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2001 J. Phys.: Condens. Matter 13 11009

(http://iopscience.iop.org/0953-8984/13/48/325)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 11009–11016 PII: S0953-8984(01)26786-1

Evidence of the quadrupolar ordering in $DyPd_3S_4$

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Received 11 July 2001, in final form 24 August 2001
Published 16 November 2001
Online at stacks.iop.org/JPhysCM/13/11009

Abstract

By means of specific heat, magnetic susceptibility, and neutron powder diffraction experiments, we reinvestigated new samples of $DyPd_3S_4$ synthesized by an improved method. We found a new phase transition at $T_Q = 3.4$ K above the two magnetic transitions around 1 K, which was characterized by a distinct peak in the specific heat and only a small anomaly in the magnetic susceptibility. The neutron powder diffraction experiment demonstrated neither new magnetic reflections nor evidence of a change of the crystal structure below T_Q. It was furthermore found that the quartet crystalline-electric-field ground state is consistent with the result for the magnetic entropy deduced from the specific heat and that T_Q increases with the external magnetic field. These results strongly imply that the new phase transition at T_Q is due to antiferroquadrupolar ordering.

1. Introduction

We previously reported on the physical properties of rare-earth (R) palladium bronzes, RPd_3S_4, with the $NaPt_3O_4$-type crystal structure [1], and discussed the possibility of systematic occurrence of a quadrupolar transition in addition to the magnetic transition for the R series. We recently performed a neutron powder diffraction experiment on typical compounds, with R = Tb and Yb, in order to clarify the relationship between the quadrupolar and the magnetic moments through the determination of the magnetic structures [2]. It was found that the transition which we previously attributed to a quadrupolar ordering is probably a magnetic

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transition of the impurity phase, R_2O_2S, since the magnetic reflections of R_2O_2S were identified below the transition temperature in the neutron diffraction [2]. X-ray powder diffraction affirmed that many main Bragg peaks of R_2O_2S coincidentally overlap with those of RPd_3S_4, especially in the case of R = Tb. Hence it was fairly difficult to recognize the presence of the impurity phase just using x-ray diffraction methods. We have carefully rechecked the x-ray diffraction patterns of the other samples of RPd_3S_4 and also confirmed a slight contamination with R_2O_2S in the case of R = Dy. We tried various methods of preparation to remove Dy_2O_2S from sintered samples. In this paper, we report on physical properties of newly synthesized clean samples of $DyPd_3S_4$ revealed by specific heat, magnetic susceptibility, and neutron powder diffraction experiments.

2. Experimental procedure

We found it difficult to prepare completely Dy_2O_2S-free samples by a solid-state reaction of Dy_2S_3 with Pd and S powder such as that described in reference [1]. In the present study, we employed the following new method: $DyPd_3$ was first synthesized by arc melting Dy (3N) and Pd (3N) under an Ar atmosphere, then mixed with four times the molar amount of S (4N). The mixture was sintered at 1173 K for four days in a BN crucible sealed in an evacuated quartz tube ($\sim 10^{-6}$ Torr). By means of x-ray powder diffraction, it was confirmed that the new sample did not contain any detectable amount of residual Dy_2O_2S, and the cubic lattice parameter was found to be 6.641 Å at room temperature.

The specific heat measurement was performed by a quasi-adiabatic heat pulse method between 0.5 K and 30 K in the magnetic field range up to 8 T. The dc magnetic susceptibility and the magnetization were measured by a SQUID magnetometer (Quantum Design, MPMS) between 2 K and 300 K up to 7 T. The ac magnetic susceptibility was measured by a mutual-inductance method from 0.5 K to 6 K. The neutron diffraction experiments were performed at the HERMES installed at the T1 thermal neutron guide tube of the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI) [3]. The measurement ranges for the temperature and the Bragg angle 2θ were 2.0 K $< T <$ 300 K and $3^\circ < 2\theta < 153^\circ$, respectively. The wavelength of the neutron beam was $\lambda = 1.8196$ Å monochromated by the (331) reflection of Ge single crystal [3].

