Resistivity in the heavy $REIn_3$ compounds (RE identical to Tb, Dy, Ho or Er)

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Resistivity in the heavy $REIn_3$ compounds (RE≡Tb, Dy, Ho or Er)

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Abstract. The temperature dependence of the magnetic contribution to the resistivity was investigated in the paramagnetic phase of the $REIn_3$ compounds where RE≡Tb, Dy, Ho or Er. It was shown that the dependences for $DyIn_3$, $HoIn_3$ and $ErIn_3$ behave in qualitative agreement with that calculated in the mean-field approximation assuming the crystal-field effect. The negative temperature coefficient of the magnetic resistivity found for $TbIn_3$ corresponds to that for $GdIn_3$ where the crystal field does not influence the resistivity. The anomalously large rise in the resistivity observed for $ErIn_3$ at temperatures close to T_N was attributed to the influence of the molecular field.

The heavy $REIn_3$ compounds crystallize with the $AuCu_3$ type of structure and show antiferromagnetic ordering (except $LuIn_3$) at low temperatures. In these compounds the RE ions possess well localized magnetic moments and the 3^+ oxidation state.

In previous papers concerned with transport properties of these intermetallics, results for the light $REIn_3$ compounds were mainly reported and a marked influence of the crystal-field (CF) effect on the resistivity was found [1–3]. Also certain preliminary results were given for the heavy $REIn_3$ compounds [4]. It was shown that the RKKY model satisfactorily describes the resistivity of the heavy $REIn_3$ compounds if the temperature is sufficiently high, i.e. all CF levels are overall populated. Then the magnetic part of the resistivity ρ_m is temperature independent; however, the spin-disorder resistivity follows the de Gennes factor for the heaviest REs only.

In the present paper we report some results of the resistivity measurements obtained in the paramagnetic region but in the temperature range where ρ_m is a temperature-dependent function. We show that the observed temperature dependence of ρ_m is in qualitative agreement with that calculated assuming the CF effect.

The measurements were performed on single-crystal samples cut off along a (001)-type direction from bulk single crystals grown from the melt [5]. The residual resistivity ratio $\rho 300/\rho 4.2$ of the samples obtained was approximately 25. The dimensions of the samples were close to 0.3 mm×0.3 mm×3.5 mm, and the standard four-probe DC method was used to measure the resistivity. An electrical current up to 100 mA was applied always along the (001)-type direction of the crystal and a Keithley 116 nanovoltmeter was used to measure the voltage across the sample. Commutation of the current avoided undesirable thermoelectric forces.

The experimental dependence $\rho_m(T)$ was calculated under the assumption of validity of Mathiessen's rule:

$$\rho(T) = \rho_r + \rho_{ph}(T) + \rho_m(T) \tag{1}$$

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where $\rho(T)$ is the total resistivity of the compound, $\rho_{ph}(T)$ is the phonon resistivity and ρ_r is the residual resistivity. As the standard for phonon resistivity, that of the non-magnetic $LuIn_3$ was used. $LuIn_3$ was chosen because its phonon properties are closer to those of the heavy $REIn_3$ compounds than are the phonon properties of the other non-magnetic compound in this family, namely $LaIn_3$. The slope of $d\rho/dT$ for $LuIn_3$ at high temperatures is the same as for the heavy $REIn_3$ compounds whereas the slope of $LaIn_3$ is 20% larger. Also the low-temperature properties of $LuIn_3$ do not show the anomalies observed for the thermal expansion [6] and resistivity [7] of $LaIn_3$.

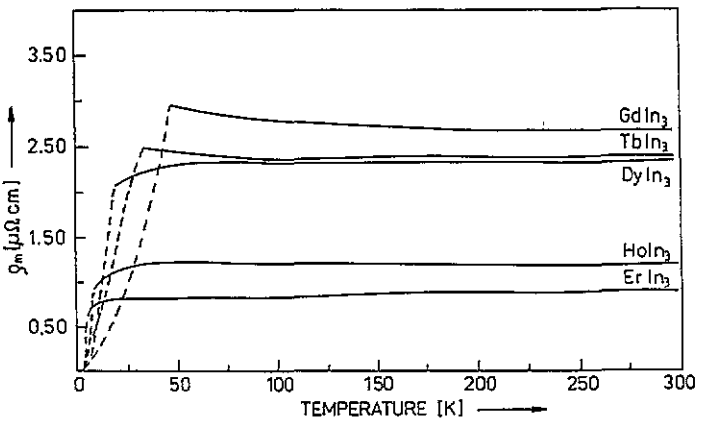

Figure 1. Temperature dependences of the magnetic part of the resistivity: at temperatures $T > T_N$. The phonon contribution in the resistivity of $LuIn_3$ was assumed to be that common to the phonon part of all $REIn_3$ compounds.

