Magnetic Properties of Polycrystalline PrCu₂: A Quadrupolar Transition Material

Jesús Rodríguez Fernández
CITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain
Reprint requests to Prof. J. Rodríguez Fernández. Fax: +34 942 201402. E-mail: rodrigufj@unican.es


Dedicated to Dr. Bernard Chevalier on the occasion of his 60th birthday

Polycrystalline PrCu₂, which has a quadrupolar transition at 7.7 K, has been investigated using electrical resistivity, magnetization and dilatometry techniques. To study dilution effects, two solid solutions of PrCu₂, (Pr₀.8La₀.2)Cu₂, and (Pr₀.8Y₀.2)Cu₂, were also studied. The quadrupolar transition decreases in temperature with doping, while it increases slightly with the magnetic field. In resistivity and thermal expansion, the magnetic contributions show a clear evidence of crystal field excitations. The analysis of both properties provided benchmark values of the Debye temperature and Grüneisen parameters.

Key words: Quadrupolar Effects, PrCu₂, Magnetic Properties, Electrical Resistivity, Crystal Field

Introduction

When ions with localized electrons such as in 4f or 5f shells have a nonmagnetic ground state, i.e. no dipolar moment in the ground state, the ions usually remain paramagnetic down to very low temperatures where ordering of nuclear moments might occur and induce electronic moments as in Pr. However, as recently pointed out [1], the ions can also undergo another type of transition induced by asymmetric charge distribution of f electrons, a so called quadrupolar transition. The nature of this quadrupolar transition is very interesting and not yet fully understood. Until now, quadrupolar transitions have been extensively studied in systems with cubic symmetry. However, this transition was also recently found to exist in compounds such as UPd₃ [2] and PrCu₂ [3, 4] with different symmetry.

PrCu₂ crystallizes in the orthorhombic KHg₂-type which can be regarded as a distorted hexagonal AlB₂ structure where the orthorhombic b axis is the hexagonal c axis of the AlB₂ structure. The C₂ᵥ local symmetry at the Pr site of PrCu₂ splits the nine-fold degenerate multiplet ⁹H₄ of the Pr³⁺ ion into nine singlets. Although the ground state is expected to be non-magnetic, it has a non-zero quadrupolar moment. It appears that the energy separation between the two lowest singlets decreases below 8 K, and Pr undergoes a quadrupolar transition. When Pr enters the quadrupolar ordered phase, quadrupole moments are coupled to each other through lattice strains leading to a crystal symmetry transformation from orthorhombic to monoclinic [5]. With lowering the temperature further, the material becomes antiferromagnetically ordered at 54 mK, which involves both the conduction electron and the nuclear spins [6–8]. Recently, muon spin rotation spectroscopy has demonstrated that this magnetic order continues to be present, at least on a short-range scale, up to at least 60 K, the quadrupolar-quadrupolar coupling being the proposed driving mechanism [9].

Naturally, crystal field excitations of PrCu₂ have been a central issue regarding the quadrupolar transition and were studied intensively using different techniques. Early specific heat measurements [10] indicated that the separation between the first two levels is Δ₁ ≪ 7 K at T ≥ 8 K and Δ₁ ∼ 15 K at 0 K. On the other hand, inelastic neutron studies [11] gave a more accurate estimate for the first four levels; separations between the ground state and the three excited states are Δ₁ = 6 K, Δ₂ = 6 K and Δ₃ = 15 K. These values change slightly below 8 K to Δ₁ = 3 K, Δ₂ = 12 K and Δ₃ = 15 K.