3. Results and discussion

Figure 1 shows the temperature dependence of the inverse susceptibility of newly synthesized $DyPd_3S_4$ measured in the magnetic field of 0.3 T. The inverse susceptibility obeys a Curie–Weiss law above about 150 K represented by the straight line shown in figure 1. The Weiss temperature and the effective Bohr magneton per unit formula were determined as 5.8 K and 10.1 μ_B, respectively. The value of the Bohr magneton agrees well with that of the free Dy^{3+} ion, 10.6 μ_B, indicating that Dy ions in the compound are trivalent at high temperatures.

Figure 2(a) shows the temperature dependence of the specific heat, C_p (denoted by open circles) and the ac magnetic susceptibility, χ_{ac} (denoted by open triangles). The overall behaviour of the C_p for our new sample is very different from that for the previous one: there are two major differences in the two sharp peaks below 1 K and the distinct new peak at 3.4 K. There is no longer a large anomaly in the specific heat around 5.0 K as observed for our previous sample, which was formerly attributed to a quadrupolar order [1]. Since our new sample does not exhibit any lines of Dy_2O_2S in the x-ray diffraction pattern as mentioned above, it is very probable that the peak of C_p observed at 5.0 K for our previous sample

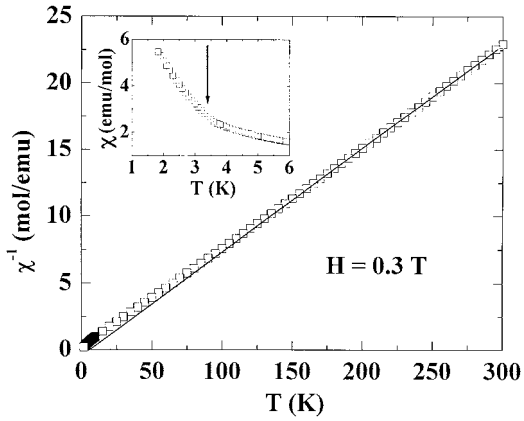

Figure 1. The temperature dependence of the dc inverse magnetic susceptibility measured at 0.3 T. The inset shows the magnetic susceptibility below 6 K.

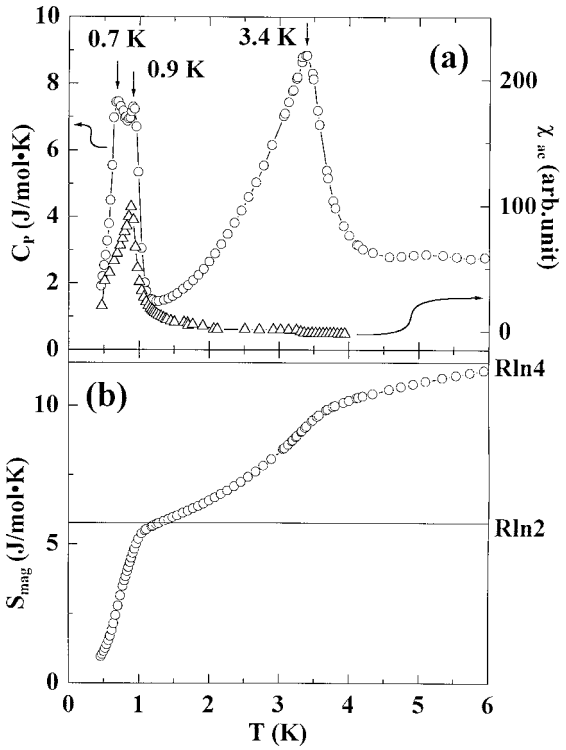

Figure 2. (a) Temperature dependences of the specific heat (open circles) and the ac magnetic susceptibility (open triangles). (b) Thermal variation of the magnetic entropy deduced from the specific heat.

is due to the magnetic transition of Dy_2O_2S whose antiferromagnetic transition is reported at 5.85 K [4].

C_p for the new sample has two successive peaks at 0.7 and 0.9 K as shown in figure 2(a), although our previous sample exhibited a broad single peak at 0.5 K. Since χ_{ac} exhibits a large

