Electron-transport properties of $R_2Fe_{14}B$ compounds

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The electrical resistivity of $R_2Fe_{14}B$ (R=lanthanide series) polycrystalline samples was measured over the temperature range of 4–700 K. Even though the overall behavior of the resistivity in $R_2Fe_{14}B$ is determined mainly by Fe atoms, interesting features follow from the presence of rare-earth atoms. At low temperatures, the resistivity ρ increases with temperature as T^2. We find that scattering of electrons by modes involving all spins, with a dispersion given by the R-Fe exchange interaction, contributes to this behavior. On the other hand, the high-temperature anomaly in ρ observed just below the Curie temperature is quite likely produced by electron-phonon scattering arising from a pronounced lattice softening in this temperature region. Saturation values of the high-temperature magnetic resistivity are in agreement with de Gennes and Friedel's prediction for spin-disorder scattering. [S0163-1829(97)00605-X]

I. INTRODUCTION

Rare-earth-transition-metal compounds of the type $R_2Fe_{14}B$ (R=lanthanide series) have been the subject of intensive research during the last decade. These alloys are important for technological applications as permanent magnets. Since the discovery of $Nd_2Fe_{14}B$,[1] numerous experimental results for the whole $R_2Fe_{14}B$ family have been reported. Structures have been characterized, their magnetization and coercive forces have been measured, crystal-field and anisotropy parameters have been determined, and magnetoelastic measurements have been done.[2–4] More recently, inelastic neutron-scattering experiments have been performed in order to improve our understanding of the magnetic properties of these materials.[5]

$R_2Fe_{14}B$ ternary intermetallic compounds crystallize in a tetragonal structure. Their unit cell, with a total of 68 atoms, is quite complicated. Rare-earth atoms have strongly localized $4f$ electrons which may interact with transition-metal (Fe) $3d$ bands. Therefore, there is an interplay between the localized magnetism and the itinerant magnetism arising from $3d$ iron atom electrons. This gives rise to a variety of interesting physical properties of $R_2Fe_{14}B$. It is also a major problem one has to deal with when discussing experimental results or performing theoretical calculations. Electronic band-structure calculations show that the Fe d bands are most important in the density of states although $4f$ narrow bands are found not far from the Fermi level.[6] R and Fe sublattice moments couple ferromagnetically for light rare-earth elements and antiferromagnetically for heavy rare-earth elements. Consequently, the magnetization in $R_2Fe_{14}B$ varies with temperature as in ferromagnetic or ferrimagnetic materials. The Curie temperature lies in the range 450-650 K. Some of $R_2Fe_{14}B$ compounds exhibit a change in magnetic structure (spin reorientation) upon cooling down from the Curie temperature. The magnetic coupling strength between R and Fe moments is about one-third of the coupling strength between Fe ions. The $R-R$ magnetic interaction is much weaker in these alloys.

Few studies have been reported on electron-transport properties of $R_2Fe_{14}B$. One of them is a short report on the resistivity anomaly observed at the spin-reorientation transition temperature in $Nd_2Fe_{14}B$ and $Tm_2Fe_{14}B$.[7] Two other papers are devoted to an anomalous electron transport in $Nd_2Fe_{14}B$ and $Y_2Fe_{14}B$.[8] It has been found that the magnetic resistivity increases rapidly with increasing temperature in both alloys. A weak resistivity singularity has been observed at the Curie temperature. The authors have associated the low-temperature anomaly with spin fluctuations, while the high-temperature ''hump'' has been related to the strong Invar effect in these compounds.

The electrical-transport properties are very sensitive to electronic structure as well as to the magnetic nature of the materials studied. In particular, it has been established that the magnetism of the inner $4f$ shell strongly affects the resistivity of rare-earth metals.[9] The anomalous behavior of the resistivity in rare-earth materials is mainly produced by the s-f exchange interaction.[10,11] This interaction is also important in transport properties of intermetallic compounds with nontransition metals.[12] Intermetallic compounds with transition metals are expected to show more complex behavior related to the itinerant magnetism of the d bands. We note that the itinerant character of most of the $3d$ electrons is not usually emphasized in the interpretation of magnetic bulk properties, even though it can play a significant role in metallic compounds. Therefore, the electrical resitivity should give relevant information about the coupling of $3d$ electrons to magnetic sublattices. Surprisingly, we find no systematic study of the resitivity behavior in the $R_2Fe_{14}B$ series. Our aim is to cast some light on the role that the nonlocalized $3d$ electrons play in electrical transport by finding correlations between the electrical resistivity and the magnetic moment of lanthanide atoms in the $R_2Fe_{14}B$ series.