Using susceptibility and magnetization results, two groups [12, 13] independently proposed similar level schemes with total crystal field splittings of 316
Table 1. Cell parameters and volume of the compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>R布拉格</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrCu₂</td>
<td>4.411(3)</td>
<td>7.058(4)</td>
<td>7.448(4)</td>
<td>231.9(5)</td>
<td>0.13</td>
</tr>
<tr>
<td>(Pr₀.8La₀.2)Cu₂</td>
<td>4.420(4)</td>
<td>7.117(5)</td>
<td>7.471(6)</td>
<td>235.0(6)</td>
<td>0.17</td>
</tr>
<tr>
<td>(Pr₀.8Y₀.2)Cu₂</td>
<td>4.387(4)</td>
<td>7.022(6)</td>
<td>7.411(5)</td>
<td>228.3(6)</td>
<td>0.19</td>
</tr>
<tr>
<td>YCu₂</td>
<td>4.305(3)</td>
<td>6.876(5)</td>
<td>7.296(5)</td>
<td>216.0(5)</td>
<td>0.15</td>
</tr>
</tbody>
</table>

and 230 K. However, in both cases, the lowest energy levels do not compare well with the inelastic neutron results. Incorporating the inelastic neutron results with susceptibility data, another level scheme was proposed by Ahmet et al. [3] with a total splitting energy nearly twice that given in refs. [12] and [13].

High-field magnetization and deHaas-van Alphen (dHvA) experiments have shown that PrCu₂ has a new type of metamagnetic transition along the c axis [14, 15]. According to these results, a magnetic hard axis (c axis) becomes an easy axis (a axis), and vice versa, above the metamagnetic transition. The conversion of easy and hard axes has been reported only for DyCu₂ [16] of the same orthorhombic PrCu₂ structure. The physical origin of the axis conversion has been interpreted in terms of the rotation of quadrupolar moments on the ac plane, which appears to be easier due to the similarity between the orthorhombic and the hexagonal AlB₂-type structure of PrCu₂ as mentioned before.

Regarding our present contribution to the study of this material, it is worth mentioning that there have been relatively few reports on the macroscopic properties of polycrystalline PrCu₂ between r.t. to lower temperatures. It is the aim of this communication to report susceptibility, thermal expansion and resistivity data of PrCu₂ between 2 and 300 K and to discuss the crystal field effects seen in these macroscopic measurements. The effects of Pr dilution have been studied as well. Because LaCu₂ has a different crystal structure, we used YCu₂ with the same KHg₂-type structure as our non-magnetic material.

Experimental Details

Stoichiometric amounts of Pr (99.99 %), Y (99.99 %) and Cu (99.99 %) were melted using an induction furnace under high vacuum. We subsequently made X-ray powder diffraction measurements (XRD) of all the samples using Bragg-Brentano geometry and CuKα radiation. The electrical resistivity was measured on parallelepiped samples using a standard ac four-point technique [17] between 2 K and r.t. For magnetic measurements, we used a SQUID magnetometer (Quantum Design, MPMS7) from 2 K to r.t. and fields up to 7 T. Thermal expansion was measured between 10 and 300 K using a strain gauge technique at Universidad de Cantabria and between 1.8 and 30 K using a capacitance cell at University College, London. High field measurements were made using an extraction magnetometer of the high magnetic field laboratory, Grenoble.

Results and Analysis

X-Ray diffraction studies

XRD patterns of the compounds were measured and then analyzed by means of the Rietveld method using the program FULLPROF [18]. We found that all samples were well crystallized, presenting a single phase (space group Imma) with lattice parameters given in Table 1. The lattice parameters of PrCu₂ are in agreement with those previously reported. La substitution increases the cell volume whereas Y substitution reduces it, as expected from the different ionic radii: Pr³⁺ (1.013 Å), La³⁺ (1.061 Å) and Y³⁺ (0.88 Å).

Electrical resistivity

A plot of the temperature dependence of the electrical resistivity for all compounds is shown in Fig. 1. Resistivity of PrCu₂ has a well defined change of curvature at \( T_{Q} = 7.7 \) K which corresponds to the quadrupolar order transition. Although the resistivity continues
to decrease below 2 K, the residual resistivity ($\rho_{\text{res}}$) can be estimated by an extrapolation to $T = 0$ K from the data above 2 K. We recall that residual resistivities usually follow the Nordheim rule with doping [19]. This is the case for the Y-doped sample, which has a $\rho_{\text{res}}$ value higher than that observed for pure PrCu$_2$ (see Table 2). However, it is unexpected to have $\rho_{\text{res}}$ of Pr$_{0.9}$La$_{0.1}$Cu$_2$ lower than that of the pure compound. This feature evidences that in spite of the additional chemical disorder due to La substitution, the total lattice disorder is lower in Pr$_{0.9}$La$_{0.1}$Cu$_2$ than in PrCu$_2$, indicating a better crystallization of the 20 % La sample.