Figure 1 illustrates the temperature dependences of $\rho_m(T)$ experimentally found in the paramagnetic range. We observe that ρ_m is temperature dependent at low temperatures whereas at high temperatures it reaches a constant value called the spin-disorder resistivity $\rho_{m\infty}$. Several mechanisms can influence the magnetic resistivity above T_N, resulting in its temperature dependence. In our opinion, if the valence of the investigated compounds is stable and the temperature is not in the critical region, the major mechanism is the CF effect. This mechanism is connected with inelastic scattering of the conduction electrons on the CF split 4f levels of the RE ion. This phenomenon causes the magnetic resistivity to be temperature dependent up to the temperature at which the split 4f levels reach a state of thermally equal population. Usually, it is a case of temperatures appropriate to the energy of the overall 4f splitting δ. In the simple model of the molecular field approximation (MFA) the influence of the CF effect on the magnetic part of the resistivity is described by the well known formula derived by Hirst [8]:

$$\rho_m(T) = \rho_0 \operatorname{Tr}(PQ). \tag{2}$$

Here, the trace is taken over the $2J + 1$ CF states and the symmetrical matrices P_{ij} and Q_{ij} are defined as follows:

$$P_{ij} = \left[\exp\left(\frac{-E_i}{k_B T}\right) \Big/ \sum_k \exp\left(\frac{-E_k}{k_B T}\right)\right] \frac{(E_i - E_j)/k_B T}{1 - \exp[-(E_i - E_j)/k_B T]}. \tag{3}$$

The first factor gives the population of the ith CF state and the second represents the integrated Fermi factors. The second matrix

$$Q_{ij} = |\langle i|J_z|j\rangle|^2 + \tfrac{1}{2}|\langle i|J_+|j\rangle|^2 + \tfrac{1}{2}|\langle i|J_-|j\rangle|^2 \tag{4}$$

contains the elements from the exchange interaction $\hat{H}$ between the conduction electrons and the RE^{3+} ions, where

$$\hat{H} = -A(g-1)\delta(\boldsymbol{r}-\boldsymbol{R})\hat{s}\cdot\hat{J}. \tag{5}$$

Here A denotes the strength of the interaction, g is the gyromagnetic factor, $\hat{s}$ is the conduction electron spin operator and $\hat{J}$ is the total angular momentum operator of the RE ion. Finally ρ_0 reads

$$\rho_0 = \tfrac{3}{8}\pi A^2(g-1)mN/e^2\hbar E_F \tag{6}$$

where m, e and E_F are the electron mass, electron charge and Fermi energy, respectively.

In order to compare the experimental and theoretical results, both are normalized to unity at high temperatures, i.e. both are divided by the spin-disorder resistivity value $\rho_{m\infty}$ which is equal in our notation to $\rho_0 J(J+1)$. The results of these comparisons are shown in figures 2–5. The full circles represent the experimental data; the lines are the theoretical dependences calculated according to equation (2). In these calculations a set of CF parameters W and x from inelastic neutron scattering [9] and specific-heat [10–12] investigations has been used. Qualitative agreement between experimental results and theoretical predictions is observed for $ErIn_3$, $HoIn_3$ and $DyIn_3$. For these compounds the experimental and the theoretical curves increase monotonically, reaching saturation at high temperatures. However, when the temperature is lowered to T_N, discrepancies appear between these results. The experimental points lie above the theoretical curve and the slope of the experimental dependence is larger than that for the theoretical data. This is particularly evident for $ErIn_3$. The case of $ErIn_3$ is discussed later in more detail.

In our opinion there are two main sources of the discrepancies. The first is associated with aspherical Coulomb scattering. This mechanism gives a temperature-dependent contribution to the resistivity in the case where the 4f shell possesses a strong quadrupolar moment and conduction electrons are scattered by direct Coulomb interaction against the quadrupoles. Then the magnetic part of the resistivity may be expressed as a linear combination of the resistivity $\rho_D(T)$ associated with dipoles and the resistivity term $\rho_Q(T)$ associated with quadrupoles:

$$\rho_m(T) = x\rho_D(T) + (1-x)\rho_Q(T) \qquad 0 < x < 1. \tag{7}$$

We calculated such a linear combination using for $\rho_Q(T)$ the formula given by Hessel-Andersen and Vogt [13] but we did not obtain better agreement between the theoretical and experimental results. On the other hand we would expect some effect of the aspherical Coulomb scattering at least for $DyIn_3$ where the ground state is the Γ_8 quartet carrying a strong quadrupolar moment. Surprisingly, just in this compound the pure dipole term calculated according to equation (2) fits experimental data better than those for $HoIn_3$ or $ErIn_3$ (see figures 3–5).

