Evidence for Strong Quadrupolar Pair Interactions in Rare-Earth Palladium Bronzes $R\text{Pd}_3\text{S}_4$

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(Received 8 July 1999)

We report an evidence of order due to quadrupolar pair interactions, taking place along the rare-earth (R) series of $R\text{Pd}_3\text{S}_4$ slightly above their dipolar magnetic order. Specific-heat measurements proved that the R ions in these bronzes possess highly degenerate ground states, which may cause large orbital effects at low temperatures. The magnetic ordering temperatures much exceed those predicted by the de Gennes scaling at both ends of the R series. The fact suggests that orbital effects dominate over the ordinary exchange-type dipolar interactions. The presumed quadrupolar ordering temperatures, on the other hand, scale with the squared Stevens factor along the R series, indicating that quadrupolar pair interactions via conduction electrons are responsible for the ordering.

It has been known that the separation of spin and charge degrees of freedom plays important roles in the superconducting cuprates and the orbital and charge ordering have recently been confirmed in several transition metal oxides like $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ [1,2]. The importance of the interaction between orbital and spin states originated from f electrons has also been recognized and the resultant charge order or complex spin order in some rare-earth (R) compounds such as Yb_4As_3 [3], CeSb [4], and CeP [5] has been disclosed. In addition, the quadrupolar striction through magnetoelastic coupling, known as the cooperative Jahn-Teller effect in DyVO_4, TmVO_4 [6], and DySb [7], etc., and ordering of quadrupoles via quadrupolar pair interactions in CeB_6 [8], $\text{Ce}_3\text{Pd}_{20}\text{Ge}_6$ [9], TmTe [10], etc., have also been put into evidence. In these phenomena occurring in rare-earth compounds, it is known that the orbital degeneracy of the ground state of R ions subjected under a specific crystalline electric field (CEF) plays a very important role.

It has been pointed out by Levy *et al.* [11] that the structural phase transitions found in TmZn and TmCd are driven by quadrupolar pair interactions via conduction electrons. This assertion was made by fitting the thermal variation of elastic constants of these compounds. If such an interaction is dominant, however, some kind of scaling may be expected to hold for the R series just like the de Gennes scaling for the dipole magnetic interaction of the RKKY type well proved for certain classes of rare-earth metallic compounds. Testing for such a scaling would then be another way to prove the existence of quadrupolar pair interactions. However it would not be usually possible to test scalings because such phase transitions scarcely occur over the R series of compounds within a certain structure type. We herein report a very rare example of such a systematic occurrence along the R series in the palladium bronzes, $R\text{Pd}_3\text{S}_4$.

$R\text{Pd}_3\text{S}_4$ of the cubic NaPt_3O_4 structure type with the space group $Pm3n$ has recently been synthesized [12] and characterized as paramagnetic metals [13–15]. R ions in these compounds which are trivalent except for Eu and Yb

form a body-centered cubic frame with eight sulfur atoms at $(1/4, 1/4, 1/4)$ and two palladium atoms on each cubic face. In this crystal structure, R atoms occupy the $2a$ site with a cubic point group, T_h, of high symmetry. An orbitally degenerated CEF ground state is, therefore, anticipated for R ions of these palladium bronzes. In the present work, we investigated 13 rare-earth sulphides of R being from La to Yb by measuring the specific heat, magnetic susceptibility, and electrical resistivity down to 0.4 K or even lower for some cases [16]. We found that all these sulphides except for LaPd_3S_4 and TmPd_3S_4 have a very degenerate ground state under a cubic CEF and magnetically order at low temperatures, as summarized with some other physical properties in Table I. It is noted here that a successful synthesis of TmPd_3S_4 has never been reported before and it would be a new compound of this series [17]. Most of the heavy-rare-earth compounds exhibit above their magnetic ordering temperature T_m another phase transition of probably nonmagnetic origin, as denoted by T_Q in the Table, which we herein interpret as quadrupolar ordering. In this Letter we demonstrate these interesting low-temperature phenomena by taking the case of DyPd_3S_4 merely as a typical example and will soon report details on the rest of the compounds elsewhere.