Resistivity of YCu$_2$ shows a typical metallic behaviour due to electron-phonon scattering. It can be fitted using the Grüneisen-Bloch law (full line in Fig. 1) with a Debye temperature $\Theta_D = 163$ K. Allowing for corrections due to the mass difference between Y and Pr, we estimate that the Debye temperatures are 147 K for PrCu$_2$ and 149.4 K for Pr$_{0.9}$La$_{0.1}$Cu$_2$. High-temperature slopes $\beta = \frac{d\rho}{dT}$ are almost the same for all three compounds and similar to those found in REPt (RE = rare earth element) compounds, $\beta = 0.125$ $\mu\Omega\text{cm}^{-1}$ [20], the only exception being the Y-doped one which has a lower value of $\beta$.

Using the $\Theta_D$ and $\beta$ values we can first calculate the phonon contributions $\rho_{\text{phon}}$ for each compound using the Grüneisen-Bloch law and, subsequently, the magnetic resistivity from the relationship $\rho_m = \rho - \rho_{\text{res}} - \rho_{\text{phon}}$ (for details see ref. [21]). Fig. 2 shows magnetic resistivities obtained from the procedure just described. In the magnetic resistivity of PrCu$_2$, we observe one clear anomaly around 7 K corresponding to the quadrupolar transition, followed by a noticeable reduction of $\rho$ upon decreasing $T$ (see the insert in Fig. 2). With doping, this anomaly at low temperature gets subdued considerably, and we do not observe a clear anomaly for the doped sample although the resistivity curvature increases at lower temperatures. From the magnetization data to be discussed below we found that the transition temperature moves towards lower temperatures upon doping. One noteworthy point about the general shape of the resistiv-

Table 2. Electrical resistivity data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\rho_{\text{res}}$ ($\mu\Omega\text{cm}$)</th>
<th>$\frac{d\rho}{dT}$ ($\mu\Omega\text{cm K}^{-1}$)</th>
<th>$\rho_m$ ($\mu\Omega\text{cm}$) at 300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>YCu$_2$</td>
<td>5.1</td>
<td>0.122</td>
<td>13</td>
</tr>
<tr>
<td>(Pr$<em>{0.9}$La$</em>{0.1}$)Cu$_2$</td>
<td>3.5</td>
<td>0.122</td>
<td>9.8</td>
</tr>
<tr>
<td>(Pr$<em>{0.9}$Y$</em>{0.1}$)Cu$_2$</td>
<td>17.2</td>
<td>0.101</td>
<td>8</td>
</tr>
<tr>
<td>Pr$_2$</td>
<td>0.6</td>
<td>0.128</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Temperature dependence of the magnetic resistivities. The insert shows the low temperature part.

We can analyze the magnetic resistivity data further, we used a model given by Rao and Wallace [23], according to which the magnetic resistivity can be written in the following form:

$$\rho = \rho_m + \frac{2}{J(J+1)} \sum_{m_i,m_i'} |\langle m_i'|sJ|m_i\rangle|^2 p_i f_{ii},$$

where $p_i = \frac{\exp[-E_i/k_B T]}{\sum_j \exp[-E_j/k_B T]}$ and

$$f_{ii} = \frac{2}{1 + \exp[-(E_i - E_{i'})/k_B T]}$$

Using this formula we calculated the $\rho_m(T)$ contribution for PrCu$_2$. We compare the calculated $\rho_m(T)$ val-
Fig. 3. Comparison between experimental and calculated $\rho_m(T)$. The CEF parameters for the a, b and c curves are taken from references [12, 13] and [3], respectively.

ues with the experimental results in Fig. 3. Lines a and b are for calculated results using crystal field parameters given in refs. [12] and [13], respectively. We also calculated the magnetic resistivity using the CEF parameters from ref. [3] (line c in Fig. 3). Qualitatively the models account for the increase of the resistivity with temperature in the paramagnetic region. However, quantitatively none of the three CEF models can fit properly the experimental data although overall line c is in better agreement with the experimental results. The largest differences between experimental data and the model are found in the low-temperature region, probably associated with the influence of the short range magnetic order observed up to 60 K [9] by muon spin rotation spectroscopy.

