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Jahn-Teller-like phase transition of $TmPd_3S_4$ around 200 K

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We report a Jahn-Teller-like phase transition in a synthesized metallic compound, $TmPd_3S_4$, of the cubic $NaPt_3O_4$ structure type. The transition causes a very large thermal hysteresis in the electrical resistivity between 120 and 230 K and a modulated structure with a modulation vector of about $\frac{1}{8}a^*$ (a^*: reciprocal-lattice unit vector) at lower temperatures which was revealed by a low-temperature x-ray powder diffraction. Analyses on the low-temperature specific heat and the magnetic susceptibility suggest that the compound becomes an exchange-induced moment antiferromagnet ($T_N = 1.1$ K) by the nonmagnetic singlet ground state of Tm^{3+} ions. [S0163-1829(99)51146-6]

Rare-earth (R) palladium bronzes, RPd_3S_4, of the cubic $NaPt_3O_4$-type structure with the space group $Pm3n$ (No. 223) have been characterized as paramagnetic metals for several R elements.[1–4] We have recently confirmed that this structure type extends throughout the series of R elements except Lu.[5] In this crystal structure, the R atom occupies the $2a$ site with a cubic point group, T_h, of high symmetry. An orbitally degenerated crystalline-electric-field (CEF) ground state is, therefore, anticipated for R ions of these palladium bronzes. The orbital degeneracy is often lifted at low temperatures by a cooperative Jahn-Teller transition or a quadrupolar ordering, which has been actually observed in some rare-earth compounds such as $TmVO_4$,[6] CeB_6,[7] and $Ce_3Pd_{20}Ge_6$.[8] Our systematic investigations on RPd_3S_4 in fact revealed that the compounds of $R=$ Sm, Tb, Dy, Ho, and Er presumably show quadrupolar ordering below about 8 K.[5] Furthermore we have found[5] that these ordering temperatures approximately scale with $J(J+1)(2J-1)(2J+3)\alpha_J^2$, where J is the total angular momentum and α_J the Stevens factor, as theoretically predicted by taking into account a quadrupolar pair interaction mediated through conduction electrons.[9] This system has thereby provided us the first opportunity for testing such scaling for quadrupolar ordering.

Unlike the other members of RPd_3S_4,[5] $TmPd_3S_4$ does not, however, show quadrupolar ordering, but a Jahn-Teller-like phase transition as high as 200 K. The transition causes a very large thermal hysteresis in the electrical resistivity between 120 and 230 K and a modulated structure at low temperatures. In this paper, we present the experimental results on these peculiar properties of $TmPd_3S_4$ which are very unique among the series of RPd_3S_4.

The sample was prepared by prereacting Tm and Pd powders with sulphur in an evacuated quartz tube for two days at 900 °C. The product was ground in an agate mortar and pressed into a pellet. It was further reacted in an evacuated quartz tube for 3 days at 900 °C. The sample quality was checked at room temperature by a x-ray powder diffraction which showed the $NaPt_3O_4$-type structure as the main phase and weak reflections of impurity phase of PdS. The lattice parameter of $TmPd_3S_4$ was determined to be $a=6.630$ Å which follows well the lanthanide contraction of the free trivalent R ions for the series RPd_3S_4.

Figure 1 shows the temperature dependence of the reciprocal magnetic susceptibility, $1/\chi(T)$, measured on cooling by a commercial superconducting quantum interference device (SQUID) magnetometer under a magnetic field of 3 kOe between 2 and 300 K. $1/\chi(T)$ follows a Curie-Weiss law represented by the solid line in the figure, although a very small thermal hysteresis is observed between 170 and 240 K as shown in the inset. The effective Bohr magneton and the Weiss temperature were estimated to be $7.12\mu_B$ and -13 K by fitting the data above about 70 K, respectively. The former value is only slightly smaller than the theoretical one ($7.57\mu_B$) for the free trivalent ion. Tm ions in $TmPd_3S_4$ are hence considered to be trivalent and the lattice parameter is consistent with the lanthanide contraction of the free R^{3+} ion, as mentioned above.