The samples were prepared by thoroughly mixing the calculated amount of the sesquisulfide Dy_2S_3, palladium powder, and sulphur in an agate mortar and by heating the mixture sealed in an evacuated silica tube at 1173 K for three days. The sample was slowly cooled to room temperature at the rate of -15 K/h, and then checked by an x-ray powder diffraction using a $\text{Cu}K_\alpha$ radiation. The product was found to be single phased and the lattice parameter of cubic DyPd_3S_4 was 6.647 Å, which is in fairly good agreement with the literature value, 6.636 Å [15].

We found that the magnetic susceptibility $\chi(T)$, measured with a commercial SQUID magnetometer at 3 kOe from 2 to 300 K, does not exhibit any noticeable anomaly down to 2 K and follows a Curie-Weiss law above about 50 K, as shown in the inset of Fig. 1. It, therefore, appears that the magnetic susceptibility does not unfortunately

TABLE I. Physical properties of RPd$_3$S$_4$.

| | a (Å) | Magnetic transition | | T_Q (K) | Effective moment $p_{\text{eff}}(\mu_B/R)$ | Weiss temp. θ (K) | Degeneracy of ground state + low-lying state |
		T_m (K)	Structure				
LaPd$_3$S$_4$	6.744	⋯	⋯	⋯	⋯	⋯	⋯
CePd$_3$S$_4$	6.716	6.0	F	⋯	2.51	−45.4	4
PrPd$_3$S$_4$	6.705	1.8	F	⋯	3.55	−43.3	4(3 + 1)
NdPd$_3$S$_4$	6.693	2.0	AF	⋯	3.78	−63.2	4
SmPd$_3$S$_4$	6.676	2.5	AF	3.0	⋯	⋯	4
EuPd$_3$S$_4$	6.682	3.4	AF	⋯	⋯	⋯	8
GdPd$_3$S$_4$	6.663	5.5	AF	⋯	7.76	−7.1	8
TbPd$_3$S$_4$	6.656	2.5	AF	7.5	9.14	−10.9	4 + α
DyPd$_3$S$_4$	6.647	0.8	F	5.0	10.9	−7.5	4 + α
HoPd$_3$S$_4$	6.642	0.8	F	2.2	10.5	−13.5	4 + α
ErPd$_3$S$_4$	6.634	0.65	F	0.9	9.17	−5.6	2 + α
TmPd$_3$S$_4$	6.630	1.1	AF	⋯	7.12	−13	1
YbPd$_3$S$_4$	6.632	1.8	AF	(2.9)	⋯	⋯	4