In this paper we report resistivity measurements in $R_2Fe_{14}B$ (R=Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm) polycrystalline samples as a function of temperature in the range from 4 to 700 K. The results obtained enable us to determine the dominant electron-scattering processes and the rare-earth contribution to them in these materials. The ex-

perimental procedure is described in Sec. II. Results of resistivity measurements are reported and discussed in Sec. III. The dependence of the magnetic resistivity on the spin of R ions enables us to estimate the role of the rare-earth ion. Conclusions are drawn in Sec. IV.

II. EXPERIMENT

The $R_2Fe_{14}B$ compounds were synthesized in a high-frequency induction furnace using the cold crucible method. The ingots obtained were annealed for three weeks at 1000 °C and checked by x-ray diffraction. The ac electrical resistivity measurements were performed with a six-probe method on bar-shaped samples. The samples were spark cut from the bulk polycrystalline material and had typical dimensions of $1\times2\times10$ mm^3. Before measurements, each sample was polished and checked for possible cracks. We used low-frequency (about 31 Hz) low excitation ($\approx$20 mA) currents in our computer controlled setup for resistivity measurements. Platinum pressure contacts were applied to the samples in the whole temperature range (4–700 K). The relative error obtained for resistivity measurements is about 0.01%; absolute values were determined to within 5%. The temperature was determined to about 1 K at high temperatures and to about 0.2 K at low temperatures using chromel-alumel and chromel-AuFe thermocouples, respectively. The Curie temperature T_C of the $R_2Fe_{14}B$ samples was determined from magnetization curves obtained in a Faraday balance. The values of T_C agree with previously reported ones to within 2%.[2]

III. RESULTS AND DISCUSSION

Figure 1 shows how the resistivity of $R_2Fe_{14}B$ varies with temperature in the range from 4 to 700 K, for all samples studied. The overall behavior of the resistivity is alike in these compounds. At low temperatures, the resistivity measured tends to a small constant value. ρ is observed to increase fast with temperature in the range from 50 K to $T\approx0.5T_C$. This increment corresponds to 80% of the total resistivity. For higher temperatures, ρ increases more slowly. All $\rho(T)$ curves show a small dip near the Curie point. The resistivity increases linearly with temperature thereafter.

First, we discuss the low-temperature behavior of the resistivity. Applying Matthiessen's rule, the total resistivity can be written as

$$\rho=\rho_0+\rho_{\rm ph}+\rho_{\rm mag}, \tag{1}$$

where ρ_0 is the temperature-independent residual resistivity, $\rho_{\rm ph}$ is the resistivity arising from electron-phonon scattering, and $\rho_{\rm mag}$ is the magnetic (spin) resistivity, respectively. We could possibly include another term in Eq. (1) arising from electron-electron scattering. As discussed below, this contribution to the total resistivity is very small. The phonon contribution to resistivity, $\rho_{\rm ph}$, can be calculated using the Bloch-Grüneisen formula. We assume a value of 420 K for the Debye temperature θ_D as values between 400 and 450 K have been found for θ_D in various $R_2Fe_{14}B$ compounds.[3] A plot of $\rho_{\rm mag}$ versus T is shown in Fig. 2 for $T\leqslant45$ K for all alloys studied. $\rho_{\rm mag}$ is proportional to T^2 in this temperature range. The values of the constant term ρ_0, obtained from a least-squares fit to the relation $\rho-\rho_{\rm ph}=\rho_0+AT^2$, vary between 5 and 30 $\mu\Omega$ cm. We attribute this variation to different sample preparations and, consequently, to sample dependent impurity concentration and static lattice imperfections. The coefficient A takes value between 1×10^{-9} and $2\times10^{-9}\Omega$ cm K^{-2}. Two mechanisms can cause the resistivity of a ferromagnetic metal to vary as T^2 at low temperatures: scattering by charge fluctuations of d electrons, and scattering by spin fluctuations. In the former case, the coefficient A is proportional to the square of the density the of d states at the Fermi level. Calculations of the band structure

