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Electrical resistivity in RAg compounds (R = Pr, Nd, Gd, Dy, Er, Lu)

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Abstract. The electrical resistivity of some intermetallic compounds RAg (R = Pr, Nd, Gd, Dy, Er, Lu) has been measured in the approximate range 10–800 K. While LuAg was fitted to the Bloch–Grüneisen formula, for all the others the experimental data can be mainly described as a sum of the phonon scattering term and the magnetic contribution. Crystal field effects occur for the Pr, Nd, Dy and Er compounds. A new examination of the previously studied compounds LaAg and CeAg provided the evaluation of the 4f instability contribution.

1. Introduction

The problem of the valence instabilities shown by some rare-earth elements in their intermetallic and semimetallic compounds aroused a growing interest in the last years, and is studied by means of different experimental techniques, such as thermal expansion, specific heat, magnetic susceptibility, x-ray photoemission spectroscopy and transport measurements.

In addition to the well known and established cases of some ytterbium and cerium compounds, many compounds containing samarium, europium, thulium and lanthanum show anomalous behaviour in their physical properties. For example, the electrical resistivity of CeAg and LaAg cannot be described only by the phonon scattering contribution (Merlo and Canepa 1987). On the other hand, the evaluation of the different contributions is strongly affected by the choice of the 'normal' reference system, so very different values of these anomalies as well as of their thermal dependences can be obtained. Since a comparison among the properties of the isotypic compounds formed by all rare earths is useful in these cases, the electrical resistivity has been measured for some other RAg compounds (R = Pr, Nd, Gd, Dy, Er, Lu).

2. Experimental details

The rare-earth metals used were products of Rare Earth Metals, UK, Michigan, USA, Nuclear Co, USA, and Koch–Light, UK, with nominal purity ranging from 99.5 to 99.9%. Silver was supplied by Johnson–Matthey Co, UK, 99.999% purity.

The samples were prepared by the semi-levitation technique in a water-cooled copper pedestal under an ultra-pure argon atmosphere. Metallographic analysis showed that all

the samples were single phase. The room-temperature lattice constants of the examined compounds, obtained by the x-ray powder method, were in agreement with literature data (Iandelli and Palenzona 1979).

The samples for resistivity measurements with typical dimensions $1 \times 1 \times 9 \text{ mm}^3$ were prepared and measurement of their geometrical factor was obtained using a method previously described (Merlo and Canepa 1987). The electrical resistivity measurements were made in the temperature range from 10 to about 800–1000 K by the four-point method, using fine copper wires spot welded to the sample. The highest measurement temperature, which should correspond to a purely phononic thermal dependence, was selected for each compound on the basis of the known magnetic transition temperatures.

3. Results

The lowest temperature achievable in the present measurements is 10 K, so the evaluation of the residual resistivity ρ_r is usually affected by a considerable error, and for PrAg it was not possible to separate ρ_r from other contributions.

Some preliminary assumptions have been made for a general interpretation of the results obtained. In all the compounds studied the thermal trend in the high-temperature range is linear. This has been considered indicative of saturation conditions occurring for magnetic, crystal-field and valence instability contributions. Following this hypothesis, the thermal behaviour of the resistivity at high temperature has been completely ascribed to phonon scattering. Since YAg (Merlo and Canepa 1987), LuAg and GdAg provide, within the calculated variance, the same value of the Debye temperature (165 K), this value was assumed as characteristic of all the RAg compounds. The Bloch–Grüneisen equation was so fitted to the experimental data of the other phases using the high-temperature linear slope and the value $\theta = 165 \text{ K}$. Anyhow, this choice does not influence seriously the results, since a change of $\pm 10 \text{ K}$ for the θ -value produces a variation of nearly $0.1 \times 10^{-8} \Omega \text{ m}$ on the calculated magnetic contribution.

