Enhanced Electrical Resistivity before Néel Order in the Metals $R\mathrm{CuAs_2}$ (R = Sm, Gd, Tb, and Dy)

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We report an unusual temperature (T) dependent electrical resistivity (ρ) behavior in a class of ternary intermetallic compounds of the type $R\mathrm{CuAs_2}$ (R = rare earths). For some rare earths (Sm, Gd, Tb, and Dy) with negligible $4f$ hybridization, there is a pronounced minimum in $\rho(T)$ far above respective Néel temperatures (T_N). However, for the rare earths which are more prone to exhibit such a $\rho(T)$ minimum due to $4f$-covalent mixing and the Kondo effect, this minimum is depressed. These findings, difficult to explain within the hitherto-known concepts, present an interesting scenario in magnetism.

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It is a fundamental fact in condensed matter physics that, in metals containing magnetic moments, the spin-disorder contribution to electrical resistivity (ρ) in the paramagnetic state is a constant adding to the lattice contribution, which decreases with decreasing temperature (T). Naturally, ρ usually exhibits a positive T coefficient down to the magnetic ordering temperature (T_0), except perhaps a weak critical point effect restricted to a narrow T range (less than a few percent of Curie temperature) [1]. However, in the event that the sign of the exchange interaction between the local magnetic moment and the conduction electrons is negative (the phenomenon called "the Kondo effect") due to covalent mixing of the relevant orbital, ρ can show a low T upturn increasing logarithmically below a characteristic temperature leading to a minimum in $\rho(T)$ well above T_0. This aspect has been very well known for Ce and Yb alloys [2]. Here, we report that, in a class of ternary intermetallic compounds of the type $R\mathrm{CuAs_2}$ (R = rare earths) [3], the rare earths with strictly localized $4f$ character (in which case one does not anticipate the Kondo effect, e.g., Sm, Gd, Tb, and Dy) exhibit a pronounced minimum in $\rho(T)$ above respective Néel temperatures (T_N). However, for R = Pr, Nd, and even Yb, no such minimum is observed in $\rho(T)$. These findings present an unusual and interesting scenario as far as electronic transport in magnetic metals is concerned.

The series of compounds under investigation, $R\mathrm{CuAs_2}$ (R = Pr, Nd, Sm, Gd, Tb, Dy, Yb, and Y) crystallize in the $\mathrm{HfCuSi_2}$-type layered tetragonal form (space group, $P4/nmm$) [3]. For the experimental details, including sample preparation and the measurements of ρ, magnetization (M), and heat capacity (C), the reader may see Ref. [4].

Figure 1 shows $\rho(T)$ behavior for all the compounds below 70 K. Let us first look at the data for R = Sm, Gd, Tb, and Dy, in which the $4f$ orbitals are known to be so deeply localized that the covalent mixing effects can be ignored. The value of ρ falls in the milliohms range around 300 K in all cases. However, since the samples are found to be porous, the measured absolute values of ρ are overestimated and, hence, should not be taken too seriously. What is important to note is that ρ decreases monotonically with T without any other feature down to 70 K (and, hence, not shown here). This establishes that all these compounds behave similar to metals. As the T is lowered, one finds that, in these compounds, ρ attains surprisingly a prominent minimum at a temperature, T_{min} (equals about 35 K for Sm, Gd, and Tb; about 20 K for Dy), below which it rises again. It should be noted that this feature is not observed for the Y compound (as well as for R = Lu, not shown here), in which case $\rho(T)$ exhibits normally expected metallic behavior down to the measured lowest temperature (apart from a weak drop at about 7 K, which is presumably due to traces of a parasitic superconducting phase). This observation indicates that the minimum in other cases is magnetic in origin.