**Magnetization and susceptibility**

Fig. 4 shows the magnetization measured in an applied magnetic field of $B = 0.1$ T. Measurements were made with increasing temperature after cooling the sample to 2 K in zero field. Magnetization of PrCu$_2$ shows a slight upturn at $T = 7.7$ K, corresponding to the quadrupolar transition. In Pr$_{0.9}$La$_{0.2}$Cu$_2$ and Pr$_{0.9}$Y$_{0.2}$Cu$_2$, there are slight upturns at lower temperatures. This behaviour is clearly revealed in the derivative of the magnetization (insert of Fig. 4), where a negative peak is observed for all three compounds. Thus, quadrupolar transition temperatures for Pr$_{0.9}$La$_{0.2}$Cu$_2$ and Pr$_{0.9}$Y$_{0.2}$Cu$_2$ are found to be 4.9 and 5.4 K, respectively. It is important to point out that alloying effects in other quadrupolar transition material, such as UPd$_3$, destroy the quadrupolar order even with percentages lower than 5 % [24].

To study the field dependence of the quadrupolar transition of PrCu$_2$, we measured the temperature dependence of the magnetization up to 7 T. Fig. 5 shows the derivative of the magnetization at several fields. The position of the peak changes very little with fields up to 7 T. Regarding this field dependence of the quadrupolar transition of PrCu$_2$, it is worth mentioning that in TmCd the quadrupolar transition temperature increases appreciably even with a small magnetic field [25].

Although all the proposed crystal field schemes for PrCu$_2$ have an overall energy level splitting larger than 230 K, the temperature dependence of the inverse magnetic susceptibility is almost linear down to 20 K.
Table 3. Main magnetic parameters.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magnetization per Pr ion (µB) at 2 K and 0.1 T</th>
<th>θp (K)</th>
<th>µeff (µB)</th>
<th>Χ₀ (emu mol⁻¹)</th>
<th>ΘQ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrCu₂</td>
<td>0.0271</td>
<td>−2.5</td>
<td>3.56</td>
<td>−2.2 × 10⁻⁴</td>
<td>7.9</td>
</tr>
<tr>
<td>(Pr₀.8La₀.2)Cu₂</td>
<td>0.0214</td>
<td>−10.4</td>
<td>3.50</td>
<td>−6.6 × 10⁻⁴</td>
<td>4.9</td>
</tr>
<tr>
<td>(Pr₀.8Y₀.2)Cu₂</td>
<td>0.0358</td>
<td>3.7</td>
<td>3.51</td>
<td>−4.8 × 10⁻⁴</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Fig. 5. Temperature derivative of the PrCu₂ susceptibility measured at different applied fields.

Fig. 6. Temperature dependence of the inverse magnetic susceptibility. The straight lines are fits to the Curie-Weiss law above 20 K. For the sake of clarity, the data for each compound are shifted upwards.

Fig. 7. Magnetic moment versus magnetic field at T = 2, 10 and 30 K.

Fig. 8. Magnetic moment versus temperature plot (not shown here). Although we acknowledge that data get somewhat scattered with increasing fields, and it becomes difficult to get dM/dT with reasonable accuracy as previously obtained with the SQUID data below 7 T, it appears that the quadrupolar transi-
Fig. 8. Magnetization curves of PrCu₂ at several temperatures up to 20 T. In circles are shown for comparison some SQUID data up to 7 T.

Fig. 9. Linear thermal expansion coefficients of PrCu₂ and YCu₂. The solid line represents the Debye fit whereas the dashed line represents the estimated phonon contribution of PrCu₂.