3.1. Results for LuAg

The measured resistivity of LuAg, reported in figure 1, follows, over the whole temperature range examined, the Bloch–Grüneisen formula $\rho = 4RT(T/\theta)^4 J_5(\theta/T)$ where θ is the Debye temperature and $J_5(\theta/T)$ is the Grüneisen function. The obtained values of R and θ , reported in table 1, agree with those reported in the temperature range from 4.2 to room temperature by Bauer *et al* (1986), namely $0.05 \times 10^{-8} \Omega \text{ m K}^{-1}$ and 170 K. The high value of the residual resistivity ($\rho_r = 4.5 \times 10^{-8} \Omega \text{ m}$) is due to the low purity of the starting lutetium metal.

3.2. Results for ErAg

The electrical resistivity of ErAg shows a small anomaly at $T_N = 15 \text{ K}$, where the compound undergoes the antiferromagnetic transition: the temperature value is in agreement with those obtained by Walline and Wallace (1964) ($T_N = 15 \text{ K}$), Pierre and Pauthenet (1965) ($T_N = 21 \text{ K}$), Nereson (1973) ($T_N = 18 \text{ K}$) and Hill (1987) ($T_N = 15 \text{ K}$). Because of the narrow temperature range examined below T_N , no analytical elaboration of the thermal dependence of the magnetic resistivity was carried out. Above the transition temperature (figure 1), where the spin disorder is nearly complete, the res-

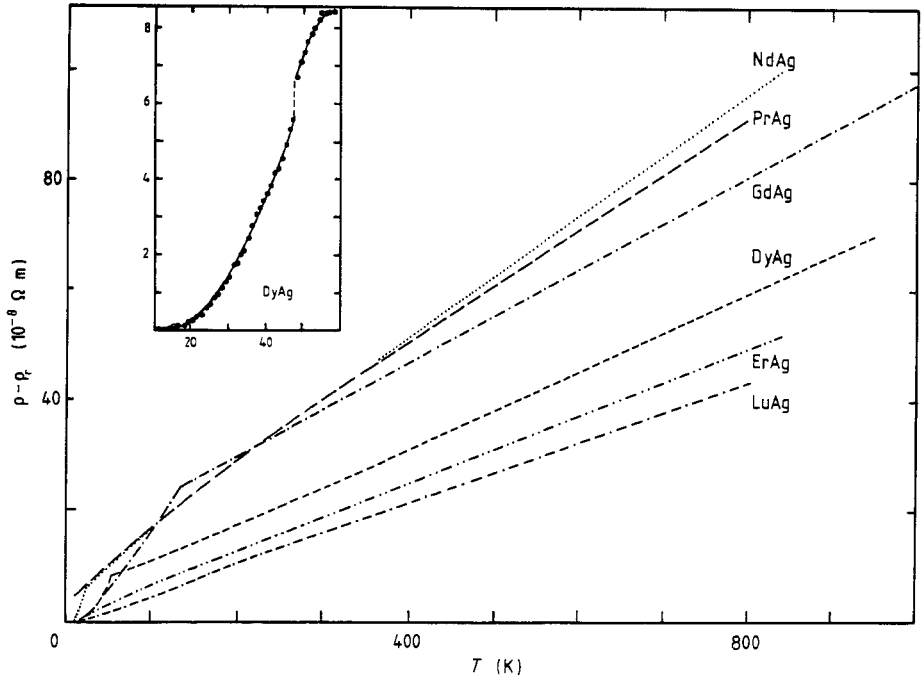


Figure 1. Thermal dependence of the electrical resistivity ($\rho - \rho_r$) for the RAg compounds ($R = \text{Pr, Nd, Gd, Dy, Er, Lu}$). For PrAg the trend contains the residual resistivity. The inset shows the low-temperature region of DyAg.