upturn around 1.0 K, suggesting the appearance of spontaneous magnetization, and the Weiss temperature takes a positive value as mentioned above, a ferromagnetic transition may occur at this temperature. In contrast, χ_{ac} reveals almost no anomaly at 0.7 K, where C_p shows a peak. We do not understand the precise nature of the transition at the moment. On the other hand, χ_{ac} shows only a small anomaly where C_p reveals such a large λ-type peak around 3.4 K. Therefore, it is difficult to assign the large anomaly of C_p to a magnetic transition. We instead attribute the peak occurring at 3.4 K to a quadrupolar transition, hereafter called T_Q. We would like to make a comment here about the relevance to anomalies of C_p found for our old samples. The specific heats C_p of the old samples reported in reference [1] often showed a very small anomaly around 2 K, which we ignored in comparison with the large anomaly around 5 K. Taking into account the new C_p for the present clean sample, we see that the quadrupolar order might have been depressed by appreciable disorder due to parasitic impurity phases in our old samples. Such a depression of the quadrupolar ordering by disorder has also been reported for CeAg, in which the depressed order recovered—on annealing—the transition temperature of about 4 K as well as the sharpness of the C_p-anomaly [5].

In the cubic crystalline electric field (CEF), the ground J-manifold of Dy^{3+} ($J = 15/2$) splits into two doublets and three quartets. Since Dy^{3+} has a half-integral J, the energy levels have at most twofold degeneracy in zero magnetic field (Kramers degeneracy). In order to examine the splitting of the ground J-manifold, we estimated the magnetic entropy, S_{mag}, from the magnetic part of the specific heat, C_{mag}, obtained by subtracting C_p for $LaPd_3S_4$ as the nonmagnetic contribution. Figure 2(b) shows the temperature dependence of S_{mag} for $DyPd_3S_4$ calculated by integrating C_{mag}/T. The entropy of about $R \ln 2$ is released around the magnetic transition temperature and T_Q. This implies that the CEF ground state is probably an orbitally degenerate quartet or a Kramers doublet closely accompanied by the first excited doublet. In the case of the latter doublet ground state, it is often called a 'pseudo-quartet' ground state. In Dy-based intermetallic compounds, such a 'pseudo-quartet' or a quartet ground state is often realized; for example, in tetragonal DyB_2C_2, an antiferroquadrupolar (AFQ) transition and a complex magnetic transition are believed to occur at $T_Q = 24.7$ K and $T_C = 15.3$ K, respectively [6]. The CEF ground state of DyB_2C_2 is reported to be a 'pseudo-quartet' of two Kramers doublets leading to the quadrupolar and the magnetic transitions. The specific heat of DyB_2C_2 reveals large λ-type peaks around T_Q and T_C, while the magnetization shows an anomaly at T_C and almost no anomaly at T_Q [6]. These behaviours of DyB_2C_2 resemble very much those of $DyPd_3S_4$ as described above. It is, hence, very probable that the quadrupolar transition at T_Q in $DyPd_3S_4$ is also caused by lifting the orbital degeneracy of one of the quartets or the pseudo-quartet.

In order to further clarify the nature of the transitions in $DyPd_3S_4$, we have measured the specific heat in the external magnetic field and display the result in figure 3(a). T_Q starts increasing with the magnetic field above about 0.3 T and apparently saturates at 4.7 K above 3 T, rapidly losing peak intensity. This behaviour is reminiscent of an AFQ order, because such an increase of T_Q with the magnetic field is commonly observed for an AFQ transition. In CeB_6, for example, T_Q increases from 3.3 K in zero magnetic field to 8.5 K at 14.5 T [7]. The increase of T_Q with the magnetic field is often anisotropic: in TmTe the AFQ transition takes place at $T_Q = 1.8$ K and T_Q increases to about 2.6 K at about 7 T applied along the [111] direction, while along the [100] direction it increases at first in low magnetic fields before decreasing above 5 T [8]. For $DyPd_3S_4$, T_Q increases up to about 3 T but the peak quickly broadens beyond this until it becomes almost invisible around 8 T, as described above. This behaviour may be a result of an anisotropy like in the case of TmTe. It would be necessary to investigate more detailed behaviour in high magnetic fields by using single crystals to establish this.

