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Magnetic properties of clathrate-like compound $Pr_3Pd_{20}Ge_6$

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Abstract

The magnetic properties of clathrate-like compound $Pr_3Pd_{20}Ge_6$ with the cubic C_6Cr_{23}-type crystal structure have been investigated by magnetic susceptibility and magnetization measurements. The temperature dependence of magnetic susceptibility of $Pr_3Pr_{20}Ge_6$ is quite isotropic regarding to the magnetic field direction and follows Curie–Weiss law above 2 K. The magnetization processes were reproduced by assuming that the crystal field ground states are doublet Γ_3 in 4*a*-site and triplet Γ_5 in 8*c*-site.

Keywords: $Pr_3Pd_{20}Ge_6$; Magnetic susceptibility; Magnetization; Crystal-field ground state; Clathrate

The ternary intermetallic compounds $R_3Pd_{20}Ge_6$ (R = rare-earth ions) show a variety of the physical properties depending on the kinds of rare-earth ion R. These compounds belong to the cubic C_6Cr_{23}-type crystal structure (space group $Fm\bar{3}m$) and have two different crystallographic sites 4*a* (point group O_h) and 8*c* (T_d) of rare-earth ions as shown in Figs. 1 and 2 [1]. $Ce_3Pd_{20}Ge_6$ shows the dense Kondo behavior in the electrical resistivity and in the specific heat, a quadrupolar ordering at $T_Q \sim 1.2$ K and an antiferromagnetic one at $T_N = 0.75$ K [2–4]. $R_3Pd_{20}Ge_6$ (R = Nd, Dy and Tb) show successive antiferromagnetic orderings due to the existence of the two kinds of rare-earth ion sites [5–7].

$Pr_3Pd_{20}Ge_6$ have been studied extensively by magnetic, ultrasonic and inelastic neutron scattering experiments. The inelastic neutron scattering have detected the energy transfer from only one site and have revealed the crystal field levels Γ_3 (0 meV)–Γ_5 (0.5 meV)–Γ_4 (4.0 meV)–Γ_1 (9.6 meV) [8]. The magnetic properties indicate that the crystal field ground state is Γ_3 doublet at least in one of the rare-earth sites [9]. The temperature dependence of elastic constants $(c_{11} - c_{12})/2$ shows a Curie-type softening toward lower temperature, which means the ground state to be doublet Γ_3 [10]. Though the magnetic- and elastic properties at low temperature are not fully described by the CEF levels reported by the inelastic neutron scattering. For example the temperature dependence of the magnetic susceptibility below 2 K and the temperature dependence of elastic constant c_{44} cannot be reproduced by Γ_3 doublet ground state [9,10]. Therefore, to investigate the 4f-electronic ground state is main issue in this compound. We report the magnetic properties and propose the 4f-electronic ground state of Pr ions based on the results of magnetic susceptibility and magnetization measurements.

Polycrystalline samples of $Pr_3Pd_{20}Ge_6$ were synthesized by arc-melting the stoichiometric constituents on a water-cooled copper hearth under argon atmosphere. Single crystalline samples of $Pr_3Pd_{20}Ge_6$ were prepared by the floating-zone method under argon atmosphere using the stick-type shaped poly-crystalline samples with the diameter of 4 mm. Magnetic susceptibility and magnetization were measured by the superconducting quantum interference device (quantum design) from 2 to 300 K.

Fig. 3 is the experimental result (a) and calculated one (b) of X-ray powder diffraction of $Pr_3Pd_{20}Ge_6$. We computed the X-ray scattering intensity using the software RIETAN-2000 [11]. The obvious other phase was not observed in our sample.

Fig. 4 shows the temperature dependence of the magnetic susceptibility χ and the inverse susceptibility $1/\chi$ of

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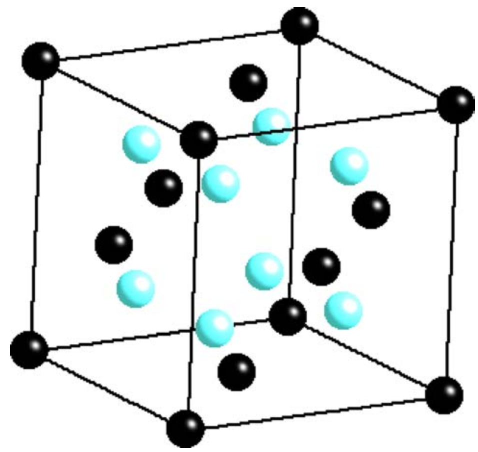

Fig. 1. Rare-earth sites in $R_3Pd_{20}Ge_6$. Black marks and white ones are 4*a* and 8*c* site, respectively. Pd and Ge ions are omitted for clarity.