In order to rule out the origin of this upturn from magnetic superzone formation [5] due to possible antiferromagnetic ordering at T_{min}, it is important to make sure from independent measurements that T_N falls well below T_{min}. In this respect, the dc magnetic susceptibility (χ) and C data shown in Figs. 2 and 3 are quite conclusive. The χ above about 100 K is found to follow Curie-Weiss behavior (not shown here) and the effective moments (μ_{eff}) obtained from this temperature range are in full agreement with that expected for respective trivalent R ions (μ_{eff} = 0.7, 7.9, 9.7, and $10.63\mu_B$ for R = Sm, Gd, Tb, and Dy, respectively). The features due to magnetic ordering appear as a well-defined peak in χ and C and/or as a sudden change in the slope of inverse χ versus T well below T_{min} as one lowers the T. The T_N thus obtained are close to 12.5, 9, 9, and 8 K for Sm, Gd, Tb, and Dy cases, respectively. (There are additional features at

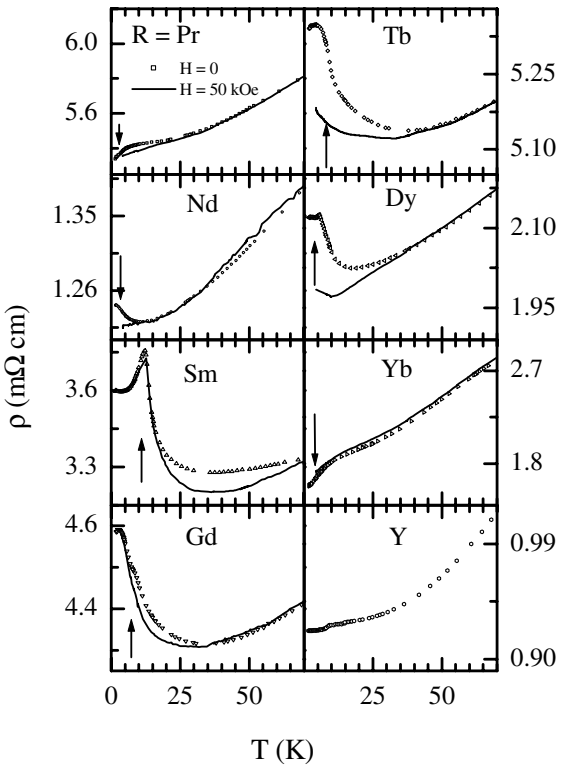

FIG. 1. Electrical resistivity behavior of RCuAs$_2$ compounds below 70 K in zero magnetic field as well as in the presence of 50 kOe. Vertical arrows mark the Néel temperatures.

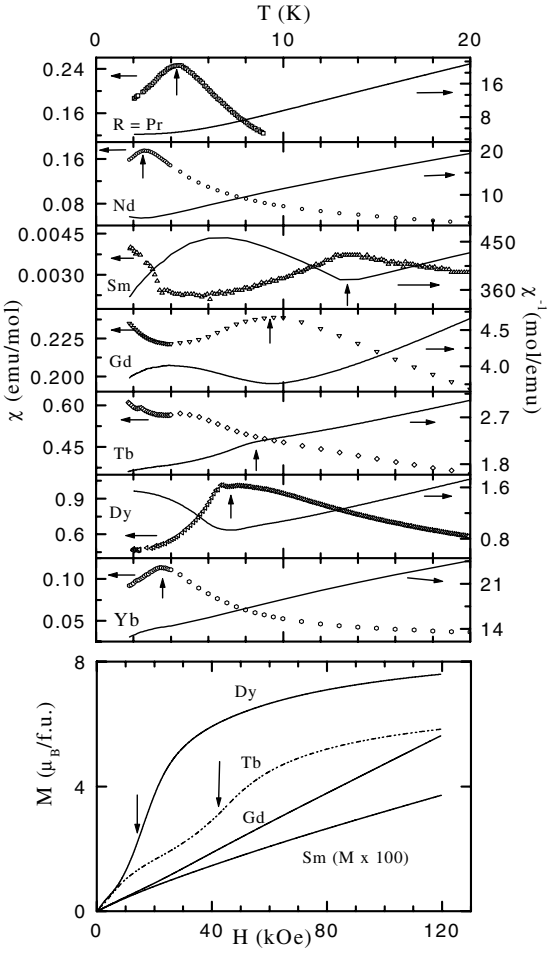

FIG. 2. (top) Magnetic susceptibility measured in a magnetic field of 100 Oe (circles) and inverse susceptibility measured in a field of 5 kOe (lines) for RCuAs$_2$ compounds. Vertical arrows mark the Néel temperatures. (bottom) Isothermal magnetization behavior for R = Sm, Gd, Tb, and Dy at 1.6 K with the arrows showing the field around which there is an upward curvature in some cases and the plots are found to be nonhysteretic.

