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LETTER TO THE EDITOR

Magnetic and electric quadrupolar anomalies in $PrCu_2Si_2$

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Abstract. There is an abnormal enhancement of the Néel temperature ($T_N \simeq 21$ K) and spin-disorder resistivity beyond that expected on the basis of de Gennes scaling in $PrCu_2Si_2$. While the electric quadrupole alignment is known to be the driving force for the moderate breakdown of this scaling in homologous heavy rare-earth members, such a mechanism is not applicable to $PrCu_2Si_2$. Contrary to the behaviour in heavy rare earths, there is no distinct anomaly in the temperature-dependent lattice constants in this compound as if the electric quadrupole moment of Pr is quenched. Thus, this compound is shown to exhibit novel magnetic and quadrupolar behaviour.

The tendency of the 4f orbital to exhibit some degree of extended character at the beginning of the rare-earth (R) series is known to cause anomalies in the magnetic properties of cerium intermetallic compounds. However, very little attention has been paid to looking for such effects in intermetallics based on Pr. In this article, we demonstrate a unique magnetic behaviour of the compound $PrCu_2Si_2$, crystallizing in the $ThCr_2Si_2$ structure [1]. We bring out further novel aspects with respect to the Pr 4f electric quadrupole moment in this compound.

According to the well known de Gennes scaling, which assumes that the exchange interaction strength does not vary in a given series, the magnetic ordering temperature for Gd should be the highest in a given R series. However, some of the Ce compounds are known to disobey this rule due to strong 4f hybridization. For the compound $PrCu_2Si_2$, the observed ratio of the Néel temperature (T_N) of Pr ($T_N \simeq 21$ K) to that of Gd ($T_N \simeq 13$ K) [1] is the largest, even when compared with such enhancement ratios ($\leqslant 1.0$) for the Ce ion in any series of compounds. The value for Pr should be at least 20 times smaller than that of Gd, according to de Gennes scaling. It may be pointed out that the T_N-values for the heavy rare-earth members of this series are moderately larger than that predicted by this scaling behaviour, and the electric quadrupole alignment with decreasing temperature has been proposed to be the driving force for this deviation in these rare-earth alloys [2]. In this article, we explore whether this explanation can be offered for the anomalous enhancement of T_N in $PrCu_2Si_2$. For this purpose, we have investigated this system by studying several pseudoternary solid solutions based on $PrCu_2Si_2$ by electrical resistivity (ρ) and magnetic susceptibility (χ) measurements. With the knowledge of the lattice constant data [3], we conclude that the origin of the breakdown of de Gennes scaling is not the same as that proposed [2] (quadrupole alignment) for the heavy rare-earth

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members of this series, thereby suggesting the unique magnetic behaviour of this compound. In fact, there is a quenching of the 4f quadrupole moment for $PrCu_2Si_2$, as indicated by the lattice constants. Thus, we show the existence of novel magnetic and quadrupolar anomalies in $PrCu_2Si_2$.

The pseudo-ternary alloys we have investigated are: $Pr_{1-x}La_xCu_2Si_2$ (x = 0.0, 0.2, 0.4, 0.6, 0.8), $Pr_{1-x}Y_xCu_2Si_2$ (x = 0.1, 0.2, 0.4, 0.6, 0.8), $Pr_{1-x}Gd_xCu_2Si_2$ (x = 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) and $PrCu_{2-x}Ni_xSi_2$ (x = 0.15, 0.3, 0.5, 1.0, 1.5, 1.75 and 2.0). The alloys $GdCu_{2-x}Ni_xSi_2$ (x = 0.0, 0.4, 0.8, 1.2, 1.6 and 2.0) were also investigated for the sake of comparison. The experimental data (2–300 K) have been published by us previously [4, 5] and we present only those results that are relevant for our discussion.

