Possible evidence for an energy gap below the Néel temperature in ternary rare-earth compounds

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Electrical-resistivity (ρ) behavior in the vicinity of the Néel temperature (T_N) of the pseudoternary alloys $R\mathrm{Cu}_{2-x}\mathrm{Ni}_x\mathrm{Si}_2$ (R = Pr, Gd, and Dy) and $R_{1-x}\mathrm{La}_x\mathrm{Cu}_2\mathrm{Si}_2$ (R = Pr and Gd) is reported. There is an increase in ρ just below T_N in several alloys, followed by the usual decrease at lower temperatures due to the loss of spin-disorder contribution. We attribute this rise in ρ to the formation of an energy gap at the Fermi surface due to antiferromagnetic ordering.

The magnetic ordering of the local moments of the rare-earth ions in metals is known to cause a large effect on the conduction electrons via the *s-f* interaction. Particularly, in antiferromagnets, the long-range order is expected to induce superzone gaps in the conduction electron energy bands. Such energy gaps at the Fermi surface in the magnetically ordered state should result in an increase of electrical resistivity with decreasing temperature below Néel temperature (T_N) and this aspect has been well documented for the pure heavy rare-earth metals.[1] However, possible existence of these distortions of the Fermi surface of rare-earth intermetallic compounds is often ignored in the current literature while interpreting experimental results. This may probably be because the existence of such effects has not been sufficiently demonstrated in the alloys containing *localized* moments.

With this motivation we have investigated the pseudoternary alloys, $R\mathrm{Cu}_{2-x}\mathrm{Ni}_x\mathrm{Si}_2$ (R = Pr, Gd, and Dy) and $R_{1-x}\mathrm{La}_x\mathrm{Cu}_2\mathrm{Si}_2$ (R = Pr and Gd), crystallizing in the $\mathrm{ThCr}_2\mathrm{Si}_2$ structure,[2] by electrical resistivity (ρ) measurements, as these compounds offer a nice opportunity to investigate Fermi surface effects for different orientations[2] of the magnetic moments *(vide infra)*. The main finding is that in several alloys we notice an increase in ρ at the onset of antiferromagnetism (followed by the loss of a spin-disorder contribution well below T_N), similar to that noted[3] for $\mathrm{URu}_2\mathrm{Si}_2$, indicating the existence of energy gaps in the conduction electron bands intersecting the Fermi surface due to antiferromagnetic ordering. Such an inference emphasizes the need to be cautious while extrapolating the experimental results in the paramagnetic state to the magnetically ordered state, such as the extraction of the linear coefficient of specific heat, spin-disorder contribution to resistivity, relaxation time data, etc.

The alloys of several compositions were prepared by arc melting followed by annealing at 1070 K to remove strains in the lattice. The samples were characterized by x-ray diffraction. Electrical resistivity (ρ) measurements were performed in the temperature interval 1.5–300 K by a conventional four-probe method employing a current of 100 mA in a medium of helium gas for temperature homogeneity; the sensitivity of voltmeter was 10 nV.

For the sake of clarity we show in Figs. 1 and 2 the resistive data only up to 40 K for all the alloys investigated. Néel temperatures for most of the specimens were independently obtained from the temperature at which dc magnetic susceptibility (χ) exhibits a sharp and well-defined peak due to magnetic ordering. Considering a minor uncertainty (about 0.5 K) in the temperature values above 10 K in both the experimental methods it is safe to state that T_N determined from χ data[4] nearly corresponds to the temperature at which resistivity starts increasing (see below). The main experimental observations are the following.

(i) With respect to Pr alloys: There is a marginal increase in ρ near T_N for $\mathrm{PrCu}_2\mathrm{Si}_2$, which becomes dominant for nickel concentrations $x = 0.15$ to 1.5 and this feature is completely absent for $\mathrm{PrNi}_2\mathrm{Si}_2$ [Fig. 1(a)]. This peak in ρ is also enhanced by La substitution and it persists even for $\mathrm{Pr}_{0.2}\mathrm{La}_{0.8}\mathrm{Cu}_2\mathrm{Si}_2$ [Fig. 2(a)].