offer us very useful information about the CEF scheme of the compound, as is often the case [18]. We discuss the CEF in the following with the aid of the magnetic entropy obtained from the specific-heat measurement. The Weiss temperature and the effective moment μ_{eff} were obtained by a least-squares fit to be −7.5 K and 10.9μ_B, respectively. The μ_{eff} is nearly equal to that of a free Dy^{3+}, 10.63μ_B, which means that the Dy ion of this compound is trivalent like other R ions except for Eu [12] and Yb, and Dy^{3+} is responsible for the magnetic behavior of the compound. Figure 1 also shows the ac magnetic susceptibility $\chi_{\text{ac}}(T)$ measured by a conventional mutual inductance technique under an ac magnetic field of 100 mOe at 123 Hz from 0.4 to 8 K. $\chi_{\text{ac}}(T)$ exhibits a peak very sharply rising below about 1 K indicating a ferromagnetic phase transition.
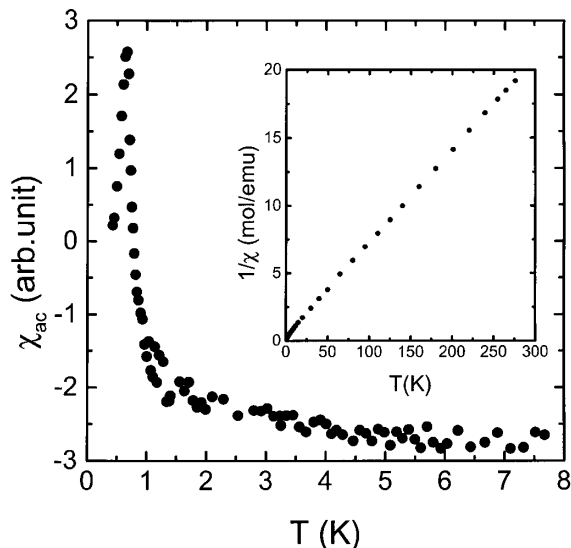
Figure 2 is the specific heat $C_p(T)$ between 0.15 and 20 K for the sample (No. 4), which exhibits two large peaks at 0.5 and 5 K. We have also measured $C_p(T)$ of another sample of slightly different quality (No. 5) in external magnetic fields up to 5 T and found that the lower-temperature peak shifts to higher temperatures showing a considerable broadening with the increasing magnetic field, while the other peak at 5 K does not shift much until it fades out above about 3 T, possibly overlapping with the low-temperature peak, as seen in the inset. So the lower transition indicates a ferromagnetic transition at $T_m = 0.8$ K and the higher one does not seem to be of magnetic origin, as also suggested from the $\chi_{\text{ac}}(T)$ shown in Fig. 1, where no detectable anomaly is seen around 5 K within the present experimental precision.

Figure 3 is the magnetic entropy $S_{\text{mag}}(T)$ which is calculated by integrating the magnetic specific heat $C_{\text{mag}}(T)$
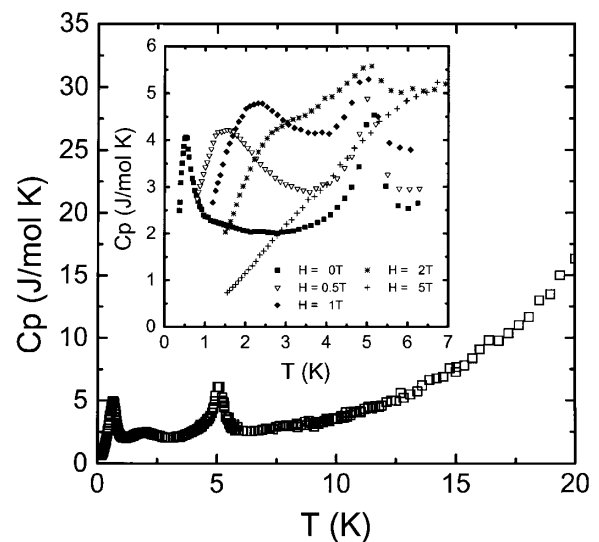

FIG. 1. $\chi_{\text{ac}}(T)$ of DyPd$_3$S$_4$. The inset shows the inverse magnetic susceptibility measured at 3 kOe from 2 to 300 K, following a Curie-Weiss law above about 50 K.

FIG. 2. $C_p(T)$ of DyPd$_3$S$_4$ (No. 4). The inset shows $C_p(T)$ of DyPd$_3$S$_4$ (No. 5) in several external magnetic fields up to 5 T.

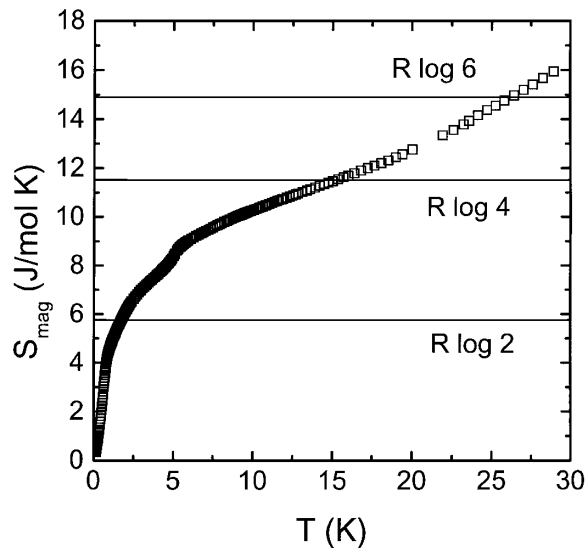FIG. 3. $S_{mag}(T)$ of DyPd$_3$S$_4$ (No. 4).