Before we discuss the enhancement of T_N in Pr with that in other heavy rare-earth members of this series, we demonstrate that the indirect exchange interaction (Ruderman–Kittel–Kasuya–Yosida mechanism, RKKY) is still responsible for mediating abnormally strong magnetic ordering in Pr, rather than, for instance, superexchange. For this purpose, we show the values of Néel temperature for some series of alloys in figure 1. It is obvious (see figure 1) that T_N for the La-substituted specimens scales with the concentration of Pr ions. Such a scaling of T_N with x is expected for a situation where the coupling between the localized moments is mediated by conduction electrons (RKKY mechanism). No other mechanism can explain such a scaling of T_N with Pr concentration. In particular, a superexchange mechanism is expected to lead to a much faster depression of T_N with the dilution of magnetic ions, as, e.g., observed in the case of $PrBa_2Cu_3O_7$ [6–8]. The dipolar mechanism cannot lead to the enhanced value of T_N either. That the RKKY mechanism is operative in controlling the magnetism in $PrCu_2Si_2$ is further supported by the similar T_N variation with x in $PrCu_{2-x}Ni_xSi_2$ and $GdCu_{2-x}Ni_xSi_2$. In both the series of alloys, T_N initially decreases with the replacement of Cu by Ni (up to about $x = 0.4$) and then increases for higher values of x. This non-monotonic dependence of T_N on x presumably results from the variations in the band structure caused by the changes in the conduction electron concentration.

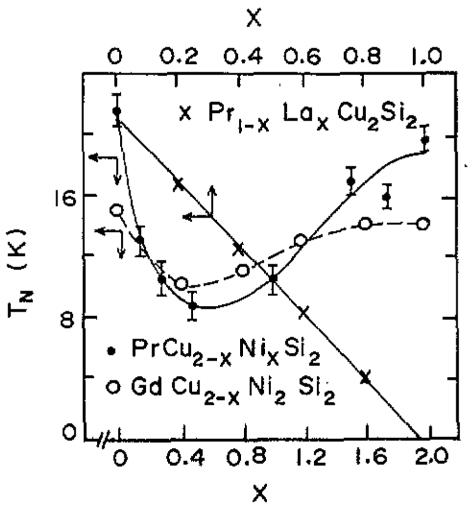

Figure 1. The Néel temperature as a function of composition in the pseudoternary alloys based on $PrCu_2Si_2$ and $GdCu_2Si_2$. The lines through the points serve as guides to the eye.

We will now show that the observed enhancement of T_N of $PrCu_2Si_2$ over its de Gennes scaled value (about 0.7 K) cannot be consistently understood within the framework of the ideas proposed for heavy rare-earth members [2]. It was argued [2] that the excess resistivity for heavy rare earths at high temperatures contains major contributions from the aspherical Coulomb contribution from the thermally fluctuating electric quadrupoles. When the quadrupole alignment sets in at low temperatures, magnetic ordering is energetically favoured, thereby giving rise to the enhancement of T_N. The lattice also responds to the quadrupole alignment [9] by a volume-conserving anomaly in the c/a ratio [3, 10]. It was shown [2] that all the measured quantities—the enhancements of T_N over the de Gennes scaled value, ρ_{sd}, the low temperature c/a anomaly and the saturated magnetostriction measured at a low temperature—scale with each other. We therefore look for this scaling in $PrCu_2Si_2$ to prove our point.

In order to derive the values of ρ_{sd}, we carefully analyse the resistivity data [4] for $Pr_{1-x}Gd_xCu_2Si_2$ alloys along the lines followed in [2]. ρ_{sd} (6.9 $\mu\Omega$ cm) for $PrCu_2Si_2$ is much larger than that noted for $GdCu_2Si_2$ (5.3 $\mu\Omega$ cm), whereas de Gennes scaling yields a value less than 0.25 $\mu\Omega$ cm for $PrCu_2Si_2$. *This experimental finding is very unusual.* In order to see whether ρ_{sd} and T_N track each other, we plot the values of T_N and ρ_{sd} in figure 2 as a function of x in this solid solution; for the sake of clarity, ρ_{sd} and T_N for $GdCu_2Si_2$ are chosen to coincide in this plot. Considering that χ, ρ and heat capacity data show the features due to magnetic ordering at slightly different temperatures [4, 5], the absolute error in T_N is estimated to be ± 1 K, although the variations of T_N as a function of x from any one of the three experimental methods is much less than 0.5 K. The error on ρ_{sd} is less than ± 0.3 $\mu\Omega$ cm. Within these experimental errors, we can confidently state that T_N and ρ_{sd} track each other. The observed ratio of ρ_{sd} (in units of $\mu\Omega$ cm) to T_N (in units of K), 0.3–0.35, is in good agreement with that noted for heavy rare earths, as if the same mechanism—quadrupole alignment—controls the enhancement of T_N throughout the series including $PrCu_2Si_2$.