$Pr_3Pd_{20}Ge_6$ at fields of 0.1 T along the [0 0 1], [1 1 1] and [1 1 0] axes. The inset shows the low-temperature part of χ and $1/\chi$ in expanded scale. Solid lines in Fig. 4 are the calculation results based on the crystal-field level, which is described later. The observed magnetic susceptibility shows a quite isotropic nature regarding to the magnetic field direction, which has been previously reported in ref. [9]. The magnetic susceptibility obeys the Curie–Weiss law in all the temperature range down to 2 K. At low temperature as shown in the inset of Fig. 4, the magnetic susceptibility shows the Curie–Weiss behavior, not van-Vleck one. The lower-temperature magnetic susceptibility by Nakayama et al. also shows the Curie–Weiss behavior down to 0.5 K and deviates from the calculated results based on the doublet Γ_3 ground state, which shows the temperature independent behavior below 2 K [9]. These results indicate that the ground state is magnetic state or including magnetic state.

To investigate the magnetic properties in higher magnetic fields we have measured field dependence of magnetization. Fig. 5 displays the magnetization of $Pr_3Pd_{20}Ge_6$ under fields along the [0 0 1], [1 1 1] and [1 1 0] axes at 1.9 K. The open marks and the closed ones in Fig. 5 are the experimental results and calculated one, respectively. Magnetizations

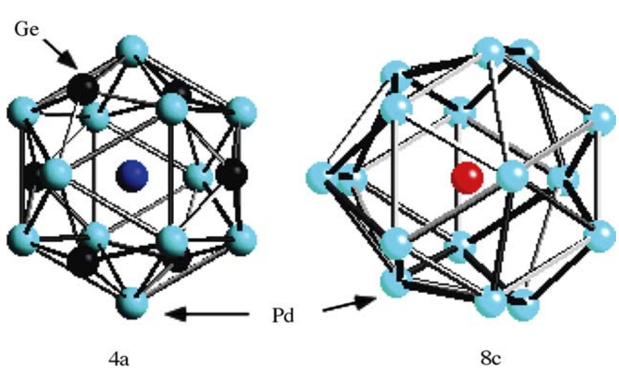

Fig. 2. Ligands of 4*a* and 8*c* sites of rare-earth ions. The centers are occupied by rare-earth ions.

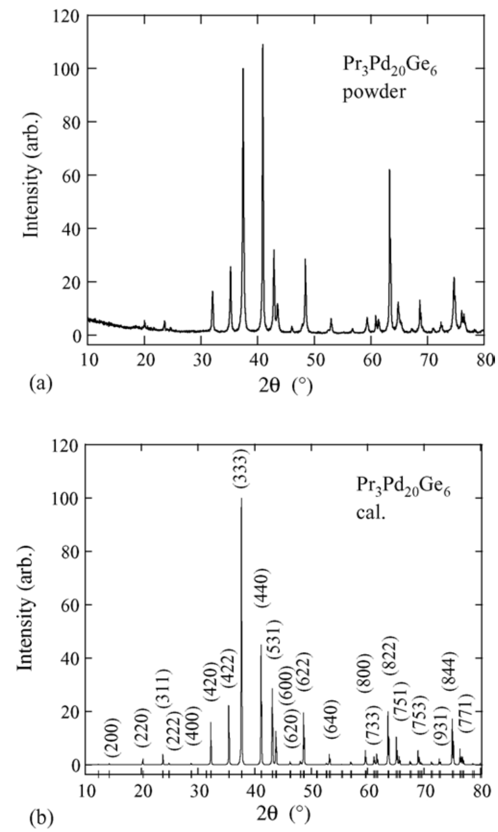

Fig. 3. The experimental result (a) and calculated one (b) of the X-ray powder diffraction pattern of $Pr_3Pd_{20}Ge_6$.

increase linearly below 1 T. The anisotropy was observed above 1 T. The previous report by ultrasound measurements revealed that the elastic softening in $(c_{11} - c_{12})/2$, which means the crystal field ground state to be Γ_3 doublet. Although, the experimental results of the elastic constant c_{44} and the magnetic susceptibility shows the deviation from the calculation based on the Γ_3 doublet ground state. This result implies the possibility that the ground state includes the state besides Γ_3 doublet. In addition, the CEF level scheme

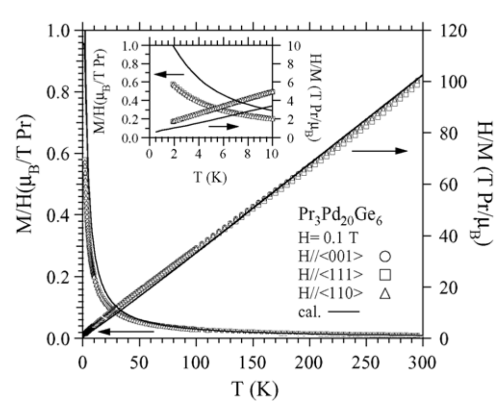

Fig. 4. The temperature dependence of the magnetic susceptibility of $Pr_3Pd_{20}Ge_6$ in fields of 0.1 T along the [0 0 1], [1 1 0] and [1 1 1] axes. The solid line is the calculated result of magnetization in fields along the [0 0 1] axis based on the CEF level in text.

