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LETTER TO THE EDITOR

Anomalous electron transport in $Nd_2Fe_{14}B$ single crystals

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Abstract. In contrast to the case of pure Fe, the increase in resistivity of $Nd_2Fe_{14}B$ at temperatures higher than half the Curie point is exceedingly small and the Curie point $d\rho/dT$ anomaly has the opposite sign. The results are related to the giant Invar effect observed in $Nd_2Fe_{14}B$. The persistence of this effect above the Curie point may lead to an apparent anomalous phonon resistivity slope in the paramagnetic phase.

At low temperatures the behaviour of ρ is dominated by the Nd^{3+} crystal field levels. A single model using realistic level splittings accounts satisfactorily for the observed behaviour.

When routinely measuring the electrical resistivity (ρ) of $Nd_2Fe_{14}B$ over a wide range of temperature (4–700 K) we found an unexpected $\rho(T)$ dependence which suggests that the contribution of the atomic Fe magnetic moments to the spin-disorder resistivity is exceedingly small in $Nd_2Fe_{14}B$. Also the Curie point anomaly is qualitatively different from the standard behaviour observed in ferromagnetic metals, e.g. in pure Fe.

Figure 1 shows the resistivity curve for a high quality $Nd_2Fe_{14}B$ single crystal prepared at the Laboratoire Louis Néel—CNRS, Grenoble, taken from the same batch previously characterized in detail with x-rays, magnetic, Mössbauer, thermal expansion and neutron diffraction methods [1–4]. For convenience the data is displayed in terms of the reduced temperature T/T_C, using $T_C = 592$ K for this sample [2]. The electrical resistivity was measured in the plane perpendicular to the [001] axis.

As $Nd_2Fe_{14}B$ has about 82% of iron atoms, at atomic distances very similar to those in Fe, it is striking that no significant increase occurs in the electrical resistivity when the Fe magnetic moments strongly disorder at high temperatures; e.g. ρ increases only by $\sim 5\ \mu\Omega$ cm between 0.6 T_C and T_C. This contrasts with the behaviour observed in pure Fe (also shown in figure 1) where spin-disorder scattering is responsible for an increase in ρ of about 60 $\mu\Omega$ cm between 0.6 T_C and T_C.

The experimental $\rho(T)$ curve in $Nd_2Fe_{14}B$ clearly shows the approach to saturation well below T_C, since about 90% of the total resistivity increase occurs between 0 and 300 K. Furthermore, the behaviour of ρ near the Curie point is anomalous, showing a slight decrease as T_C is approached from below.

In order to characterize further this anomalous behaviour we performed direct measurements of the temperature derivative of the electrical resistivity over a wide

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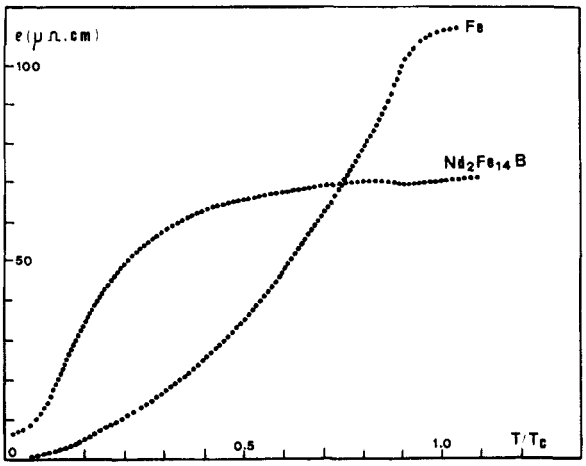

Figure 1. Dependence of the electrical resistivity (ρ) of Fe and $Nd_2Fe_{14}B$ on the reduced temperature T/T_C (T_C = 592 K).