Thermal expansion

We measured the thermal expansion of the compounds PrCu₂ and YCu₂. The relative change of length ΔL/L between 4 and 300 K is 4200 × 10⁻⁶ and 5500 × 10⁻⁶ for YCu₂ and PrCu₂, respectively. Fig. 9 shows the temperature dependence of the thermal expansion coefficient α = (1/L) (dL/dT). The curve of the non-magnetic YCu₂ shows a typical behaviour due to phonons. We can fit the YCu₂ data using a relation between thermal expansion and specific heat (Cᵥ) α = ΓχCᵥ/3Vm, where Γ is the Grüneisen parameter, χ is the compressibility and Vm the molar volume.

Thermal expansion coefficient of PrCu₂

Fig. 10. Magnetic contribution to the linear thermal expansion coefficient of PrCu₂. The insert shows the low temperature part.

The best fit (solid line in Fig. 9) is obtained with a Debye temperature ΘD = 340 K and Γχ = ∂lnΘD/∂P = 2.8 Mbar⁻¹. This ΘD is larger than that calculated using the resistivity. Differences between ΘD values obtained using different techniques have previously been reported for other compounds [26]. For example, for YNi and LaNi the Debye temperature obtained from thermal expansion is also higher than that from resistivity [27]. At r.t. the α value is lower for PrCu₂ than for YCu₂. This, we think, is due to the smaller value of Γχ for PrCu₂ (Γχ = 2.6 Mbar⁻¹) than that for YCu₂ (Γχ = 2.8 Mbar⁻¹). In order to extract the magnetic contributions to the thermal expansion (αₘ), we have subtracted the phonon contribution αₘag = α − αₘphon using the data for YCu₂. We estimated the upper limit for the phonon contribution from the Debye model after performing the corresponding mass corrections [28] and using the maximum possible value for Γχ (dotted line in Fig. 9). The magnetic contribution is shown in Fig. 10. A narrow and strong peak appears at the quadrupolar transition, indicating a large reduction in the cell volume when the quadrupolar moments become ordered. In the paramagnetic region, we observed a broad hump centred around 50 K, which is likely to be due to crystal field effects. We analyzed the hump using the phenomenological model given in [29]: according to this model the contribution of the CEF splitting to α(αₘag) follows the equation:

αₘag = \frac{\chi}{3Vmk_B^2} \langle E_i^2 Γ_i \rangle - \langle E_i \rangle \langle ε_i Γ_i \rangle

where k_B is the Boltzmann constant, Γ_i is the Grüneisen parameter, and χ is the Grüneisen parameter.
Conclusions

The substitution of Pr by 20 % La/Y does not modify the crystalline structure of pure PrCu$_2$ and only increases/decreases the cell volume in agreement with the different ionic radii. The quadrupolar transition does not disappear with doping, but shifts from $T = 7.7 \text{ K}$ to lower temperatures nearly in proportion to the Pr percentage. The small difference between the transition temperatures in Pr$_{0.8}$La$_{0.2}$Cu$_2$($T_Q = 4.9 \text{ K}$) and Pr$_{0.8}$Y$_{0.2}$Cu$_2$($T_Q = 5.4 \text{ K}$) could be due to the different Pr–Pr distances in both compounds. In this sense, the increase of the Pr–Pr distance in the La doped compound with respect to the Y doped one reduces the quadrupolar interactions between the Pr ions and thus decreases the temperature of the quadrupolar transition. In addition we have found that the quadrupolar transition in PrCu$_2$ is very robust against magnetic field and does not disappear up to 20 T. Regarding the metamagnetic transition observed at high magnetic fields in single crystalline compounds, we have not found any sign of it in our polycrystalline samples. The electrical resistivity and the thermal expansion provide clear evidence of crystal field excitations at high temperatures. For the resistivity, neither of the previously proposed CEF models can account quantitatively for the experimental data, however for the thermal expansion the model proposed in [12] fits our results reasonably well. These analyses, in which the separation of the phonon and magnetic contributions was necessary, have allowed us to obtain benchmark values for Debye temperatures and Grüneisen parameters.

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References