The temperature dependence of the electrical resistivity, $\rho(T)$, measured by a conventional dc four-probe method

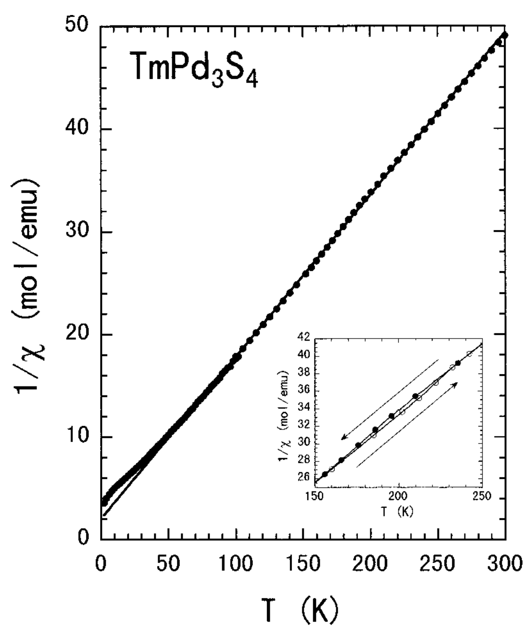

FIG. 1. The temperature dependence of $1/\chi$ of $TmPd_3S_4$ measured on cooling. The solid line represents a Curie-Weiss law fitted above about 70 K. The inset shows the thermal hysteresis observed between 170 and 240 K.

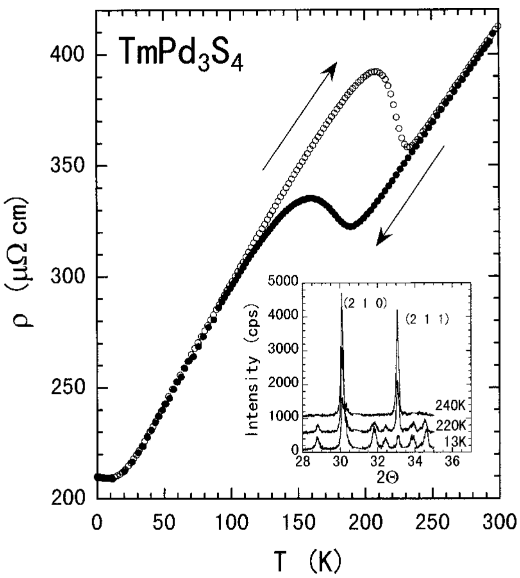

FIG. 2. The temperature dependence of ρ of $TmPd_3S_4$ measured with increasing (○) and decreasing (●) temperature. The inset shows the low-temperature x-ray powder diffraction pattern measured on heating. Only indices of the fundamental reflections are given. Several weak reflections of impurity phases are eliminated and the origin for the ordinate is shifted for clarity.

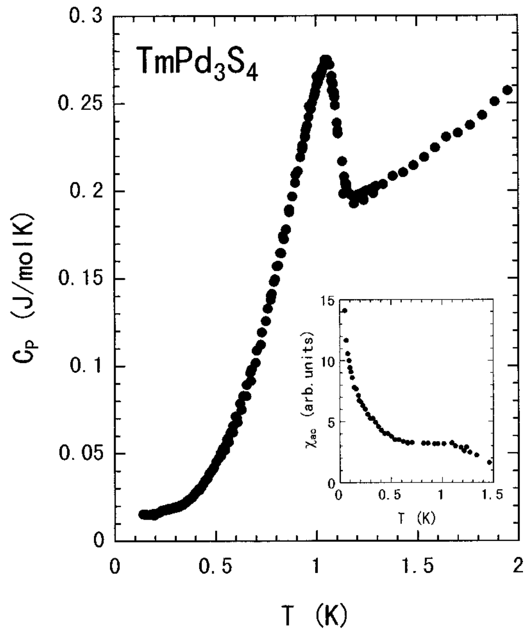

FIG. 3. The low-temperature C_P of $TmPd_3S_4$. The inset shows the low-temperature χ_{ac} showing a small anomaly around 1.1 K.