(ii) With respect to Gd and Dy alloys: For $\mathrm{GdCu}_2\mathrm{Si}_2$ and $\mathrm{DyCu}_2\mathrm{Si}_2$, there is no peak in ρ at T_N. However, this peak develops for large concentrations of nickel, but appears to be absent for total replacement of Cu by Ni. *Interestingly, for some Gd alloys [see Fig. 1(b)] the increase in the resistivity is quite dramatic on two accounts; firstly, it spreads to as much as 10 K below T_N and, secondly, the observed magnitude of increase is comparable to or even larger than the decrease due to the loss of spin disorder contribution.* La substitution in $\mathrm{GdCu}_2\mathrm{Si}_2$, does not result in a peak in ρ at the onset of magnetic ordering in contrast to the observation for the corresponding Pr alloys. We take this as an indication for the absence of contributions from possible spin-disorder effects following the chemical substitutions to such peaks in the latter cases. In addition to the above findings we also note for $\mathrm{GdNi}_2\mathrm{Si}_2$ an increase in ρ with decreasing temperature over a wide temperature range well above T_N; this feature is somewhat unusual for Gd systems and can probably result[5] from significant variations of the lattice constants with temperature above 15 K. Since this feature is presumably not related to magnetic ordering we will not discuss this aspect any further in this paper.

The major observation of present interest to us is the existence of a rise in ρ below T_N in several alloys, notably