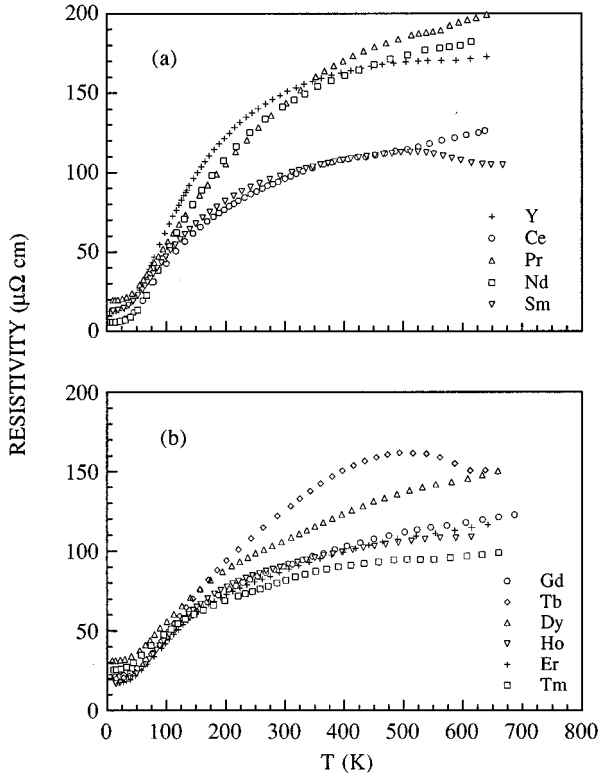

FIG. 1. Resistivity data points versus temperature in $R_2Fe_{14}B$ alloys: (a) R=light rare earth ions, (b) R=heavy rare earth ions. Only a small number of the data points are shown to improve clarity.

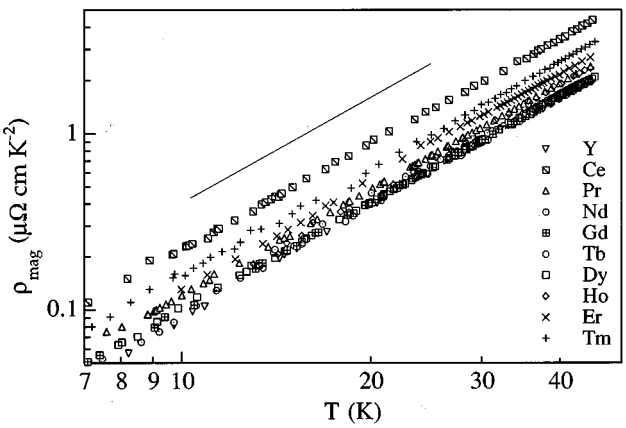

FIG. 2. The total resistivity less the phonon and residual contribution versus T in the temperature range 4 K$\leqslant T\leqslant$45 K. The solid line shows a T^2 dependence.

for $R_2Fe_{14}B$ give density of d states at the Fermi level that varies little as the rare-earth component changes.[6] Unfortunately, we have not found any further data that would enable us to estimate a value of A for electron-electron scattering in the materials studied. Such values have however been found for other ferromagnetic compounds.[13] They are much smaller than the values determined experimentally in $R_2Fe_{14}B$ alloys. Furthermore, the values found for A vary systematically with the spin value of rare-earth ions as shown below. This suggests that electron-electron scattering in our samples contributes negligibly, and that contributions to the T^2 coefficient must therefore come from magnetic scattering.