further lower temperatures, which could be due to spin-reorientation effects.) There could be a small ambiguity in precisely locating T_N from the C data, as the peak positions can be shifted to a lower T or the C tail may continue to a higher T, depending on the complexities of the magnetic structure [6]. But the fact remains that the features due to the onset of magnetic transition appear well below $T_{\min}$ in all cases. Therefore, the minimum in $\rho(T)$ well above 12 K cannot be attributed to magnetic superzone gap formation. (ρ increases further below T_N in some cases, rather than exhibiting a drop due to the loss of spin-disorder contribution, which may be attributed to this gap effect.) It may be stated that χ for both the field-cooled and the zero-cooled conditions of the specimens are essentially the same, which establishes that there is no spin-glass freezing in the T range of investigation. Isothermal M in the magnetically ordered state, measured until magnetic field (H) = 120 kOe (see Fig. 2, bottom, for instance, for the data at 1.6 K), varies sluggishly with H without any hysteresis; in fact for R = Sm and Gd, M varies linearly with H, whereas Tb and Dy exhibit metamagneticlike features. These establish that the magnetic ordering is indeed of an antiferromagnetic type and not of a ferromagnetic type.

It may be recalled that we have earlier reported a similar ρ behavior for some Gd systems, e.g., Gd_2PdSi_3, crystallizing in a AlB_2-derived ternary hexagonal structure [7], but other rare-earth members of those series do not exhibit such a minimum in $\rho(T)$. The present series of compounds is thus unique in the sense that the observation of $\rho_{\min}$ spans over the entire rare-earth series (but not restricted to Gd alone). It is this finding that provides compelling evidence for a more-common hitherto-unrecognized magnetism-related electron scattering effects in the paramagnetic state. There is also another noteworthy difference between these two classes of compounds: The minimum is very sensitive to the presence of an external H in the case of Gd_2PdSi_3, whereas the application of a H of 50 kOe does not depress this minima in the present compounds, most notably for R = Gd and Sm (see Fig. 1). In other words, the magnetoresistance $\{MR = [\rho(H) - \rho(0)]/\rho(0)\}$ is quite small varying sluggishly with H; this also rules out any explanation in terms of possible grain boundary effects at least

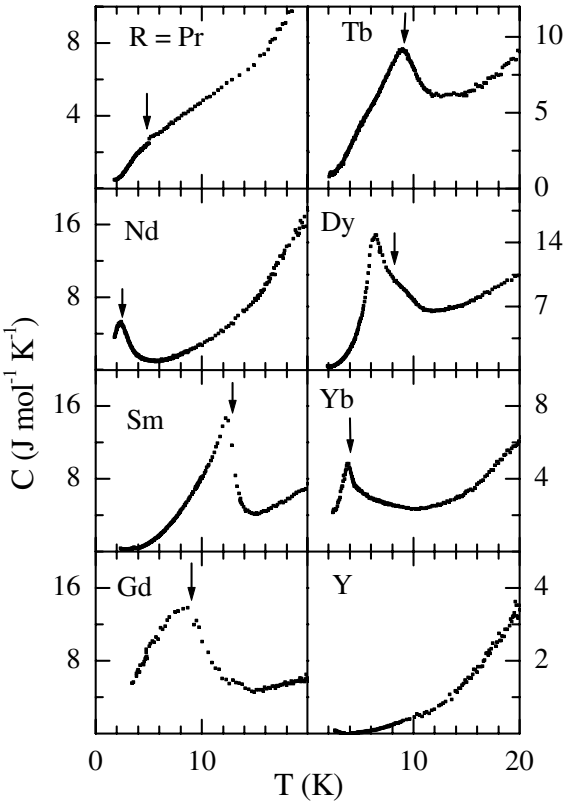

FIG. 3. Heat capacity as a function of temperature for RCuAs$_2$ compounds. Vertical arrows mark the Néel temperatures, as inferred from the magnetic susceptibility data.