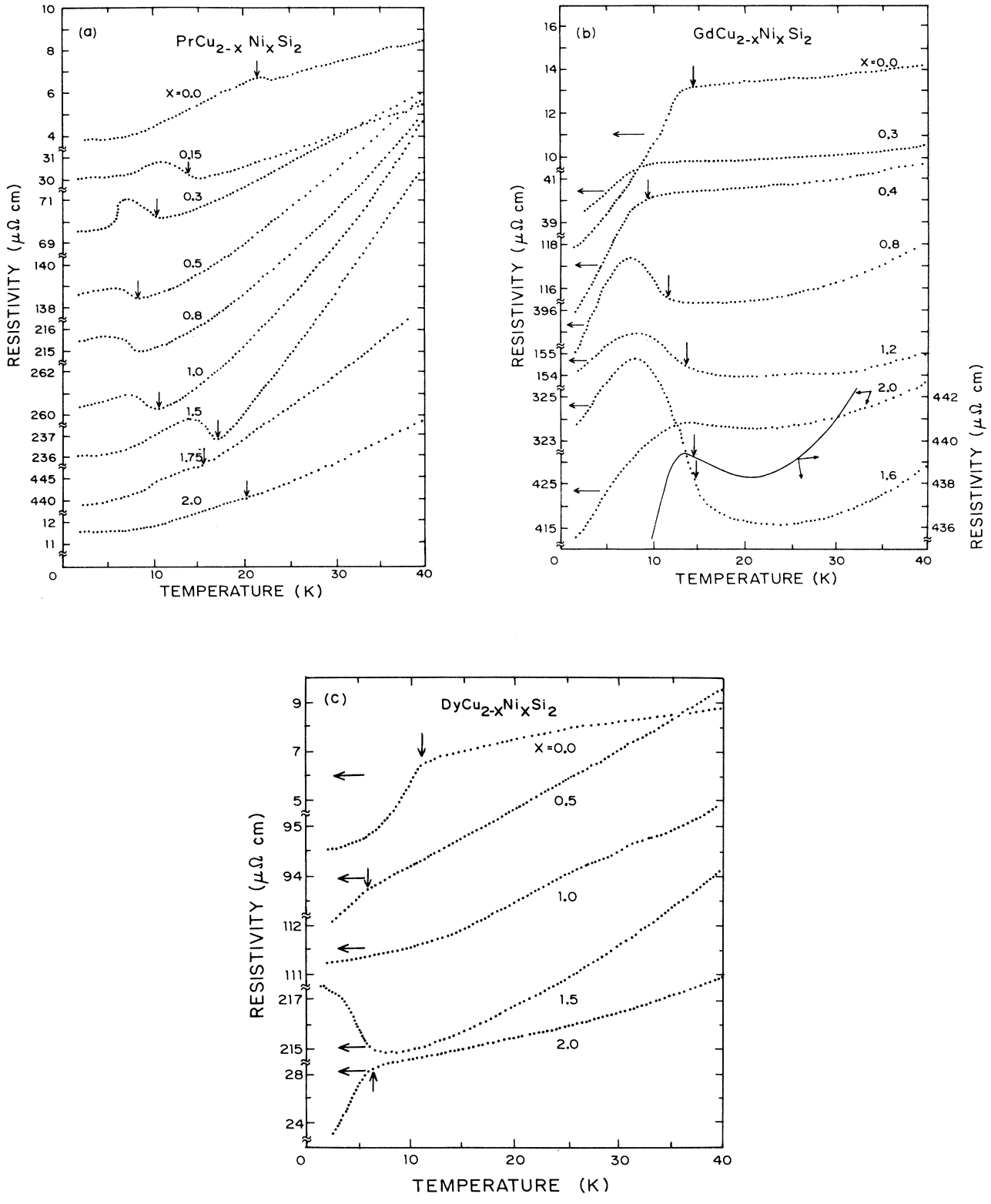

FIG. 1. Electrical resistivity as a function of temperature (1.5–40 K) for several alloys for (a) $PrCu_{2-x}Ni_xSi_2$ series, (b) $GdCu_{1-x}Ni_xSi_2$ series, and (c) $DyCu_{2-x}Ni_xSi_2$ series. Vertical arrows for (a) and (b) indicate the temperature at which dc magnetic susceptibility exhibits a well-defined peak due to the onset antiferromagnetism and for (c) they represent the temperature at which resistivity starts decreasing due to the loss of spin-disorder contribution. In (b) the data for $GdNi_2Si_2$ are plotted in an expanded scale also by a continuous curve to highlight the existence of a minimum well above T_N.

significant for a few Gd cases. This feature has been observed for isotropic URu_2Si_2 ($T_N = 17$ K), exhibiting a magnetic structure similar to that of $PrCu_2Si_2$ and it has been attributed to spin-density waves resulting in the formation of energy gaps at the Brillouin-zone boundaries intersecting the Fermi surface.[3] In view of similarities of the observed features we believe that the same argument is applicable to the present series of alloys also. However, there is a fundamental difference in the origin of gap formation in URu_2Si_2 and the alloys under investigation; that is, U $5f$ electrons can exhibit itinerant character thereby contributing to the conduction band, but the $4f$ electrons in these rare-earths are localized.