divided by T with respect to T. $C_{mag}(T)$ was deduced by subtracting the specific heat of LaPd$_3$S$_4$ from that of DyPd$_3$S$_4$. $S_{mag}(T)$ increases somewhat monotonously with temperature, attaining $0.75R\ln2$ at $T_m = 0.8$ K and $0.7R\ln4$ at $T = 5$ K. This thermal variation of $S_{mag}(T)$ strongly suggests the relatively closely distributed CEF energy levels above the ground state quartet Γ_8 for DyPd$_3$S$_4$. It is known that the lowest J-multiplet of Dy^{3+} ($J = 15/2$) splits into two doublets (Γ_6 and Γ_7) and three quartets (Γ_8) in a cubic CEF [19]. The peak of nonmagnetic origin at $T = 5$ K is thereby originated possibly from quadrupolar ordering due to the degenerate Γ_8 ground state, as in CeB$_6$ [8] and Ce$_3$Pd$_{20}$Ge$_6$ [9].

The electrical resistivity $\rho(T)$ of a sintered sample was measured from 0.4 to 300 K, which confirms that DyPd$_3$S$_4$ is a metal with a T-linear resistivity above 150 K and a residual resistivity ratio, RRR $\approx$ 4.5[$\rho(300$ K$) = 180(\mu\Omega \cdot$ cm$)$]. The onset of the ferromagnetic transition around 0.8 K and a small anomaly as a change of the slope around 6 K were discernible on the $\rho(T)$ curve. DyPd$_3$S$_4$ is thereby a new metallic sulfide according to the temperature dependence of the electrical resistivity $\rho(T)$, as earlier reported for LaPd$_3$S$_4$ [13,15], NdPd$_3$S$_4$, and EuPd$_3$S$_4$ [15].

Of the two distinct peaks observed at 0.5 and 5 K in the specific heat of DyPd$_3$S$_4$, the lower-temperature peak is attributed to a ferromagnetic transition at $T_m = 0.8$ K and the other one of nonmagnetic origin is therefore attributable to quadrupolar ordering of the ground state quartet of Dy ions. Similar low-temperature behavior has been observed also in TbPd$_3$S$_4$, HoPd$_3$S$_4$, and ErPd$_3$S$_4$, for which a distinct peak in the specific heat has been disclosed at T_Q, just like in DyPd$_3$S$_4$ and the variation of the specific heat in applied magnetic fields suggests that the magnetic transition in all these compounds except for TbPd$_3$S$_4$ seems to

be ferromagnetic. The combined degeneracy of the ground state and immediate excited states under the cubic symmetry estimated from $S_{mag}(T)$ is given in the last column of the Table. It is obvious that most of these R ions possess highly degenerate low-lying states. These high orbital degeneracies are expected to bring about various orbital effects like quadrupolar ones at low temperatures. We will briefly comment here on TmPd$_3$S$_4$. We recently found that the compound exhibits a Jahn-Teller-like transition causing a very large thermal hysteresis in the $\rho(T)$ between 120 and 230 K, and a modulated crystal structure below the transition [17]. Furthermore, it exhibits below 1.1 K the exchange-induced moment antiferromagnetism by the singlet ground state of Tm^{3+} ions. Hence TmPd$_3$S$_4$ is a very unique member of the RPd$_3$S$_4$ family.