for R = Sm and Gd, as any extra scattering from the magnetic ions at the grain boundaries has been in general known to be strongly suppressed by small applications of H. Thus, for $H = 50$ kOe, the magnitude of MR in the T region of interest is much less than or close to 2%, which could be compared with the net increase (about 14%, 6%, 4%, and 4% for R = Sm, Gd, Tb, and Dy, respectively) of zero-field ρ as measured at T_N relative to that at $T_{\min}$. Though smaller in magnitude, there is a noticeable influence of H for R = Tb and Dy. Possibly, there is a subtle difference in the origin of $\rho(T)$ minimum between the present Gd and Sm compounds on the one hand and Gd_2PdSi_3 on the other with Tb and Dy compounds lying somewhere between these two limits.

In order to explore whether the upturn in ρ below $T_{\min}$ in the paramagnetic state could be understood in terms of hitherto-known concepts, we plot the data in the range 12.5 to 31 K (region of interest) in various ways in Fig. 4, for instance, for $SmCuAs_2$. Clearly, the upturn cannot be attributed to the Kondo effect due to deeply localized nature of the $4f$ orbital. Though, occasionally, Sm compounds show the Kondo effect [2], this phenomenon cannot be expected for Gd, Tb, and Dy. The absence of the Kondo effect even in this Sm compound is further supported by the nonlogarithmic variation of ρ [Fig. 4(d)]. We have verified this by obtaining the $4f$ contribution (ρ_{4f}) to ρ [Fig. 4(f)] after subtracting the lattice part from the knowledge of $\rho(T)$ of the Y analogue as described by Cattaneo and Wohlleben [8]. We arrive at a similar conclusion even when we employ the data of the Lu sample for lattice contribution. The plot of $\ln(\rho)$ versus $1/T$ is not linear [Fig. 4(c)] and the absence of activated behavior rules out the formation of any type of gap as a possible cause of this upturn. The plots of $\ln(\rho)$ versus $T^{-1/4}$ and $T^{-1/2}$ are also not linear [Figs. 4(a) and 4(b)], thereby ruling out an explanation in terms of variable range hopping and Coulomb gap formation mechanisms [9]. Apparently, there is no $T^{1/2}$ dependence of ρ as well [Fig. 4(e)], which implies that presently known