When investigating the $RECu_2Si_2$ compounds, Cattaneo and Wohlleben [14] found an influence of the quadrupoles on the magnetic resistivity. However, in their case both the spin-disorder resistivity and the Néel temperature did not scale well with the de Gennes

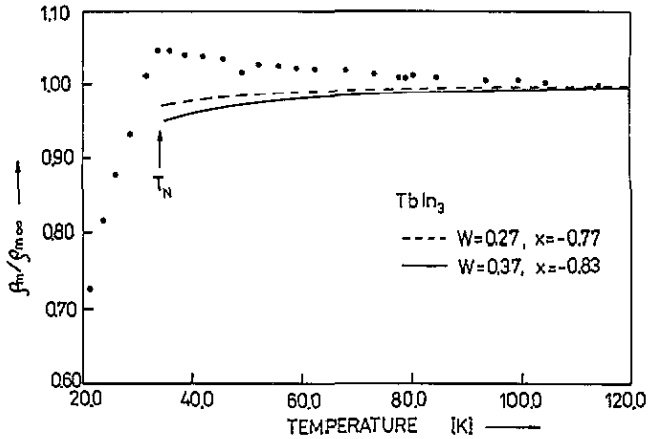

Figure 2. Comparison of the measured (●) and calculated (——) magnetic contributions to the resistivity of $TbIn_3$. The CF parameters were taken from [11].

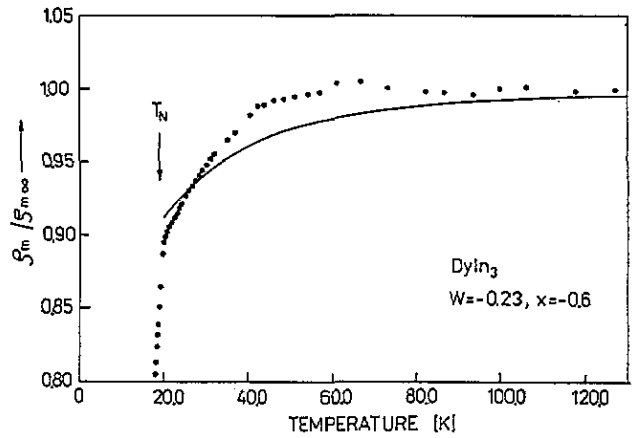

Figure 3. Comparison of the measured (●) and calculated (——) magnetic contributions to the resistivity of $DyIn_3$. The CF parameters were taken from [12].

factor, and a correlation between these two factors was clearly seen. This is not the case for the $REIn_3$ compounds; see data in [3]. Therefore the aspherical Coulomb scattering alone may not be responsible for the observed discrepancies.

Another mechanism not considered in the model described above is the effect of collective excitations, leading to the formation of bands from the CF levels. Calculations made in the random-phase approximation (RPA) for the singlet ground-state $PrIn_3$ compound [15] gave better agreement between theoretical and experimental results than that in the MFA [2]. Additionally, the calculations [15] clearly showed that their final product depends explicitly on the reduced caliper of the Fermi surface. If this caliper is sufficiently small for ferromagnets, the RPA resistivity may even exhibit a peak just above T_C. However, for antiferromagnets a similar result is obtained for a sufficiently large Fermi vector corresponding to Q of the new periodicity for the magnetic structure below T_N. If the Fermi vector approaches Q, the RPA resistivity is strongly enhanced [16]. It was also

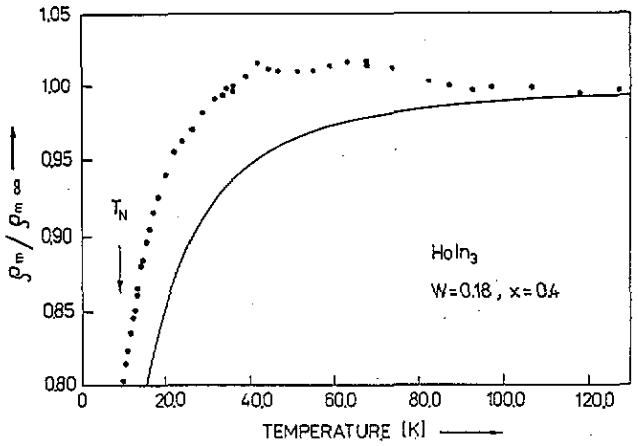

Figure 4. Comparison of the measured (●) and calculated (——) magnetic contribution to the resistivity of HoIn$_3$. The CF parameters were taken from [9].