T_Q and T_m of RPd$_3$S$_4$ are plotted in Fig. 4 along the R series together with the de Gennes factor, $(g_J - 1)^2 J(J + 1)$, which is denoted by a dot-dashed curve. At sight T_Q appears to scale fairly well with the de Gennes factor, while T_m does not scale so well, i.e., T_m for the heavy rare earths seems to be somewhat depressed and that for the light rare earths is, on the other hand, enhanced relative to that of GdPd$_3$S$_4$. Particularly, T_m of CePd$_3$S$_4$ is very much enhanced in spite of the Kondo effect confirmed in this compound [16]. We do not know at the moment the reason for this peculiar behavior of the compound. In any case this overall tendency of T_m along the R series implies that the isotropic indirect exchange interaction of the RKKY type is not a unique one operating in this series of compounds, as ordinarily observed in many rare-earth compounds but an additional one or a more complex anisotropic indirect pair interaction prevails in addition to CEF effects in the present compounds [20]. The magnetic transition in these compounds may have been affected to a certain extent by magnetoelastic interactions through the quadrupolar effect which becomes predominant at higher temperatures.
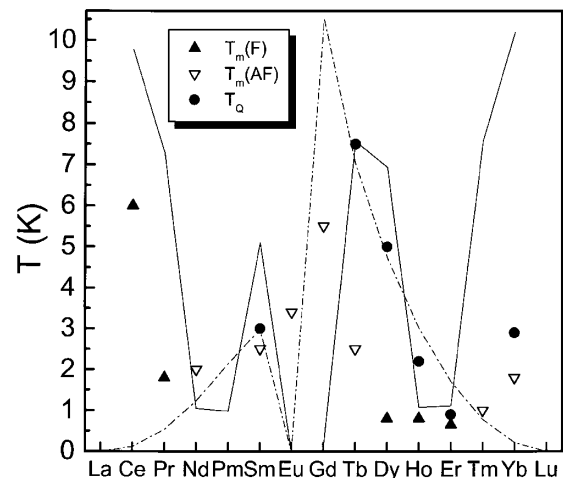

FIG. 4. T_m and T_Q of RPd$_3$S$_4$ are shown with the de Gennes factor (denoted by the dot-dashed line) and $\langle O_2^0 O_2^0 \rangle \cdot \alpha_J^2$ (denoted by the solid line), both normalized at Tb.

Anisotropic couplings between R ions in metallic substances derived from orbital effects through indirect exchange interactions have been theoretically investigated so far by many authors in various approximations [21,22]. It is not easy, however, to apply these theories directly to real systems, but we are now able to test them, for example, by observing the systematic occurrence in the R series. However, it must be borne in mind in doing so that the coupling constants which we now consider are two of many contributions obtained for the cubic symmetry group under many assumptions; the multipolar interionic interaction in the absence of CEF effects may be written in the molecular-field approximation by [22],

$$H = -J(0) \sum_i \langle J \rangle \cdot \mathbf{J}_i$$

$$- K_1(0) \sum_i [\langle O_2^0 \rangle O_{2 \cdot i}^0 + 3 \langle O_2^2 \rangle O_{2 \cdot i}^2]$$

$$- K_2(0) \sum_i [\langle P_{xy} \rangle P_{xy \cdot i} + \langle P_{yz} \rangle P_{yz \cdot i} + \langle P_{zx} \rangle P_{zx \cdot i}],$$

where $J(0)$, $K_1(0)$, and $K_2(0)$ are an average dipolar exchange constant, tetragonal and trigonal quadrupolar constants, respectively. O_2^0, O_2^2, and P_{xy}, etc., are the quadrupolar operators for the cubic symmetry. The bilinear and quadrupolar coupling constants have been derived, each of which consists of six terms and the dominant term of these couplings is proportional to the de Gennes factor and the squared Stevens factor, α_J^2, respectively. In Fig. 4 the latter factor, $J(J+1)(2J-1)(2J+3)\alpha_J^2$ is included as a solid line, according to Schmitt and Levy [22]. It appears that T_Q scales better with this factor based on the quadrupolar pair interaction rather than the dot-dashed curve of the de Gennes factor, particularly at Yb, although its T_Q is a bit too low. The low T_Q of YbPd$_3$S$_4$ may be ascribed to the low proportion (only about 32%) of Yb^{3+} in the sintered sample. In an attempt to increase the Yb^{3+} proportion a high-pressure synthesis at 4 GPa was tried but found unsuccessful.