Table 1. Results of the resistivity–temperature curves for the RAg compounds ($R = \text{Pr, Nd, Gd, Dy, Er, Lu}$). ($T_N = \text{Néel temperature}$, $\rho_r = \text{residual resistivity}$ (the value reported for PrAg contains also the saturation magnetic resistivity), $\theta = \text{Debye temperature}$ (the value for PrAg, NdAg, DyAg and ErAg is assumed), $R = \text{slope of } \rho(T) \text{ at high temperature}$, $\rho_{m\infty} = \text{saturation magnetic resistivity}$, $\rho_m(T_N) = \text{magnetic resistivity at } T_N$, $\Delta T = \text{temperature range for the validity of the Bloch–Grüneisen formula.}$)

Compound	T_N (K)	ρ_r ($10^{-8} \Omega \text{ m}$)	θ (K)	R ($10^{-8} \Omega \text{ m K}^{-1}$)	$\rho_{m\infty}$ ($10^{-8} \Omega \text{ m}$)	$\rho_m(T_N)$ ($10^{-8} \Omega \text{ m}$)	ΔT (K)
PrAg	12	(8.8)	(165)	0.104	—	—	200–800
NdAg	25	1.7	(165)	0.110	8.0	5.5	200–840
GdAg	134	1.8	165	0.085	12.7	14.2	200–990
DyAg	55	2.6	(165)	0.071	2.1	6.0	400–960
ErAg	15	3.3	(165)	0.059	1.4	0.8	50–850
LuAg	—	4.5	165	0.054	—	—	10–800

istivity follows the Bloch–Grüneisen formula with the assumed Debye temperature of 165 K (table 1). The magnetic contribution, obtained by subtracting the phonon scattering term from the total resistivity, saturates at around 50–55 K at a value of $\rho_{m\infty} = 1.4 \times 10^{-8} \Omega \text{ m}$ (figure 2).

3.3. Results for DyAg

DyAg shows the transition to the antiferromagnetic phase at $T_N = 55 \text{ K}$ (figure 1). This value agrees with those of Walline and Wallace (1964) ($T_N = 55 \text{ K}$, from magnetic

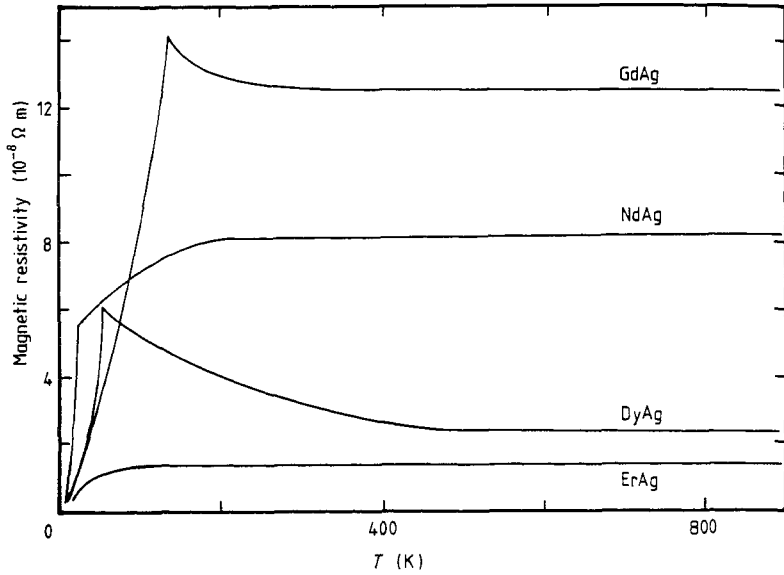


Figure 2. Magnetic resistivity ρ_m of NdAg, GdAg, DyAg and ErAg.