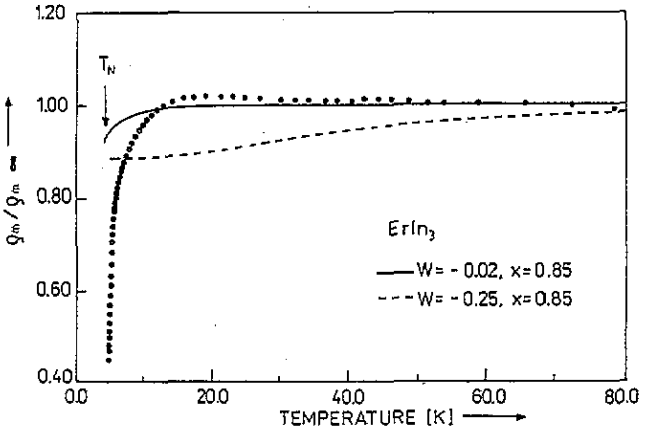

Figure 5. Comparison of the measured (●) and calculated (——, - - -) magnetic contributions to the resistivity of ErIn$_3$: - - -, results obtained for CF parameters taken from [10]; ——, modified CF parameters taken from [9].

shown that the distance dependence of the exchange interaction plays an essential role in the approximation [17] and the presence of RKKY-type interactions in solids enhances this effect.

Although the mechanism connected with collective excitations may influence the resistivity of all the REIn$_3$ magnetic compounds, it is, in our opinion, the main mechanism leading to the anomalous behaviour of ρ_m observed for TbIn$_3$ (see figure 2). We reported very similar behaviour of $\rho_m(T)$ for GdIn$_3$ previously [18]. It is characteristic that the two compounds having the highest Néel temperatures of the REIn$_3$ family but completely different CF influences (Gd is an S-state ion whereas in TbIn$_3$ the overall CF splitting is about 50 K) exhibit such an unusual and similar anomaly. This excludes the CF effect as the source of the anomaly. In our opinion, sources of such behaviour should be sought in the conduction band where a branch or branches with the Fermi vector close to Q may

appear.

Now let us consider the $ErIn_3$ case. A few experimental facts ought to be emphasized for this compound. The first is the very low value of the temperature at which $\rho_m(T)$ saturates. In this compound it is only about 15 K, whereas for the other CF-influenced $REIn_3$ compounds this temperature is usually much higher, in the range 50–150 K (see figures 2–5; see also [1,2] where results for $PrIn_3$ and $NdIn_3$ are reported.

Such a low value of the temperature at which $\rho_m(T)$ saturates is in our opinion clear evidence that the overall CF splitting is small. From our estimation this splitting does not exceed 15 K. Values of the CF parameters are almost unknown for this compound. One can find mentioned in the literature two sets of the LLW CF parameters. The first $W = 0.02, x > |W|$, is roughly estimated from the inelastic neutron scattering experiment [9] and the second $W = -0.25$, $x = 0.85$, where sixfold degeneration of the ground state and the negative sign of the W was deduced, comes from specific-heat studies [10]. In figure 5 we compare the experimental data on $\rho_m(T)/\rho_{m\infty}$ with the theoretical dependences calculated for the two above-mentioned parameter sets. For a better comparison in the first set $W = 0.02, x > |W|$, we have changed the sign of W and put $x = 0.85$ to obtain the same sixfold-degenerate ground state. Figure 5 shows that the second parameter set is not correct. The curve calculated according to these parameters does not resemble the experimental curve even qualitatively. The discrepancy almost certainly arises because the W-value is too high ($W = -0.25$ gives an overall CF splitting of about 100 K). The curve calculated for $W = -0.02$ and $x = 0.85$ (overall splitting of about 10 K) conserves all features of the experimental dependence. It saturates at about 15 K and decreases when the temperature approaches T_N from above. However, in this temperature range we observe that the slope of the experimental curve is almost 15 times that for the theoretical curve. To our knowledge such a dramatic change in $\rho_m(T)$ in the paramagnetic range has not been observed until now in any other CF-influenced material. Since it was not possible to create theoretically the sharp dependence in the model given above for any sequence of CF levels split by an energy of 10–15 K, therefore we are of opinion that the observed behaviour of $\rho_m(T)$ is a reflection of the additional phenomena taking place in $ErIn_3$ at temperatures close to T_N. This assumption seems to be confirmed by data on the temperature dependence of the entropy S obtained by Czopnik *et al* [19] where a strong dependence of $S(T)$ was observed at the above-mentioned temperatures.