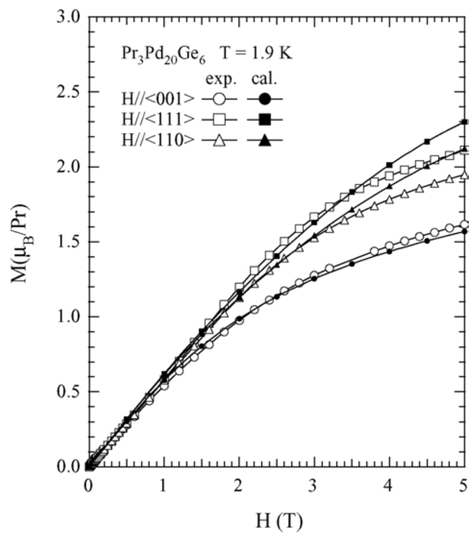

Fig. 5. The magnetic field dependence of the magnetization of $Pr_3Pd_{20}Ge_6$ in fields along the [0 0 1], [1 1 1] and [1 1 0] axes at 1.9 K. The open symbols and closed ones are the experimental result and calculated ones based on the CEF levels described in Fig. 6, respectively.

in which the ground state is doublet Γ_3 cannot reproduce our results of magnetization processes. On the other hand, the simple CEF level in which the ground state is triplet Γ_5 leads the overestimation of the magnetization in the all field directions. Therefore, we assumed that the ground states are different in the two sites 4*a* and 8*c*. However the inelastic neutron scattering by Keller et al. detected the energy transfer from the single site of Pr ions. Therefore we chose the CEF parameters, which make the ground state doublet Γ_3 being replaced by the first excited triplet Γ_5 and the higher-energy states lying at the fixed energies as shown Fig. 6. Keller et al. estimated the CEF parameters to be $x = -0.709021$ and $W = -1.8894$ K in the Lea–Leask–Wolf's notation [12]. To exchange the ground-state doublet Γ_3 and the first excited triplet Γ_5, we chose the CEF parameters to be $x = -0.76$ and $W = -2.05041$ K. The solid marks with lines in Fig. 5 are calculated results based on the CEF level in Fig. 6. By assuming this CEF level scheme the magnetization process are reproduced more quantitatively than in the case of simple Γ_3 ground state or simple Γ_5 ground state. Moreover, by assuming this CEF level scheme the temperature dependence of magnetic susceptibility in Fig. 4 are also reproduced qualitatively. The calculated result indicated by lines in Fig. 4 is similar to the lower temperature part of the magnetic susceptibility by Nakayama et al. The suggested crystal field ground state has to be checked by the other experimental methods.

We have measured the magnetic properties of the single crystal of the clathrate-like compound $Pr_3Pd_{20}Ge_6$. Our experimental results of the magnetic susceptibility and the magnetization confirmed the data previously reported. The temperature dependence of the magnetic susceptibility shows a quite weak anisotropy in the three principal axes of the cubic crystal. The temperature dependence of magnetic susceptibility follows Curie–Weiss law and shows no indication of the van-Vleck paramagnetism above 2 K. This result means that the crystal field ground state is not simply non-magnetic doublet Γ_3, but includes the magnetic state. We tried to fit the magnetic susceptibility and magnetization data by assuming that the 4*a*- and 8*c* sites have different ground states. The magnetization and magnetic susceptibility were reproduced by assuming that the ground state of the 4*a* site is magnetic triplet Γ_5 and that of 8*c* site is non-magnetic Γ_3 doublet.

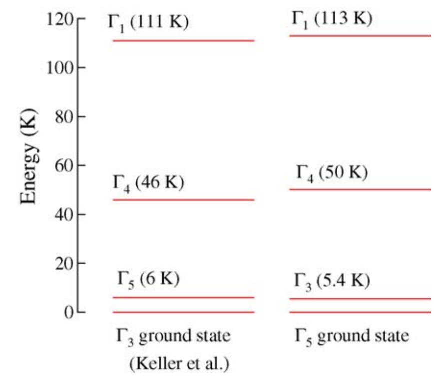

Fig. 6. CEF energy level scheme. Left hand side is determined by the inelastic neutron scattering (4*a* site) and right hand side is proposed from the results of magnetization measurements (8*c* site).

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