneva and Rennes found that the paramagnetic rare-earth metals also formed superconductors whereas earlier the addition of paramagnetic rare-earth impurities was always found to lower T_c. Recently, Matthias et al[2] reported that in a new group of ternary borides, MRH_4B_4, either ferromagnetism (M=Gd,Tb,Dy,Ho) or superconductivity (M=Y,Nd,Sm,Th,Er,Tm and Lu) existed. In Table I we list the transition temperatures of some of the rare-earth compounds. We see a sharp break from magnetism (T_c^m) and superconductivity (T_c^s) in going from Ho to Er. Of considerable interest has been the later discovery[3] of re-entrant magnetism (at T=0.9 K) accompanying a transition to a normal metallic state in $ErRh_4B_4$, a rare-earth superconductor with T_c^s = 8.7 K; this has also generated considerable excitement as to 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.

In this paper, we discuss the origin of these phenomena using results of <u>ab initio</u> self-consistent energy band calculations carried out on three of these MRH_4B_4 systems, with M = Er, Y (an 11.3 K superconductor) or 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) were 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 $ErRh_4B_4$.

II. METHOD OF CALCULATION

Since we wished to understand (i) the existence of either magnetism or superconductivity, (ii) the switch-over from magnetism to superconductivity in going from Ho to Er and (iii) the transition from superconductivity to magnetism in the same system ($ErRh_4B_4$) with lowering of temperature, we chose for our studies 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) as representatives of the systems studied.

Details of the energy band calculations will be given in a more extended publication. Here we note that the calculations were done for the full 18 atom/unit cell structures self-consistently using the Linear Muffin-Tin Orbital (LMTO) and related methods[4]. The potential contained the Hedin-Lundqvist treatment for 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. Although not an exact scheme, the LMTO method of Andersen[4] is computationally rapid and efficient in 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.

In our calculations, the energy eigenvalues were determined at 18 k points in the tetragonal irreducible wedge of the Brillouin Zone (BZ) and ℓ_{max} was 1 for boron atoms and 2 for the other atoms, resulting in 122 x 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 3mRy for energy states below the Fermi level. The matrix elements included the corrections to the overlapping spheres.

III. RESULTS

In order to interpret the band structure results on a physical basis, we determined the total density of states (DOS) and the separate ℓ-decomposed contributions to the DOS arising from the two M atoms, the eight Rh atoms and the eight B atoms which comprise a single unit cell. We give results of the DOS at the Fermi energy, E_F, in Table II. We find that E_F falls - in all three cases - at a peak in the DOS and that this peak structure arises from the structure in the Rh 4d contributions. (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[3] yields $\lambda = 0.96$ and indicates that in strong coupling theory a large T_c^s value would result.

We now focus our attention on the $ErRh_4B_4$ results. The Er5d DOS at E_F, 8.9 states/Ryd-cell spin, is quite a bit smaller (~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.

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 Matthias et al.[2] 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 $(g-1)^2 J(J+1)$. Further, 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[2] magnetic ordering temperature, $T_c^m \sim 6.6$ K).

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 onset of the superconducting state is reduced and so $T_c^s > T_c^m$. The observed value of T_c^m in Er (cf. Table I) 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 to produce a sufficiently large exchange field to then destroy the superconducting state. This results in the low observed temperature of the re-entrant magnetically ordered state at T=0.9 K.

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Table I

Magnetic transition temperatures (T_c^m) and superconducting transition temperatures (T_c^s) for some rare-earth ternary borides (in degrees Kelvin). (after references 2 and 3)

	Y	Gd	Tb	Dy	Ho	Er	Tm	Lu
T_c^m		5.62	7.08	12.03	6.56	0.9		
T_c^s	11.3					8.7	9.8	11.8

Table II

Total and the $\ell=2$ decomposed DOS values by atom type at E_F (in states/Ryd-cell spin) obtained in the self-consistent LMTO calculations for the M=Y, Er and Ho compounds.

		Total DOS	$\ell=2$ DOS
YRh_4B_4	Y	10.7	9.4
	Rh	55.6	44.9
	B	11.9	--
$ErRh_4B_4$	Er	10.2	8.9
	Rh	63.5	53.3
	B	11.7	--
$HoErRh_4B_4$	Ho	10.6	9.3
	Rh	57.4	45.9
	B	13.4	--