Since in the case of the CF-influenced materials the changes in both the entropy and ρ_m are proportional to the temperature population of the CF levels, we conclude that at temperatures close to T_N the number of higher CF states which are populated increases rapidly. This, in our opinion, may be attributed to the inner Zeeman effect. We assume that between the levels forming the ground state (Γ_8 quartet and Γ_7 doublet according to Czopnik *et al* [19]) there is a gap comparable with T_N. Therefore, at $T < T_N = 4.9$ K, owing to the additional Zeeman splitting in the molecular field the highest states of the ground manifold are in fact out of reach of the thermal population. When the temperature increases and reaches T_N, the inner Zeeman effect following sublattice magnetization quickly disappears, and suddenly at $T = T_N = 4.9$ K the population of those higher-lying degenerate states of Γ_7 and Γ_8 levels is less than would be expected according to Boltzmann statistic. Such a thermodynamically unstable state forces a very rapid population process to occur in these degenerate CF states. The process may be responsible for the observed dramatic changes in ρ_m and entropy in the vicinity of T_N. Additional facts which may confirm such a conclusion are the dependence of the critical index of the specific heat α on the external magnetic field and the anomalous behaviour of the thermoelectric power (TEP). The specific-heat measurements of $ErIn_3$ showed [19] that the critical index α is anomalously large and

magnetic field dependent. The stronger the magnetic field, the smaller is α. Finally α reaches a value of 0.3 which is typical for antiferromagnets in a magnetic field of 2.7 T. This clearly shows that the magnetic field has a direct influence on the anomalous properties of $ErIn_3$ at T_N.

In our earlier paper concerning the TEPs of $REIn_3$ compounds [20] we reported that the TEP of $ErIn_3$ shows two maxima. The first—a broad maximum at about 35 K caused probably by the phonon drag—and the second—a sharp maximum at 8 K. Figure 6 shows this maximum in more detail. An anomaly (maximum or minimum) of the TEP connected with the anomalous contribution caused by the influence of the CF effect is expected, according to [21], at temperatures of about $\frac{1}{3}\delta$, where δ is the overall CF splitting. Experimentally, one usually observes it below $T = \frac{1}{2}\delta$. If we assume, following our above conclusion, that δ for $ErIn_3$ is equal to about 15 K, then the maximum found at 8 K is exactly at the place expected for the anomalous contribution to TEP. Thus it is justified to attribute the dramatic and almost linear temperature dependence of the TEP at temperatures $T < 6.5$ K to an anomalous mechanism connected with the CF influence.

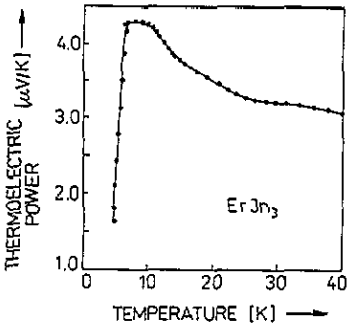

Figure 6. Temperature dependence of the TEP of $ErIn_3$.

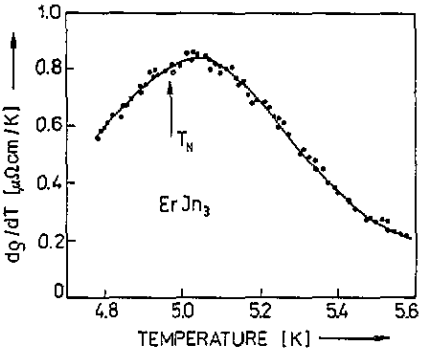

Figure 7. Temperature dependence of the resistivity derivative of $ErIn_3$.

The resistivity derivative also behaves anomalously in this compound. Investigating the $REIn_3$ compounds we have noticed that the transition to the antiferromagnetic state was always accompanied by a well defined and sharp divergence of $d\rho_m/dT$ and it did not depend on whether the $REIn_3$ compound was or was not influenced by the CF effect. The distinct but broad anomaly observed in the temperature dependence of the resistivity derivative, the shift of its maximum to temperatures above T_N (figure 7) and the lack of correspondence between the $d\rho_m/dT$ data and the specific-heat data are anomalies. Such behaviour may also indicate that an additional scattering process appears in the vicinity of T_N and masks the simple critical phenomena.

Acknowledgments

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