However, the temperature dependence of the lattice constant behaviour reported in the literature [3, 10] is in total contradiction with the existence of any quadrupole alignment in $PrCu_2Si_2$. The heavy rare earths exhibit a significant increase of c and a decrease of a below 100 K as a consequence of a quadrupole alignment in the field gradient of non-cubic RCu_2Si_2. On the basis of the scaling, if the enhanced values of T_N and ρ_{sd} truly represent the size of the quadrupolar effects, the largest anomalies in c and a are expected to be below 100 K for $PrCu_2Si_2$, in the event of a quadrupole alignment. Instead it is found that the temperature dependence of the lattice constants in $PrCu_2Si_2$ is practically the same as that in $GdCu_2Si_2$ down to 4.2 K [3], without any significant deviations from that due to thermal contraction. The value of the saturated magnetostriction [3, 11] (measured down to 4.2 K) for Pr ions doped in YCu_2Si_2 is small, consistent with the magnitude of the c/a anomaly. These experimental observations imply that the quadrupole moment is quenched down to low temperatures. Therefore, the origin of the breakdown of de Gennes scaling of T_N and ρ_{sd} in $PrCu_2Si_2$ cannot lie in an alignment of the 4f electric quadrupole in the field gradient of the non-cubic Pr site. The cause of this anomaly is, therefore, conceptually different from that in heavy rare-earth members of this series, in spite of the fact that *the magnetic coupling between the rare-earth ions is brought out by the same mechanism (RKKY type) throughout the entire series*; this baffling finding makes this compound a novel one. However, the scaling between the two quantities, T_N

and ρ_{sd} (see figure 2), is expected on the basis of de Gennes scaling also, *but with an enhanced value for the exchange integral J (by a factor of about 5).* This unusual enhancement of J may result from the spatial overlap of the radially extended Pr 4f orbital with the valence band of neighbouring atoms [12].

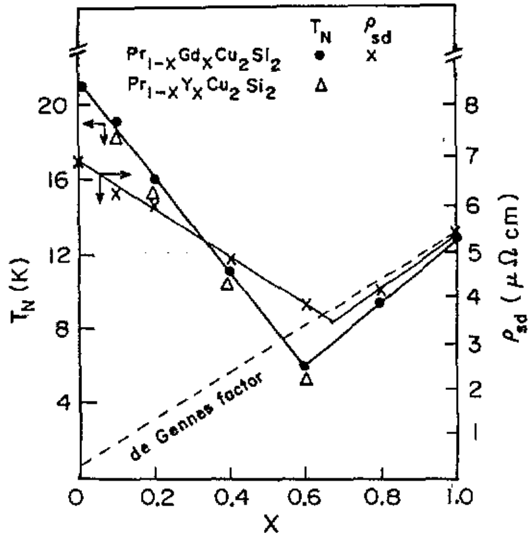

Figure 2. The Néel temperature (T_N) and spin-disorder resistivity (ρ_{sd}) as a function of composition in $Pr_{1-x}Gd_xCu_2Si_2$ alloys. The lines through the data points are guides to the eye. The values of T_N in the corresponding Y-based series are also shown by triangles.

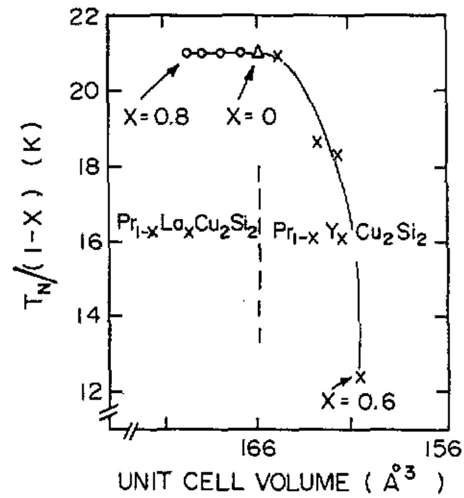

Figure 3. The Néel temperature normalized to the concentration of Pr ions as a function of unit-cell volume for the alloys $Pr_{1-x}R_xCu_2Si_2$ (R = La and Y). A line is drawn through the points as a guide to the eye.