We shall now briefly discuss the scattering of conduction electrons by spin fluctuations in ferromagnetic metals as it applies to our intermetallic compounds. Moriya, using a self-consistent renormalization theory of spin fluctuations, has found $A \propto [M(0)]^{-1}$ for weak itinerant ferromagnets.[14] [$M(0)$ is the spontaneous magnetization at $T=0$ K.] However, the complex systems studied here are strong ferromagnets with localized $4f$ moments and such a treatment may be not applicable. One can expect to find spin waves in these materials with a quadratic dispersion relation in the long-wavelength limit that gives rise to the T^2 resistivity dependence. Indeed, inelastic neutron-scattering experiments done on some $R_2Fe_{14}B$ alloys show several magnon modes.[15] A classical spin-wave model predicts three low-lying modes, two of which are dispersive. One is an acoustic mode involving spins of both rare-earth and iron ions with a dispersion given roughly by the R-Fe exchange interaction and the other mode is strongly dispersive involving Fe spins with a spin-wave stiffness constant similar to that of Fe metal. The third mode, which is nearly flat, comes from precession of the R spins in the exchange field of neighboring Fe spins. Since the coefficients A obtained vary with the rare-earth component in the $R_2Fe_{14}B$ series, we consider the R-Fe mode more closely. For the isotropic case and in the limit of long wavelength, we find (from linearized equations of motion) the following relation for scattering of electrons by this mode:[9]

$$\rho_{\mathrm{mag}}/T^2 \propto J_{\mathrm{Fe}R}^{-2}(S_{\mathrm{Fe}}S_R)^{-1}(S_{\mathrm{Fe}} \pm S_R N_R/N_{\mathrm{Fe}}), \qquad (2)$$

where S_{Fe}, N_{Fe} and S_R, N_R are the spin and the number of iron and rare-earth ions, respectively; $J_{\mathrm{Fe}R}$ is the exchange interaction constant between iron and rare-earth ions. Here, the sign ''+'' corresponds to light rare-earth ions and ''−'' to heavy rare-earth ions, respectively. For $R_2Fe_{14}B$ compounds, $N_R/N_{\mathrm{Fe}}=1/7$, and $S_{\mathrm{Fe}}=1.17$.[16] In Fig. 3 we plot ρ_{mag}/T^2 versus the expression on the right side of Eq. (2). We used the values of $J_{\mathrm{Fe}R}$ determined from inelastic neutron-scattering data.[5] The experimental point for $R=$Ce is not shown since there are no data available for J_{FeCe}. Clearly, the values found for the coefficient A follow relation (2). The value of A for an alloy with a nonmagnetic R component, extrapolated from the linear dependence shown in Fig. 3 is about 1×10^{-9}, in a good agreement with the experimental value of 1.1×10^{-9} obtained for $Y_2Fe_{14}B$. The scattering of electrons by Fe spin waves is expected to be most important in this case. It is important as well for other rare-earth ions since its amplitude is larger than one half of the coefficient A. Therefore, the experimentally found T^2 variation of the magnetic resistivity at low temperatures can

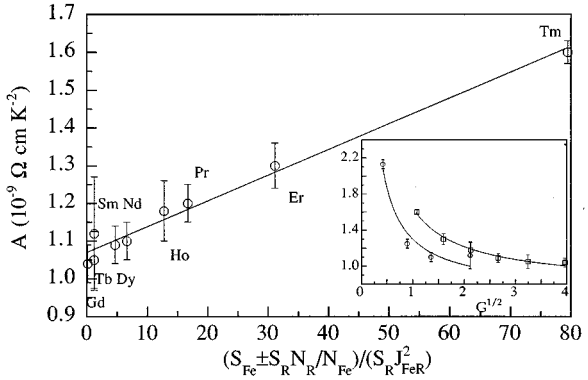

FIG. 3. The values of coefficient A (from $\rho_{\mathrm{mag}}=AT^2$) versus the amplitude of electron scattering by Fe-R magnons in $R_2Fe_{14}B$ alloys. The inset shows A versus the square root of the de Gennes factor. Solid lines are $G^{-1/2}$ fits for heavy rare-earth (upper line) and light rare-earth (lower line) atoms, respectively.

be attributed to scattering of conduction electrons by spin waves with the dispersions given by the Fe-R and Fe-Fe exchange interactions. In the inset of Fig. 3, the values of A are shown as a function of the square root of the de Gennes factor, $G[=(g_R-1)^2J_R(J_R+1)]$. Here, g_R and J_R are the rare-earth g-factor and total angular momentum, respectively. The data points divide into two classes depending on the nature of the R-Fe coupling. The upper curve is for the ferrimagnetic (heavy R) alloys and the lower curve for the ferromagnetic (light R) materials. A two-branch smooth variation with the $\sqrt{G}$ is also observed for the Curie temperature of $R_2Fe_{14}B$ compounds.[4]