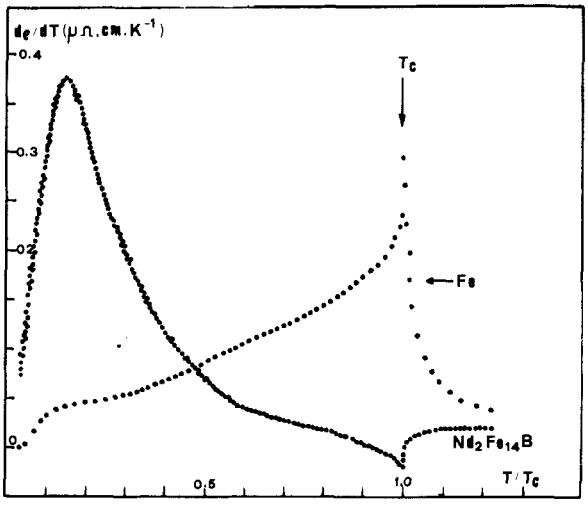

Figure 2. Temperature derivative of the electrical resistivity ($d\rho/dT$) versus T/T_C in $Nd_2Fe_{14}B$ and Fe.

range of temperature, the results being displayed in figure 2, again as a function of reduced temperature. To our knowledge, this is the first experimental study of $d\rho/dT$ in single crystals over such a wide range of temperature; in particular, no data is available in the low temperature range where crystal field level contributions may dominate in the electrical resistivity (the available results in polycrystalline sample [5] are only restricted to the spin reorientation transition region).

Since the area under the $d\rho/dT$ curve gives ρ, it is clear that the significant resistivity increase at low temperatures is associated with the high maximum observed in $d\rho/dT$ around 75 K. As shown below, this peak is in fact a normal feature in $Nd_2Fe_{14}B$, and

could be explained in terms of electron scattering by the Nd ions. The anomalous feature is the exceedingly small spin-disorder effects in $d\rho/dT$ at high temperatures (in spite of the sharp decrease of the spontaneous magnetization) and the very weak $d\rho/dT$ singularity at T_C when compared with the case of pure Fe (see curve in figure 2; from [6]). Moreover, the sign of the $d\rho/dT$ Curie point anomaly is reversed in $Nd_2Fe_{14}B$ with respect to the case of Fe.

The main increase of resistivity in $Nd_2Fe_{14}B$ occurs at low temperatures, certainly when the almost fully ordered Fe magnetic moments give a negligible contribution to ρ (in pure Fe the resistivity is only 4 $\mu\Omega$ cm at 200 K [6]). Such initial increase of resistivity is thus mainly caused by the strong thermal disorder in the Nd magnetic moments, favoured by their smaller exchange coupling constants. $J_{Nd\text{-}Nd} \ll J_{Nd\text{-}Fe} \ll J_{Fe\text{-}Fe}$ [7]; previous measurements in fact indicate that the spontaneous reduced magnetization of Nd is only 0.5 at 300 K [7, 8]. On the other hand, Nd^{3+} ions display strong crystal field effects at low temperatures, and then thermal disorder is controlled by the splitting of such crystal field levels.

Elliott first developed a simple theory to treat the effects of the crystal field levels on the electrical resistivity [9], followed by more complete accounts of the problem [10–13]. Assuming an effective crystal field splitting Δ, the electrical resistivity due to this effect can be written in the form:

$$\rho_{CF}(T) = \rho_{CF}(\infty)/\cosh^2(\Delta/2kT) \tag{1}$$

where $\rho_{CF}(\infty)$ has the standard saturation value

$$\rho_{CF}(\infty) = C(g_J - 1)^2 J(J+1) G_f^2 n_{CF}. \tag{2}$$

G_f is the interaction constant between a conduction electron and a 4f localized spin. $H_{int} \sim G_f(g_J - 1)s\,J$, J being the rare earth total angular momentum; C is a constant depending on the conduction electron band and n_{CF} is the number of scattering (crystal field) centres per unit volume.

Assuming that the low temperature *magnetic* resistivity comes from Nd scattering it suffices to remove from ρ the small phonon (ρ_{ph}) and the residual ($\rho_0 = 6.5$ $\mu\Omega$ cm) resistivities to obtain the resistivity contribution from Nd. For ρ_{ph} we use the known value for pure Fe, $\rho_{ph} = 0.03 \times T$ $\mu\Omega$ cm at high temperature [6] and extend the data to low temperatures using the Bloch–Grüneisen function, with $\Theta = 414$ K [14].