measurements), Arnold *et al* (1967) ($T_N = 51$ K, from neutron diffraction data) and Kaneko *et al* (1987) ($T_N = 56.6$ K, from magnetic measurements). A second smaller anomaly in the resistivity was found at $T^* = 46.5$ K (inset of figure 1), in good agreement with the value found by Kaneko *et al* (1987) ($T^* = 46.5$ K). These authors showed, by means of neutron diffraction data, that this transition is related to a change between different magnetic configurations. The sharp change in the resistivity reflects the rapid distortion of the Fermi surface by new Brillouin zone boundaries (superzone boundary effects). In the approximate range 10–46 K, the magnetic contribution to the resistivity was least-squares fitted to the equation $\rho_m(T) = aT^n$ and the values $n = 3.6$, $a = 3.8 \times 10^{-14} \Omega \text{ m K}^{-3.6}$ were obtained. The result agrees satisfactorily with the hypothesis of a linear dispersion law of the spin waves in an antiferromagnetic phase, for which a $\rho_m(T) = aT^4$ dependence is expected (Gratz and Zuckermann 1982). The magnetic part of the resistivity of DyAg saturates well above the Néel temperature, at about 400 K (see figure 2), providing a value $\rho_{m\infty} = 2.1 \times 10^{-8} \Omega \text{ m}$. Above 400 K the thermal trend is described by the Bloch–Grüneisen formula assuming $\theta = 165$ K.

The observed value of the thermal gradient in the high-temperature range ($R = 0.071 \times 10^{-8} \Omega \text{ m K}^{-1}$) is slightly at variance with the slope reported by Chao (1966) for the data up to 250 K ($R = 0.06 \times 10^{-8} \Omega \text{ m K}^{-1}$), where the saturation of the spin disorder contribution is still incomplete.

3.4. Results for GdAg

As can be seen in figure 1, the resistivity of GdAg exhibits the characteristic behaviour of a magnetic coupling, with a pronounced decrease below the Néel point ($T_N = 134$ K). This temperature is in agreement with those found by Walline and Wallace (1964) ($T_N = 138$ K) and Chao (1966) ($T_N = \text{about } 137\text{--}140$ K). Above T_N , after a slight negative curvature, due to short-range magnetic order, the resistivity shows a trend well described

by a simple phonon scattering. The Bloch–Grüneisen fitting provided the value of the Debye temperature (165 K) at that found for LuAg. The value of the slope ($R = 0.085 \times 10^{-8} \Omega \text{ m K}^{-1}$) can be compared with that obtained by Chao (1966) ($R = 0.07 \times 10^{-8} \Omega \text{ m K}^{-1}$) in the approximate temperature range 4.2–250 K, as for DyAg; also this lower value occurs because the magnetic contribution has not yet attained saturation conditions, which correspond, according to the present data, to $12.7 \times 10^{-8} \Omega \text{ m}$. Below T_N the magnetic resistivity (figure 2), obtained as for the other magnetic compounds by subtracting the phononic contribution from the experimental measurement, follows the power law $\rho_m(T) = aT^{1.5}$ with $a = 9.0 \times 10^{-11} \Omega \text{ m K}^{-1.5}$. This theoretically unexpected dependence is very similar to that found for $\text{Gd}_2\text{Zn}_{17}$ (Olivier *et al* 1987).

3.5. Results for NdAg

The antiferromagnetic transition of NdAg is well characterised by a sharp kink at $T_N = 25 \text{ K}$ (figure 1). Other known values are 22 K (Walline and Wallace 1964) and about 24–28 K (Chao 1966). Above T_N , a normal phonon scattering behaviour is recognisable in the approximate range 200–840 K where the Bloch–Grüneisen formula was fitted to the experimental data assuming $\theta = 165 \text{ K}$. The thermal trend of the resistivity shows the highest slope value among the examined phases ($R = 0.110 \times 10^{-8} \Omega \text{ m K}^{-1}$), and cannot be compared with the value of $0.15 \times 10^{-8} \Omega \text{ m K}^{-1}$ obtained by Chao (1966) below 200 K. The magnetic contribution (figure 2) reaches the saturation value $\rho_{m\infty} = 8.0 \times 10^{-8} \Omega \text{ m}$ at about 200 K, comparing with a magnetic resistivity of $5.5 \times 10^{-8} \Omega \text{ m}$ at T_N . Below T_N , $\rho_m(T)$ follows a $T^{3.5}$ power law, with $a = 9.2 \times 10^{-13} \Omega \text{ m K}^{-3.5}$, in reasonable agreement with the theoretically expected trend.