As the temperature increases, the rate of variation of the resistivity goes through a maximum at $T \approx 0.14T_c$(70−100 K); after that it decreases and becomes negative close to T_C, where it shows a minimum. The temperature derivatives of ρ, obtained numerically from the data shown in Fig. 1, are exhibited in Fig. 4 for various samples studied. We note that the temperature T_{sf}, where the maximum of $d\rho/dT$ is located, scales with the Curie temperature in $R_2Fe_{14}B$ alloys.

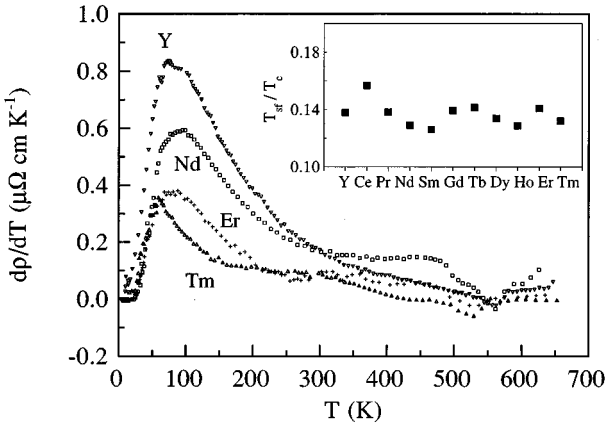

FIG. 4. The temperature derivative of the electrical resitivity versus temperature for various $R_2Fe_{14}B$ alloys. The inset shows values of the reduced temperature T_{sf}/T_c for different rare-earth components in the $R_2Fe_{14}B$ series. (The maximum of $d\rho/dT$ occurs at T_{sf}.)

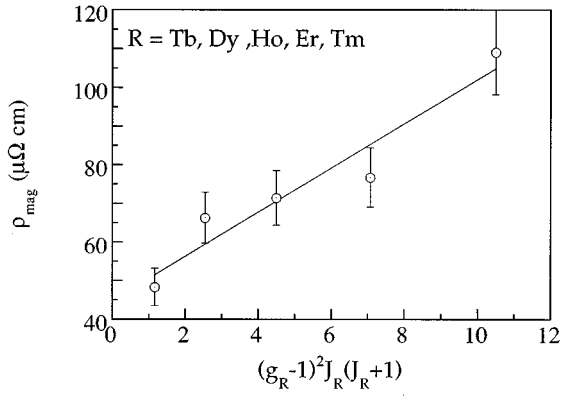

FIG. 5. Saturation values of the magnetic resistivity versus the de Gennes factor for heavy rare-earth ions in $R_2Fe_{14}B$ compounds.

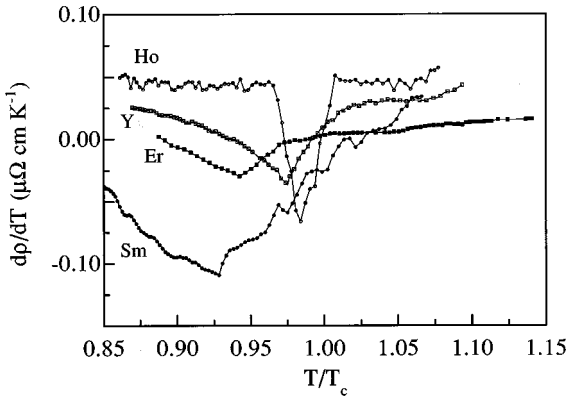

FIG. 6. The temperature derivative of the resistivity as a function of the reduced temperature T/T_c in the vicinity of T_c for various $R_2Fe_{14}B$ samples.