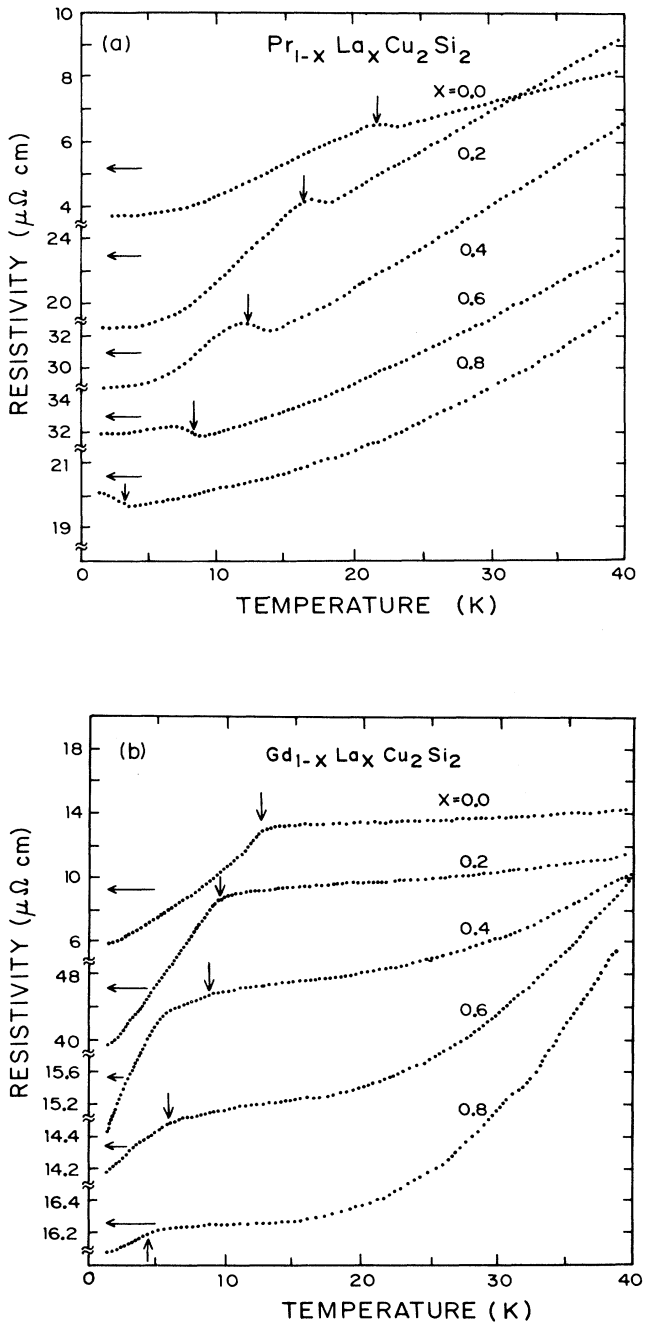

FIG. 2. Electrical resistivity as a function of temperature (1.5–40 K) for the alloys for (a) $Pr_{1-x}La_xCu_2Si_2$ series and (b) $Gd_{1-x}La_xCu_2Si_2$ series. The meaning of vertical arrows in (a) and (b) is the same as that in Figs. 1(a) and 1(c), respectively.

At this juncture, it is worthwhile to recall the nature of the alignment of the magnetic moments in all the end members. The common feature in all these antiferromagnets is that the intraplanar interaction is ferromagnetic, whereas interplanar interaction is antiferromagnetic.[2] $PrCu_2Si_2$ exhibits type-I antiferromagnetic ordering and the magnetic structure is commensurate with the lattice.[6] However, for $PrNi_2Si_2$, there is a sinusoidal modulation of magnetic moments along the c axis[7] and hence the magnetic lattice is incommensurate. For $GdCu_2Si_2$ the easy axis of magnetization is in the basal plane,[8] whereas for $GdNi_2Si_2$, the angle between Gd moments and the c axis is approximately 70° (Ref. 8). For $DyCu_2Si_2$, the ordering consists of ferromagnetic (101) planes coupled antiferromagnetically with the sequence $+-+-$ requiring thereby the doubling of the a and c axes resulting in an orthorhombic unit cell.[2] The neutron diffraction pattern of $DyNi_2Si_2$ shows a broad magnetic maximum at 1.4 K indicating the presence of a short-range magnetic order at this temperature; the magnetic moments are normal to the c axis but make an angle of 11° with the a axis (AF-III type).[9] Thus, it is clear that all of the six antiferromagnetic end members exhibit a variety of magnetic structures and it is difficult to find a correlation between these magnetic structures and the presence or the absence of the resistivity peak below T_N. In cases like $PrNi_2Si_2$, one expects[1] additional energy discontinuities (relative to that in $PrCu_2Si_2$) due to the sinusoidally modulated incommensurate magnetic structure, but we do not see this peak in this compound. The trend in the resistivity behavior as a function of Cu or Ni concentration in Fig. 1, may be explained assuming that the Fermi surface moves continuously across the magnetic Brillouin-zone boundary gaps with the changes in the number of conduction electrons and the unit-cell volume; this suggests that in those alloys where the above peak is missing, Fermi surface does not intersect such gaps. It is also expected[10] that the magnitude of the gaps and hence of the above resistivity anomaly are proportional to the oscillating amplitude of the $4f$-spin moments. These two factors qualitatively account for the overall differences in the magnitude of the resistivity anomalies below T_N among Pr, Gd, and Dy alloys exhibiting this peak in Fig. 1. Careful neutron diffraction studies are warranted on all these alloys to gain better knowledge of the magnetic structures. A faster loss of the $4f$ contribution to ρ at T_N can also compensate the increase due to the energy-gap effect thereby wiping out the above peak in some cases. This point is nicely demonstrated in the case of $DyCuNiSi_2$; in this alloy we observed a well-defined peak in susceptibility at 4 K due to the onset of antiferromagnetism, however, resistivity does not exhibit any anomaly [see Fig. 1(c)] at this temperature, not even the usual decrease due to the loss

of spin-disorder contribution.