More detailed experiments are certainly required to elucidate the quadrupolar interactions prevailing in the present palladium bronzes and work is at present being undertaken.

[1] B. J. Sternlieb, J. P. Hill, U. C. Wildgruber, G. M. Luke, B. Nachumi, Y. Moritomo, and Y. Tokura, Phys. Rev. Lett. **76**, 2169 (1996).

[2] Y. Murakami, H. Kawada, H. Kawata, M. Tanaka, T. Arima, Y. Moritomo, and Y. Tokura, Phys. Rev. Lett. **80**, 1932 (1998).

[3] M. Kohgi, K. Iwasa, J.-M. Mignot, A. Ochiai, and T. Suzuki, Phys. Rev. B **56**, R11 388 (1997).

[4] J. Rossat-Mignod, P. Burlet, H. Bartholin, O. Vogt, and R. Lagnier, J. Phys. C **13**, 6381 (1980).

[5] M. Kohgi, T. Osakabe, K. Ohoyama, and T. Suzuki, Physica (Amsterdam) **213B&214B**, 110 (1995).

[6] G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. A **38**, 1 (1975), and references cited therein.

[7] P. M. Levy, J. Phys. C **6**, 3545 (1973).

[8] J. M. Effantin, J. Rossat-Mignod, P. Burlet, H. Bartholin, S. Kunii, and T. Kasuya, J. Magn. Magn. Mater. **47&48**, 145 (1985).

[9] J. Kitagawa, N. Takeda, M. Ishikawa, T. Yoshida, A. Ishiguro, N. Kimura, and T. Komatsubara, Phys. Rev. B **57**, 7450 (1998).

[10] T. Matsumura, H. Shida, and T. Suzuki, Physica (Amsterdam) **230B–232B**, 738 (1997).

[11] P. M. Levy, P. Morin, and D. Schmitt, Phys. Rev. Lett. **42**, 1417 (1979).

[12] D. A. Keszler and J. A. Ibers, Inorg. Chem. **22**, 3366 (1983).

[13] D. A. Keszler, J. A. Ibers, and M. H. Mueller, J. Chem. Soc. Dalton Trans. **1985**, 2369 (1985).

[14] M. Wakeshima, T. Fujino, N. Sato, K. Yamada, and H. Masuda, J. Solid State Chem. **129**, 1 (1997).

[15] N. Sato, M. Wakeshima, H. Masuda, K. Yamada, and T. Fujino, High Temp.-High Press. **29**, 113 (1997).

[16] K. Abe, Master's thesis (in Japanese), University of Tokyo, 1999; K. Abe, J. Kitagawa, E. Matsuoka, N. Takeda, and M. Ishikawa (to be published).

[17] J. Kitagawa, E. Matsuoka, N. Takeda, and M. Ishikawa, Phys. Rev. B (to be published).

[18] P. Fulde, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Elsevier, Amsterdam, 1979), Vol. 2, p. 295.

[19] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[20] B. Barbara, M. F. Rossignol, E. Belorizky, and P. M. Levy, Solid State Commun. **46**, 669 (1983).

[21] T. A. Kaplan and D. H. Lyons, Phys. Rev. **129**, 2072 (1963); T. Kasuya and D. H. Lyons, J. Phys. Soc. Jpn. **21**, 287 (1966).

[22] H. H. Teitelbaum and P. M. Levy, Phys. Rev. B **14**, 3058 (1976); D. Schmitt and P. M. Levy, J. Magn. Magn. Mater. **49**, 15 (1985).