The values of T_{sf}/T_C lie in the range $0.13-0.14$ for all samples except for R=Ce for which T_{sf}/T_C is a little bit larger (0.16), as shown in the inset of Fig. 4. The maximum in $d\rho/dT$ may be related to spin-fluctuations.[14] However, the evidence for this is inconclusive thus far. In the Tm and Er compounds an anomaly in $d\rho/dT$ is observed at the spin-reorientation temperature as had been reported earlier.[7] We do not find any resitivity anomaly at the spin-reorientation transitions in the Nd and Ho compounds.

Finally, we discuss the high-temperature behavior of the resistivity in $R_2Fe_{14}B$ compounds. In the paramagnetic region ($T>T_C$), the magnetic resistivity becomes constant. According to a model developed by de Gennes and Friedel, and Kasuya,[11,10] scattering from the completely disordered spin system gives a resistivity contribution proportional to GJ_{sf}^2 where G is the de Gennes factor and J_{sf} is the interaction constant between conduction electrons and *4f* localized spins. In Fig. 5 we show how the values of $\rho_{\rm mag}$, obtained by the extrapolation of the high-temperature linear part of $(\rho-\rho_0)$ to $T=0$ K, vary with the de Gennes factor for the heavy earth ions in $R_2Fe_{14}B$ alloys. Good agreement is found in this case. However, data points for $\rho_{\rm mag}$ for light rare-earth ions are much more scattered. As already mentioned, the resistivity of all samples studied shows anomaly near T_C. A small dip in ρ and the corresponding minimum in $d\rho/dT$ are observed just below T_C. This is shown in Fig. 6 for some of $R_2Fe_{14}B$ compounds measured. Theory predicts a peak in $d\rho/dT$ just above the Curie temperature if spin fluctuations are taken into account at the critical point,[11,17,18] which is opposite to the anomaly observed here. It has been suggested in a number of papers reporting a similar anomaly in intermetallic alloys that this effect arises from Invar-type coupling.[19] At high temperatures ($T>\theta_D$), thermal expansion becomes appreciable and can alter the θ_D value of the lattice, hence the amplitude of the lattice vibration and, consequently, resistivity. This introduces an additional term into the usual expression for $\rho_{\rm ph}$,

$$\rho_{\rm ph}(T)=(C/B)(1+2\gamma\omega)T, \tag{3}$$

where C is constant, B is the bulk modulus, γ is the Grüneisen's constant, and ω is the lattice expansion. $R_2Fe_{14}B$ alloys show the Invar-type anomaly in the lattice expansion close to T_C.[20] Using data from Ref. 20, we can estimate the variation of $d\rho/dT$ arising from this effect. We get a value of about 1×10^{-8}, which is five to ten times smaller than the experimental one although of the right sign. However, in Invar-type alloys a volume increment below T_C produces also a minimum in the bulk modulus. Consequently, a corresponding variation in ρ should be observed. Longitudinal and shear elastic moduli of $Nd_2Fe_{14}B$ and $Y_2Fe_{14}B$ have been measured from 4.2 K up to above the Curie point.[21] These data give an estimated relative change in the average bulk modulus of about 30% just below T_C. The observed relative changes in $\rho_{\rm ph}$ are between 5% (R=Tm) and 25% (R=Tb) which agree with the bulk modulus variation. We neglect in this calculation spin-disorder effects on resistivity. Nevertheless, our results lead us to believe that the lattice softening near T_C may account for the observed high-temperature anomaly in the resistivity of $R_2Fe_{14}B$ alloys.

IV. CONCLUDING REMARKS

We have measured the resitivity as a function of temperature in various $R_2Fe_{14}B$ compounds. The low-temperature behavior of the magnetic resitivity ($\rho_{\rm mag}\propto T^2$) can be attributed to scattering of electrons by magnons that involve iron atoms and both rare-earth and iron atoms. The contribution of the rare earth sublattice is inversely proportional to the total angular momentum of R and to the square of the exchange interaction constant between Fe and R. In the intermediate-temperature range, the electrons are scattered mainly by spin disorder. At high temperatures ($T>T_c$), the magnetic resitivity saturates but the total resistivity increases linearly with temperature due to phonon scattering. The anomalous behavior of ρ just below T_C may be produced by strong lattice softening in this region. A different anomaly which has been observed at the spin-reorientation temperature in some $R_2Fe_{14}B$ compounds is currently being studied.

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