with both decreasing and increasing temperature between 40 mK and 300 K is shown in Fig. 2. ρ(T) shows a metallic conductivity, but a very large thermal hysteresis is remarked between 120 and 230 K, where $1/\chi$(T) shows a very small one as shown in the inset of Fig. 1. The specific heat, C_P, measured by a semi-adiabatic heat-pulse method from 170 to 300 K by once cooling down to about 80 K clearly demonstrated a distinct anomaly of second order at 230 K with an entropy change of about $\frac{1}{2}$ $R\ln 2$. We also confirmed that the supercooled state does not show any anomaly above 210 K. The extremely weak anomaly of χ around 200 K as mentioned above suggests that this phase transition is not of magnetic origin but presumably related to a structural deformation. In order to clarify it, we have performed a low-temperature x-ray powder diffraction from 13 to 300 K in a ^{4}He gas flowing cryostat. Many satellite reflections appear besides fundamental ones on heating between 220 and 240 K, as shown in the inset of Fig. 2, where only a part of the spectra is shown for clarity. It is further noted that the temperature interval where the satellite peaks appear corresponds well to the resistive transition on the heating curve of Fig. 2.[10] The intensity of satellite reflections becomes stronger with decreasing temperature at the expense of that of fundamental ones. These results indicate that a modulated crystal structure is induced by the transition causing the large thermal hysteresis. Most of the satellite reflections can be tentatively indexed by assuming a modulation vector, $k \sim \frac{1}{8}a^*$, where a^* is the reciprocal-lattice unit vector. The modulation vector was determined by using about 30 satellite reflections for $25° \leqslant 2\theta \leqslant 60°$. It should be noted here that the lattice parameter determined by the fundamental reflections does not change drastically around 200 K. Although the precise nature and the modulated structure are not known yet at the moment, the appearance of such distinct satellite lines in powder diffraction as in the inset of Fig. 2 may imply that the presumed modulation is due to a displacive modulation of heavy atoms such as R ions induced probably by a strong Jahn-Teller type interaction inferred from the highly degenerated CEF states in RPd_3S_4.[5] At sight the ordering temperature of $TmPd_3S_4$ appears to be very high for rare-earth compounds. The cooperative Jahn-Teller distortions driven by the interaction between the orbital states of R ions and the crystal lattice are usually known to occur at relatively low temperatures compared with those involving transition-metal ions.[6,11] There are, however, scarce examples of rare-earth compounds showing a strong Jahn-Teller effect. We here merely refer to the case of $PrAlO_3$, which is known to exhibit the Jahn-Teller transition at as high as 151 K.[12]

Low-temperature $C_P(T)$ measured from 0.14 to 20 K and the ac magnetic susceptibility, χ_{ac}, measured by an impedance bridge employing a SQUID as a null detector are shown in Fig. 3 and the inset, respectively. These results obviously indicate that $TmPd_3S_4$ undergoes a magnetic transition of second order around 1.1 K. This transition is smeared out under a magnetic field above about 1 T and then of antiferromagnetic (AFM) type. If it is assumed that the point group of the site of Tm ion is not affected by the modulation of the crystal structure and remains cubic symmetry, the 13-fold degeneracy of the J multiplet of the free Tm^{3+} ion splits into two singlets, a doublet, and three triplets under a cubic CEF.[13] The CEF ground state is deduced from the temperature dependence of the magnetic entropy, $S_{mag}(T)$, which is calculated by integrating the magnetic part of C_P,C_{mag}, with respect to the temperature. C_{mag} is obtained by subtracting C_P of $LaPd_3S_4$ from that of $TmPd_3S_4$. S_{mag} attains only 0.13 J/Tm mol K at the Néel temperature of 1.1 K and 3.8 J/Tm mol K at 20 K. This implies that the CEF ground state of Tm^{3+} is the nonmagnetic singlet and the AFM order at 1.1 K is due to exchange-induced moments, as commonly known for magnetic ordering in singlet ground-state systems. For example, Pr_3Tl and Pr_3In are reported as an induced-moment ferromagnet and antiferromagnet with a singlet ground state, respectively.[14] The C_P anomaly of these induced-moment systems is much reduced compared with that of conventional systems[15] and S_{mag} associated with the AFM ordering, for example, is only 0.91 J/Pr mol K,[14] which is somewhat similar to the case of $TmPd_3S_4$, as mentioned above.

We have very recently synthesized and characterized a metallic palladium bronze $TmPd_3S_4$. Our analyses on $C_P(T)$ and $\chi(T)$ indicated that $TmPd_3S_4$ exhibits the exchange-induced moment AFM below 1.1 K due to the nonmagnetic singlet ground state of Tm^{3+} ions. The compound showed a phase transition accompanied by a large thermal hysteresis in $\rho(T)$ between 120 and 230 K. Low-temperature x-ray powder diffraction indicated a modulated structure below the transition, which may be induced by a Jahn-Teller type interaction. The more precise nature of the transition and the modulated structure must be clarified and understanding why only $TmPd_3S_4$ exhibits such a transition of high ordering temperature among the series of RPd_3S_4[5] would be of particular importance. More detailed experiments including the growth of single crystals are presently in progress.

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