3.6. Results for PrAg

Two magnetic structures are known to occur for PrAg, namely an antiferromagnetic order below $T_N = 11\text{--}14 \text{ K}$ (Morin and Schmitt 1982, Kadomatsu *et al* 1984), and a ferromagnetic order at the Curie temperature of 10.5 K (Brun *et al* 1974a, b). In the temperature range studied the antiferromagnetic transition was found at $T_N = 12 \text{ K}$. Well above T_N , from 200 to 800 K, the observed resistivity values follow the Bloch–Grüneisen formula, assuming $\theta = 165 \text{ K}$, with a calculated slope of $0.104 \times 10^{-8} \Omega \text{ m K}^{-1}$ (figure 1). The fit parameter $\rho_0 = 8.8 \times 10^{-8} \Omega \text{ m}$ obtained contains both the saturation value of the spin disorder and the residual resistivity. The temperature dependence of the spin disorder resistivity, including the residual resistivity, is shown in figure 3. It was not possible to evaluate these contributions separately.

4. Discussion

The results of the present work can be compared with those obtained previously for LaAg and CeAg (Merlo and Canepa 1987). The temperature trend of the resistivity of these two compounds, very similar and definitely S-shaped, have been reexamined and described following the same approach used for the other RAg phases. Assuming the Debye temperature $\theta = 165 \text{ K}$, the resistivity data for LaAg were fitted to the Bloch–Grüneisen equation in the approximate range 400–800 K; the thermal dependence

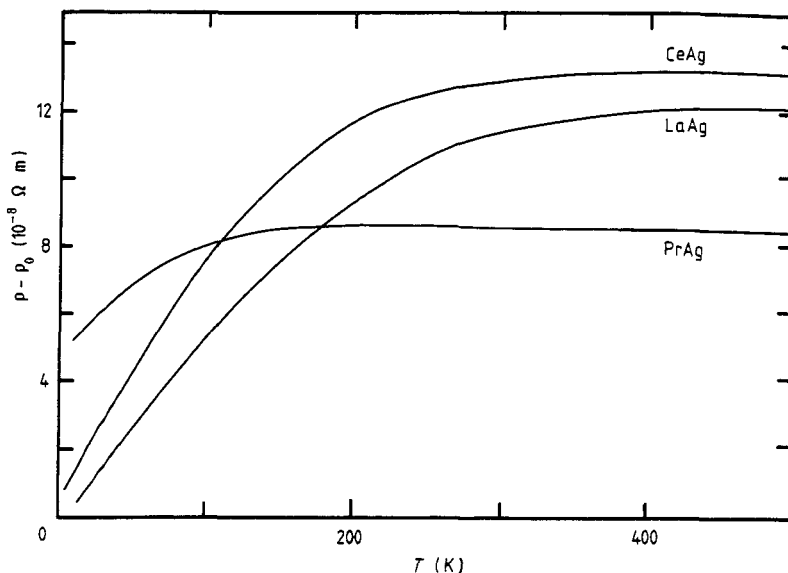


Figure 3. Temperature dependence of $(\rho - \rho_0)$, where ρ_0 is the phonon contribution (PrAg), the phonon and residual contribution (LaAg), the phonon, residual, crystallographic and spin disorder at T_N contribution (CeAg).

obtained was $R = 0.101 \times 10^{-8} \Omega \text{ m K}^{-1}$. The same fit holds for the CeAg data in the approximate range 300–800 K, providing $R = 0.106 \times 10^{-8} \Omega \text{ m K}^{-1}$.