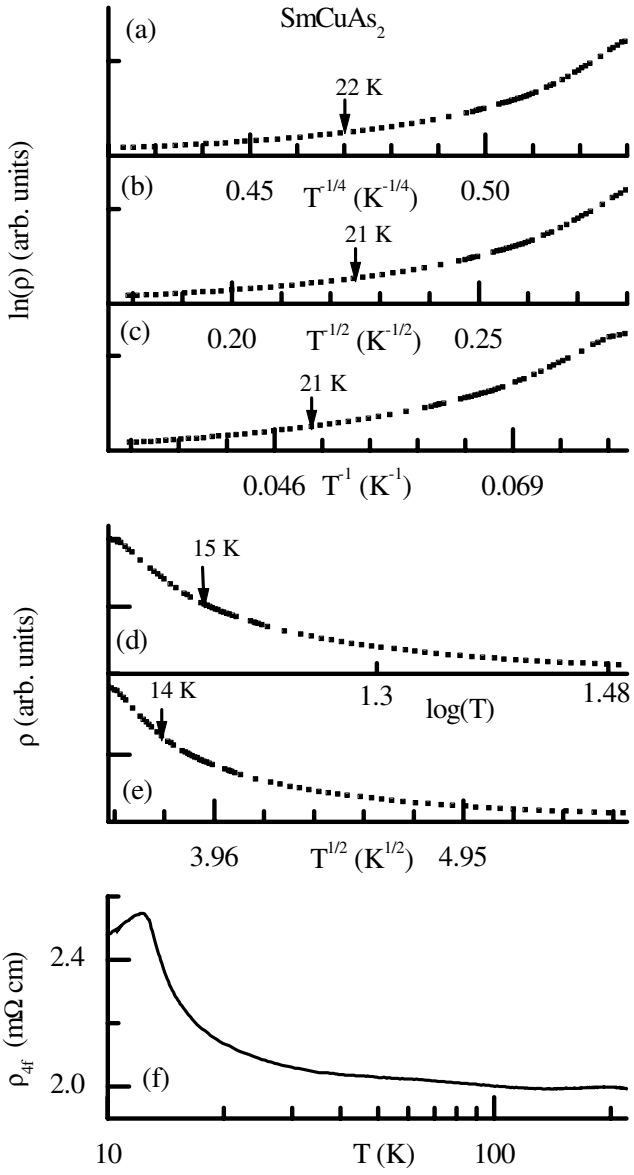

FIG. 4. The electrical resistivity in the temperature range 12.5–31 K plotted in various ways for $SmCuAs_2$ compounds. Plot (f) shows the $4f$ contribution in the logarithmic temperature scale in the T range 10–225 K.

weak-disorder-induced electron localization ideas discussed by Lee and Ramakrishnan[10] are not adequate to describe the anomalies. Another mechanism that could be advanced is in terms of the formation of magnetic polarons, as proposed for EuSe (Ref. [11]), EuB_6 (Ref. [12]), and $Tl_2Mn_2O_7$ (Refs. [13]), but the application of a H is expected to have a pronounced depressing effect on the ρ upturn resulting in a large negative MR, in contrast to the observation. For the same reason, the s-f exchange model (considering a strong scattering of $5d$ conduction electrons by the localized $4f$ electrons) [14] proposed to explain the large MR behavior of GdI_2 may not be applicable; additionally, this model assumes ferromagnetic ordering at low temperatures, whereas the present compounds are antiferromagnets; it is not clear whether this model can be modified to explain the features. The fact that ρ behavior in Y and Lu analogues is normal in this regard establishes that the origin of the above ρ anomaly does not lie in the band structure. Thus, there is no straightforward explanation for the above-mentioned enhanced scattering, though it is clear that magnetism plays a role.

We now inspect the ρ behavior of Pr, Nd, and Yb compounds (Fig. 1) along with the χ and C behavior (Figs. 2 and 3). $PrCuAs_2$ exhibits a distinct feature due to antiferromagnetic ordering at about 4 K, as evidenced by the feature in χ. Nd and Yb compounds are found to order magnetically close to 2.5 and 4.0 K, respectively, as marked by the features in C and χ data. It is worth mentioning that, though the T_N values in this series are in general larger than that expected on the basis of de Gennes scaling, this Yb compound turns out to be one of the few Yb compounds exhibiting a high magnetic ordering temperature [15]. This makes this Yb compound interesting in its own right. Following the behavior in other members of this series described above, one would naively expect that there should be a minimum in the plot of $\rho(T)$ above T_N. However, it is striking to note that no such minimum could be observed for Pr and Yb compounds and the MR is also negligible. For the Nd compound, there is a weak upturn below 15 K to the tune of 1% only. We speculate that, at least for these cases, the origin of this suppression of $\rho_{\min}$ may lie in a non-negligible degree of $4f$ mixing, characteristic not only of Yb, but also of Pr and Nd under favorable circumstances [16], though there could be other controlling factors [17]. In the case of the Yb compound, this covalent mixing manifests itself usually as the Kondo effect; the observed behavior of $\rho(T)$ plot above T_N is typical of Yb-based Kondo lattices [18], and the temperature (around 130 K) at which ρ starts falling as T is lowered represents the onset of coherent scattering among the Kondo centers [19]. The positive sign of MR (see Fig. 1) arising out of destruction of Kondo coherence by the application of H is consistent with this explanation [19]. Therefore, we tend to believe that the Kondo coherence somehow suppresses the upturn in ρ as T_N is approached. With respect to the trends among light rare earths, the spatial mixing of $4f$, though it does not result in the Kondo effect, is apparently effective in depressing $\rho_{\min}$. It is quite well known [16] that the strength of $4f$ hybridization decreases progressively as one moves from Ce to Sm and the observation of a similar trend [20] in $\rho_{\min}$ supports this interpretation, at least for these cases.

In conclusion, the findings reported here imply that the understanding of the electronic transport in the paramagnetic state of relatively simple magnetic metals is far from complete. We propose that the ideas based on weak localization [10] may have to be extended *incorporating strongly enhanced magnetic critical scattering effects extending over a wide temperature range above* T_0.

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