From the above it is clear that, in the compound under discussion, the quadrupole moment is apparently absent, although the Pr ion, with aspherical charge distribution, is known to exhibit a large quadrupole moment, the free-ion value of which is comparable to those of some of the heavy rare-earth ions [13]. We speculate that the apparent diminishing of the quadrupole moment is due to the screening of the radially extended Pr 4f charge cloud by outer shells [14] (quadrupolar Kondo effect? [15]) or non-thermal quadrupole fluctuations; these fluctuations can arise from the mixing of the higher-lying crystal-field levels (associated with different electric quadrupole moments) into the ground state due to enhanced 4f hybridization as a result of 4f spatial overlap [12]. It is worth pointing out that the electric quadrupolar Kondo effect for UBe_{13} is proposed to be responsible for the heavy-electron anomaly [15]. We speculate that this phenomenon causes the heavy-fermion-like heat capacity anomaly [4] in $PrCu_2Si_2$ also.

An observation we make, which is interesting in its own right, is that there is a positive pressure effect on the value of T_N, without any noticeable effect arising from the negative pressure. To demonstrate this, we show the values normalized to Pr concentration in $Pr_{1-x}La_xCu_2Si_2$ and $Pr_{1-x}Y_xCu_2Si_2$ alloys as a function of unit-cell volume in figure 3. Since the ionic radii of Y and Gd are very close to each other, Y and Gd substitutions yield similar values of T_N, as marked also in figure 2. It is clear from these data that the unit-cell volume reduction caused by Y/Gd substitution results in a noticeable decrease of the Néel temperature, while the same magnitude of expansion caused by La substitution does not alter the normalized value of T_N. While the positive pressure dependence is known to result from the spin Kondo effect in Ce systems, such an effect does not seem to be responsible for this depression of T_N in $PrCu_2Si_2$. We rule out the existence of spin Kondo effect in $PrCu_2Si_2$ on the following grounds.

(i) As a signature of the existence of spin compensation effects in Ce systems, a logarithmic increase of the 4f part of the resistivity with decreasing temperature is always observable above T_N [16]. However, there is no evidence for such effects in the 4f-derived resistivity in any of the Pr alloys under investigation even in the dilute limit [4]. Instead, $d\rho/dt$ is positive down to T_N [4].

(ii) The magnetic moment in the magnetically ordered state should be considerably quenched due to the spin-compensation effects compared to the theoretically expected value, as demonstrated in the literature for Ce systems. On the other hand the magnetic moment at 4.2 K in $PrCu_2Si_2$ as determined by neutron diffraction studies [1] is 2.5 μ_B. The theoretical value for the fully degenerate state of trivalent Pr ion is 3.2 μ_B. The experimentally observed value is very large, considering that the theoretical value for the crystal-field-split ground state should be much smaller than 3.2 μ_B.

(iii) The magnitude, compared to the value of T_N, and the sign of the Curie–Weiss temperature should be large and negative respectively in the presence of a strong spin Kondo effect. However, in the Pr alloys under investigation, its value is very small (< 5 K) and the sign is positive in many alloys. Hence the spin Kondo effect is not the main source of the non-magnetic tendency in $PrCu_2Si_2$. We believe that the quadrupolar fluctuations in quenching magnetism may also play a dominant role for the compression (i.e., with increasing hybridization strength [14, 15]), although the pressure dependence of the strength of crystal-field effects [17] can also contribute to this behaviour.

To conclude, the magnetic and the electric quadrupolar properties of $PrCu_2Si_2$ are novel when compared with those in the heavy rare-earth members of this series. In the rare-earth literature, while the spin-compensation (otherwise called spin Kondo) effect is very well known [18], possible quenching of the electric quadrupolar moment and its consequences for the solid state properties have not been thoroughly explored. We hope that the findings for $PrCu_2Si_2$—the absence of a spin Kondo effect and the apparent quenching of the quadrupolar moment—will motivate future investigations looking for similar materials, which may eventually lead to new aspects of rare-earth physics.

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In these articles, we have shown a strong positive pressure dependence of the heat capacity above T_N. However, we do not see such a decrease of heat capacity due to the negative chemical pressure exerted by La substitution for Pr (details to be published). These properties are typical of heavy-fermion systems. We wonder whether the positive pressure effect is the result of a simultaneous increase in the quadrupolar fluctuation frequency, following the ideas in [15].

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