The contribution responsible for the sigmoidal trend of the LaAg resistivity can now be obtained by subtracting the residual resistivity and the phonon scattering term from the experimental data. The resulting trend, shown in figure 3, saturates at $T = 300 \text{ K}$ to a value of $12.5 \times 10^{-8} \Omega \text{ m}$. If the approach used is applied to the other La compounds with the same S-shape in the resistivity, such as LaAl_2 (Bauer *et al* 1985, Müller *et al* 1982), LaRh_2 (Diesling 1985, as quoted by Wohlleben and Wittershagen 1985), LaCu_6 (Brück *et al* 1986) and LaGa_6 (Tagawa *et al* 1986), similar behaviour of this anomaly should be obtained. The most probable reason for this behaviour in all these phases lies in a weak interaction between conduction electrons and empty 4f electron states. The so-called 4f instability can arise from a mixing with a band having high values of $N(E)$; the negative curvature of $\rho(T)$ indicates that E_F is separated by kT from a region with a sharp break in the density of states. This hypothesis agrees with the band structure calculations (Bauer *et al* 1986).

The situation for CeAg appears more complex. If the residual resistivity, the contribution arising from the crystallographic transition at 16 K, the spin disorder resistivity at T_N , and the phonon scattering dependence are subtracted from the total experimental data, the trend in figure 3 is obtained. Both the temperature dependence and the saturation value of $13.0 \times 10^{-8} \Omega \text{ m}$ are similar to those of LaAg. But for CeAg crystal-field effects (CEF) are also present, according to magnetic measurements (Walline and Wallace 1964, Pierre 1970) and neutron spectroscopy (Schmitt *et al* 1978, Frick *et al* 1983, Morin 1988). As can be seen in figure 3, the resistivity anomaly of CeAg shows a higher contribution at low temperature as regards LaAg, so the saturation conditions are already achieved at 250 K. If we assume the same 4f instability contribution for the two compounds, LaAg can be used as reference for CeAg. The difference between the

two curves yields a temperature trend with a flat maximum of about $2-3 \times 10^{-8} \Omega \text{ m}$ in the approximate range 100–250 K. This may be indicated as the CEF contribution for CeAg, and it is fully developed at about 350 K, in agreement with crystal-field splitting of 265 K previously obtained (Schmitt *et al* 1978, Frick *et al* 1983).

The resistivity anomaly of CeAg can thus be ascribed mainly to a 4f instability, and to a minor extent to CEF effects. Nevertheless, this hypothesis is not conclusive, as single-ion phenomena (Kondo effect or 4f instability) can mimic the temperature dependence of ion-ion interaction, and a clear separation between the different contributions is difficult.

Concerning the other RAg examined phases, the deviations observed in the temperature range just above T_N can be ascribed to CEF effects in the Pr, Nd, Dy and Er compounds. Such behaviour is in agreement with the magnetic susceptibility, inelastic neutron scattering and specific heat results (Walline and Wallace 1964, Brun *et al* 1974a, b, Furrer 1975, Morin and Schmitt 1982, Hill 1987).

A special note can be devoted to PrAg and NdAg. Morin and Schmitt (1982), using CEF parameters determined from neutron spectroscopy experiments, calculated the CEF contribution to the resistivity of PrAg. According to these authors the comparison with the experimental data of LaAg leads to the conclusion that in PrAg the CEF contribution is probably small above T_N . So, it cannot be excluded that in the RAg phases formed with the light rare earths a part of the observed resistivity anomaly may arise from the 4f instability present in LaAg.

A further confirmation of the different behaviour shown by the light rare earths as regards the heavy rare earths, is given by the relationship between some magnetic quantities and the de Gennes factor $G = (g - 1)^2 J(J + 1)$. For the RAg compounds, the spin disorder resistivity values can be divided into two groups, the first formed by the heavy rare earths and the second by Ce, Pr, Nd. Each group of data is roughly proportional to G , but with a strongly higher scaling factor for the light rare earths. Such a double trend has been already observed in other isotypic series of lanthanide compounds, such as R_2Zn_{17} (Olivier *et al* 1987) and RCd (Pinto *et al* 1988), and can be due to the occurrence of contributions other than the spin disorder and CEF resistivity. Only detailed band structure calculations should account for the variations encountered across isostructural rare-earth compounds.

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