We could use this expression to fit our ρ data at low temperatures, but a stringent test can be made by comparing experiment and theory for the more structured $d\rho/dT$ function

$$\frac{d\rho_{CF}}{dT} = \frac{4K}{\Delta}\rho_{CF}(\infty)\frac{\exp(-\Delta/kT) - \exp(\Delta/kT)}{[1+\exp(\Delta/kT)]^2[1+\exp(-\Delta/kT)]^2}\left(\frac{\Delta}{kT}\right)^2. \tag{3}$$

We then adjust Δ in (3) so as to locate the maximum in $d\rho/dT$ at the observed value of $T = 75$ K, adjusting $\rho_{CF}(\infty)$ to reproduce the magnitude of $d\rho/dT$ at the peak. We obtain an effective level splitting $\Delta = 210$ K. This magnitude of Δ compares satisfactorily with the calculated separation between the two lowest crystal field levels of Nd, when split by the exchange internal field at low temperatures $\Delta \equiv 290$ K both for 4f or 4g sites [15–17]. Since the next higher level is far from the lower one (~500 K), its effect in ρ is expected to be small. This explains the good description of the low temperature $\rho(T)$ data with a simple two-level scheme.

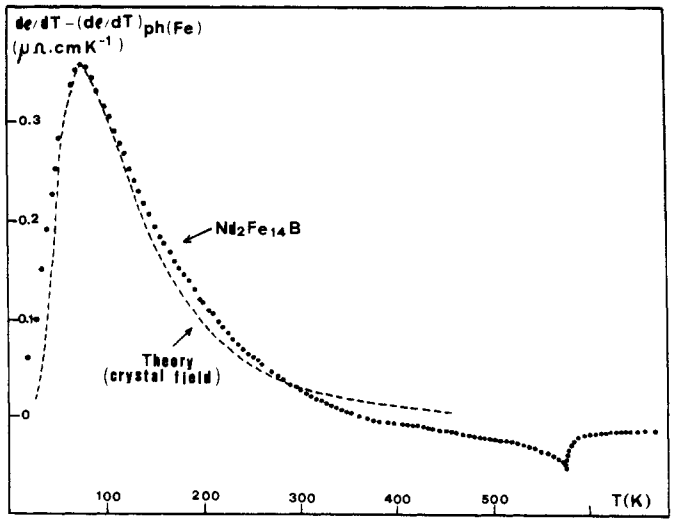

Figure 3. Comparison between $d\rho/dT$ in $Nd_2Fe_{14}B$ (after subtracting the phonon contribution of Fe) and the curve calculated according to crystal field theory (broken line; see equation (3) in text).

As shown in figure 3 the low temperature details of the electrical resistivity derivative are remarkably well reproduced by (3), even in quantitative terms. This is evidence that the low temperature behaviour of ρ in $Nd_2Fe_{14}B$ is dominated by inelastic electron scattering by the Nd^{3+} crystal field levels.

We should recall that the Zeeman splitting superimposed on the Nd^{3+} crystal field levels, due to the internal molecular field, is temperature dependent. However this temperature dependence is very small at low temperatures (Fe moments almost fully ordered; Nd giving a small contribution), which justifies the use of a *constant effective splitting* Δ. At higher temperatures the use of a constant Δ becomes incorrect, the decrease of the spontaneous magnetization considerably reducing the effective level splitting [7]. However, when $kT \gg \Delta$ all the levels are equally populated and expression (1) reduces to $\rho_{CF}(\infty)$, independent of the particular level splitting. So we have sound information on the Nd resistivity contribution both at low and high temperatures. Since this term increases monotonically with T, a smooth interpolation between both ends of temperature suffices to describe the main features of $\rho_m(T)$ due to Nd over the whole range of temperature. This is shown in figure 4, directly as a function of T since crystal field effects do not scale with T_C.

Knowing ρ_0, $\rho_{ph}(T)$ and $\rho_m(T; \text{Nd})$ we can now estimate the magnetic resistivity due to Fe,

$$\rho_m(T; \text{Fe}) = \rho(T) - \rho_0 - \rho_{ph}(T) - \rho_m(T; \text{Nd}). \tag{4}$$

The corresponding curve is shown in the inset of figure 4 directly compared with ρ_m in pure Fe (since we have only 82% Fe atoms in $Nd_2Fe_{14}B$ we multiplied ρ_m in pure Fe by a factor of 0.82). It becomes clear that the scattering power of the Fe atoms is of the same order in $Nd_2Fe_{14}B$ and Fe at reduced temperatures below ~0.45, but it is much smaller at higher temperatures, reaching an estimated decrease by a factor of 20 at the Curie point.