Finally, we would like to state that the possible role of magnetorestriction effects due to magnetic ordering have not been taken into account in this manuscript and this may be justified considering that no such anomaly in the temperature-dependent lattice-constants data near T_N was found for any of the $R\,Cu_2Si_2$ compounds.[11] We believe that the inference we have made here bears significant relevance to the interpretation of the experimental data of Ce-based Kondo-lattice systems, in which case a complicated resistive behavior due to a Kondo-type logarithmic increase below a certain temperature and Kondo-coherence effects[12] often masks the presence of such features. Even in $CeCu_2Si_2$, an isostructural compound of great interest due to heavy fermion superconductivity,[13] spin-density waves below 1 K are believed to exist[14] and hence present findings on $PrCu_2Si_2$ and its alloys should be kept in mind while drawing any major conclusion on such compounds. The results based on $Pr_{1-x}La_xCu_2Si_2$ also seem to emphasize that the energy gap formation does not require complete periodicity of the magnetic sublattice and it may exist even for a moderately dilute concentration of magnetic ions. Theoretically, it will be of interest to investigate the modifications, if any, of the polarization of the conduction band due to the intersection of the Fermi surface with the magnetic-superzone boundary gaps following antiferromagnetic ordering in such alloys. We call for an urgent verification of our conclusions by energy gap measurements in view of its significance.

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[1]See, for a review, S. K. Sinha, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneider, Jr., and L. Eyring (North-Holland, Amsterdam, 1978), Vol. 1, p. 489; see also *Magnetic Properties of Rare-Earth Metals,* edited by R. J. Elliott (Plenum, New York, 1972); R. J. Elliott and F. A. Wedgewood, Proc. Phys. Soc. **81**, 846 (1963).

[2]A. Szytula and J. Leciejewicz, in *Handbook on the Physics and Chemistry of Rare-earths,* edited by K. A. Gschneidner, Jr., and L. Eyring (North-Holland, Amsterdam, 1989), Vol. 12, p. 133.

[3]U. Rauschschwalbe, Physica **147B**, 1 (1987), and references cited therein.

[4]Clearly, T_N undergoes a nonmonotonic variation with the replacement of Cu by Ni and this is a consequence of the variations in the conduction electron density and unit-cell volume caused by Ni substitution. T_N (denoted by vertical arrows in Fig. 2) for the La-substituted specimens scales with the concentration of the magnetic ions as expected on the basis of well-known Ruderman-Kittel-Kasuya-Yosida mechanism.

[5]R. D. Parks, in *Magnetism and Magnetic Materials 1971 (Chicago)* (AIP Conf. Proc. No. 5), edited by C. D. Graham, Jr., and J. J. Rhyne (AIP, New York, 1971), p. 630.

[6]A. Szytula, W. Bazela, and J. Leciejewicz, Solid State Commun. **48**, 1053 (1983).

[7]J. M. Barandiaram, D. Gignoux, D. Schmitt, and J. C. Gomez Sal, Solid State Commun. **57**, 941 (1986).

[8]I. Nowik, I. Felner, and M. Seh, J. Magn. Magn. Mater. **15-18**, 1215 (1980)

[9]V. N. Nguyen, F. Tcheou, and J. Rossat-Mignod, Solid State Commun. **45**, 209 (1983).

[10]H. Miwa, Prog. Theor. Phys. **29**, 477 (1963).

[11]W. Schlabitz, J. Baumann, G. Neumann, P. Plumacher, and K. Reggintin, in *Crystalline Electric Field Effects in f-Electron Magnetism,* edited by R. P. Guertin, W. Suski, and Z. Zolnierek (Plenum, New York, 1982), p. 289.

[12]See several articles in J. Magn. Magn. Mater. **47&48** (1985).

[13]F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schafer, Phys. Rev. Lett. **43**, 1892 (1979).

[14]C. Tien, Phys. Rev. B **43**, 83 (1991).