# Absence of anomalously large conduction-electron polarization in superconducting rare-earth ternary compounds

A. M. Stewart
*Department of Solid State Physics, Research School of Physical Sciences, Australian National University, P. O. Box 4, Canberra, A. C. T. 2600, Australia*
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An analysis of the paramagentic susceptibility of $SmRh_4B_4$ indicates that conduction-electron polarization effects are relatively small in the $RRh_4B_4$ compounds, where $R$ is a rare earth. The coexistence of superconductivity and magnetism is therefore allowed by the smallness of the exchange interaction between the rare earth and the conduction electrons. An expression for the paramagnetic susceptibility of metallic samarium compounds is successful in explaining recent measurements on polycrystalline rhombohedral samarium metal.

There has recently been considerable interest in the crystallographically ordered ternary intermetallic compounds of composition $RRh_4B_4$, where $R$ is a rare earth, because in some of them magnetic order and superconductivity occur together.[1,2] The size of the exchange integral $I$ in the exchange interaction $-2I\vec{S}\cdot\vec{s}$ between a rare-earth spin $\vec{S}$ and a conduction-electron spin $\vec{s}$ is of great importance, because only if $I$ is small enough are superconductivity and magnetism normally permitted to coexist.

Recently Tse *et al.*[3] have claimed, on the basis of susceptibility and nuclear magnetic resonance measurements on $(Y_{1-x}Er_x)Rh_4B_r$, that anomalously large conduction-electron polarization effects, which imply a large $I$, are present in these compounds, and this has led them to propose unusual mechanisms for their superconductivity. Part of the evidence that Tse *et al.*[3] based their arguments upon were their measurements of very large paramagnetic moments for the erbium ion. Although these values were subsequently withdrawn in an erratum[3] and replaced by ones much closer to the free-ion value, it seems worthwhile to examine the magnitudes of the effective moments of the $RRh_4B_4$ compounds, because from them very direct estimates of $I$ may be obtained.

The purpose of this present note is to point out that the paramagnetic susceptibilities of the $RRhB_4$ compounds, in particular of $SmRh_4B_4$ show that conduction-electron polarization effects, and hence $I$, are in fact, if anything, unusually *small*, and that on this basis there is no reason to suppose that the mechanism for superconductivity in the $RRh_4B_4$ compounds is anything other than the usual one due to the electron-phonon interaction.

Recently Hamaker *et al.*[4] have measured the paramagnetic susceptibility $\chi$ of $SmRh_4B_4$. They found that it could be fitted to an accuracy of several percent by the sum of a temperature-independent term and a Curie-Weiss term between 1 and 300 K. Specifically they obtained

$$\chi=[\mu_{\text{eff}}^2/3(T-\theta)+\mu_B^2/\delta]N_A/k \quad , \tag{1}$$

with $\mu_{\text{eff}}=0.632\mu_B$, $\theta=-1.93$ K, and $\delta=377$ K, where $T$ is the temperature, $\mu_B$ the Bohr magneton, $N_A$ Avogadro's number, and $k$ the Boltzmann constant. It has been shown previously[5-7] that this form of temperature dependence is expected for metallic samarium compounds when account is taken of exchange interactions, conduction-electron polarization, the admixture of the samarium multiplet levels, but *not* crystal-field effects[8] (crystal-field splittings are reported to be relatively small in the $RRh_4B_4$ compounds[2]). The effective moment $\mu_{\text{eff}}$ in Eq. (1) is given by this theory as[5]

$$\mu_{\text{eff}}/\mu_0=1+2I\rho(g-1)/g-(1+2I\rho)\theta/T_0 \quad , \tag{2}$$

where $\mu_0$ is the bare moment of $Sm^{3+}(0.845\mu_B)$, $g$ is the Landé factor, $\rho$ is the conduction-electron density of states, and $T_0(=322$ K$)$ is related to the splitting between the $J=\frac{5}{2}$ and $\frac{7}{2}$ multiplet levels. Since $(g-1)/g$ is greatest for samarium $(=-2.5)$ its effective moment is more sensitive to conduction-electron polarization effects than that of any of the other rare earths.

We have been able to obtain an improved fit to the susceptibility data of Hamaker *et al.*[4] on $SmRh_4B_4$ to an accuracy of 0.5% between the temperatures of 50 and 280 K, using the parameters $\mu_{\text{eff}}=0.715\mu_B$, $\theta=-13.7$ K, and $\delta=399$ K in Eq. (1). The points below 50 K were omitted because it is at these low temperatures that crystal-field splittings have their greatest influence. The points above 280 K were omitted because the thermal population of the $J=\frac{7}{2}$

 

multiplet level of $Sm^{3+}$ becomes significant there.[5] If we substitue the fitted values into Eq. (2) we obtain $I\rho = +0.022$. [If the parameters obtained by Hamaker *et al.*[4] were used in Eq. (2) we would obtain $I\rho = +0.052$. This value, which is also comparatively small, would not alter the thrust of our argument.]

Our value of $I\rho$ is relatively small compared to those in the rare-earth metals[5] ($I\rho \approx +0.1$) or in compounds of rare earths with nontransition metals such as $RZn_{12}$ (Ref. 6) ($I\rho \approx +0.04$). If we use the value of 0.57 $eV^{-1}$ for $\rho^4$ we get $I = +0.04$ eV. This value is in good agreement with the value of 0.04 eV for the modulus, obtained from the rate of depression of $T_c$ in $(La_{1-x}Ho_x)Th_4B_4$,[2] and is consistent with the result that other $RRh_4B_4$ compounds have paramagnetic moments close to the free-ion value.[2,4]

In conclusion we have found no evidence for any anomalously large conduction-electron polarization effects in those $RRh_4B_4$ superconducting ternary compounds which contain magnetic rare-earth atoms in all the $R$ sites. This suggests that the coexistence of superconductivity and magnetism is permitted by the small value of exchange coupling between the conduction electrons and local moments. The observation by Tse *et al.*[3] of large conduction-electron polarization effects in $(Y_{1-x}Er_x)Rh_4B_4$ at small $x$ would imply that $YRh_4B_4$ possesses a large Pauli paramagnetic susceptibility which decreases as erbium is added.

Finally, the method of analyzing the susceptibilities of samarium compounds used above cannot be regarded as plausible, ignoring as it does the effects of the crystal field,[8] unless it can at least give a consistent description of the behavior of elemental samarium metal. The first analysis[5] made of the susceptibility of rhombohedral samarium metal was not valid, because at the time the magnetic ordering temperature of samarium had not been well established. However, since then, Arajs *et al.*[9] have made very accurate measurements of the susceptibility of polycrystalline rhombohedral samarium metal in the paramagnetic state. Between temperatures of 120 and 300 K they found that the susceptibility could be represented by a Curie-Weiss form $\chi = [8.40 + 160/(T + 3.17)] \times 10^{-6}$ $cm^3/g$. From this we obtain $\mu_{eff} = 0.439\mu_B$ and $I\rho = +0.098$. This is in excellent agreement in sign and magnitude[5] with the values of +0.10 for double-hexagonal-close-packed samarium metal, +0.08 for gadolinium metal and +0.07 for europium.[5] This provides further confirmation that conduction-electron polarization effects are extremely large in samarium metal itself (in contrast to $SmRh_4B_4$) as had been predicted[5] and then later confirmed[10] by an analysis of the magnetic form factor of samarium obtained from neutron scattering experiments.[11]


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