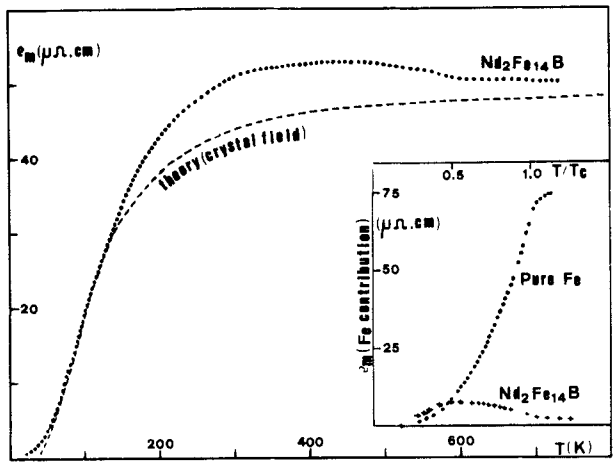

Figure 4. Temperature dependence of the magnetic resistivity of $Nd_2Fe_{14}B$ and the calculated curve according to crystal field theory (broken line; equations 1 and 2). Inset: Comparison between the iron magnetic contribution to the resistivity in pure Fe multiplied by 0.82 and in $Nd_2Fe_{14}B$.

The great reduction of the Fe resistivity in $Nd_2Fe_{14}B$ implies either a severe decrease of the corresponding scattering constant G, or of the iron magnetic moment μ(Fe) or important changes in the lattice constants indirectly affecting the electrical resistivity.

Since $\rho_m \propto G^2$, a decrease in G by a factor $\sqrt{20} = 4.5$ would be sufficient to account for the reduced order of magnitude, but it cannot explain the negative temperature dependence of ρ_m due to the Fe atoms. On the other hand, if there is any decrease in μ(Fe) with the temperature, it has to be small: the paramagnetic susceptibility behaves very much the same as in pure Fe [14]. Therefore we cannot explain a drastic reduction in ρ due to a very slight reduction in μ(Fe).

On the other hand we notice that the magnetic resistivity contribution due to Fe (inset of figure 4) is non-monotonic in temperature, having a maximum around 300 K. We thus associate the subsequent decrease of ρ_m(Fe, T) with the anomalous behaviour of the thermal expansion over the same temperature range (giant Invar effect) [18]. The corresponding spontaneous volume magnetostriction has in fact the highest value observed in a ferromagnet. This effect is directly related to the itinerant magnetism in Fe, since similar Invar anomalies are observed in $Y_2Fe_{14}B$ [18] and $La_2Fe_{14}B$ [18].

We recall that the magnetic resistivity depends on the sum [19]

$$\rho_m(T) = \rho_m(\infty) \sum_s f(K_f R_s)\Gamma(R_s, T)$$

where $f(K_f R_s)$ is an oscillatory structure factor due to the interference of electron diffracted waves. Γ is the magnetic correlation function for spins at distance R_s, and $\rho_m(\infty) \propto G^2$.

It is clear that changes in lattice parameters can affect G (different 3d–3d overlap and subsequent changes in 3d conduction electron coupling) and also the magnitude of the structure factor $f(K_f R_s)$; the effect in Γ is presumably much weaker.

Fermi surface details (K_f, anisotropies) could also change with lattice expansion, leading to subsequent effects on the electrical resistivity.

The anomalous behaviour of ρ_m(Fe) in $Nd_2Fe_{14}B$ with respect to pure iron is also observed in the magnetoresistance: $\Delta\rho/\rho$ is positive in $Nd_2Fe_{14}B$ whereas in pure Fe the reverse effect occurs. In both cases, the increase of magnetic order, either by lowering the temperature or through the application of a magnetic field, leads to an *increase* of resistivity.

The thermal expansion results show the persistence of an anomalous tail associated with the Invar effect for more than 100 K above T_C. This could explain the apparent smallness of $d\rho/dT$ in $Nd_2Fe_{14}B$ above T_C (0.02 $\mu\Omega$ cm K^{-1}) when compared with the case of Fe (0.03 $\mu\Omega$ cm K^{-1}).

It would be interesting to perform a comparable study of ρ and $d\rho/dT$ in single crystals of $Y_2Fe_{14}B$ and $La_2Fe_{14}B$. Here, the absence of the rare earth element (responsible for the rise in ρ at low temperatures) and the presence of the Invar effect [18, 20] could lead to a fairly small magnetic resistivity over the whole temperature range.

On the other hand, changing the sample composition so as to modify the size of the Invar anomaly might lead to non-negligible changes in the high temperature resistivity slope.

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