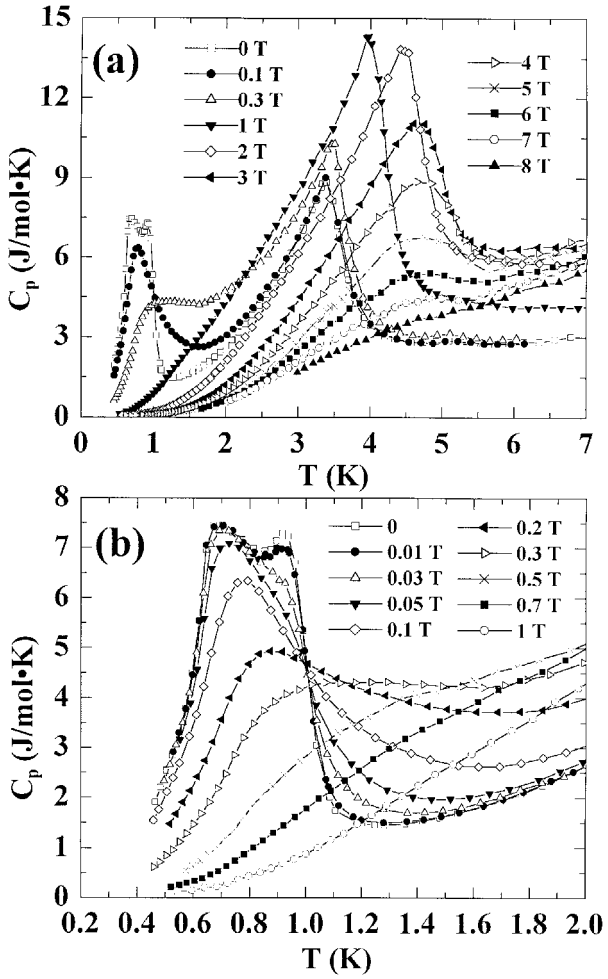

Figure 3. (a) Temperature dependences of the specific heat measured in several magnetic fields. (b) The low-temperature part for lower magnetic fields.

It is further noted that there exists a very small anomaly in the dc magnetic susceptibility, as shown by the arrow in the inset of figure 1 and that the temperature of this anomaly increases with the magnetic field at a similar rate to that of the specific heat anomaly, although it was observable only below 1 T. This type of anomaly in the magnetic susceptibility at T_Q has also been observed for CeB_6 up to about 14.5 T [7].

The low-temperature part of figure 3(a) is shown for several lower magnetic fields in figure 3(b). It is evident that the peaks at 0.7 K and 0.9 K in zero magnetic field become broad at very low magnetic fields: the peak at 0.7 K shifts to higher temperatures in increasing magnetic fields, while that at 0.9 K has already become indiscernible at about 0.05 T without appreciably shifting. Such behaviours of these peaks are not inconsistent with those for a ferromagnetic transition in external magnetic fields, which are hence consistent also with the results for the ac susceptibility shown in figure 2(a). These magnetic transitions found in the present compound may, however, imply a rather complex magnetic structure, which may be disclosed by low-temperature neutron diffraction or magnetization experiments. Compounds

that exhibit quadrupolar ordering are known to exhibit a complex magnetic structure. For example, the magnetic structure of CeB_6 is represented by the double-$\boldsymbol{k}$ structure with the wave vectors $\boldsymbol{k}_1 = (1/4, 1/4, 1/2)$ and $\boldsymbol{k}_2 = (1/4, -1/4, 1/2)$ [9]. Quadrupolar order confines a possible orientation of the magnetic moment and such a magnetic structure is believed to arise. The complex magnetic structure conjectured above may, in turn, give a hint of the occurrence of quadrupolar ordering in $DyPd_3S_4$.

Figures 4(a) and 4(b) show the neutron diffraction patterns measured above and below T_Q, respectively. Nuclear Bragg peaks of $DyPd_3S_4$ were indexed as in figure 4(a), where two peaks for the Al sample holder are also seen besides the Bragg peaks of $DyPd_3S_4$. It should be noted here that any Bragg peaks of Dy_2O_2S are indiscernible for this sample, as proved also by x-ray diffraction investigation. The lattice constant derived from these nuclear peaks is $a = 6.633(1)$ Å. At 2.4 K, no new peaks appear, indicating that T_Q is not really a magnetic transition temperature. In addition, the intensities and the positions of the nuclear Bragg peaks did not change within the experimental error. These facts, together with above-mentioned results, strongly suggest that the AFQ ordering is realized below T_Q in $DyPd_3S_4$. In the case of ferroquadrupolar (FQ) ordering, the structural transition occurs simultaneously at T_Q. In CeAg, for example, the FQ ordering is realized at 15.9 K with a structural phase transition from cubic symmetry to a tetragonal one, and the splittings of the nuclear Bragg peaks were observed in the neutron diffraction experiment [10].

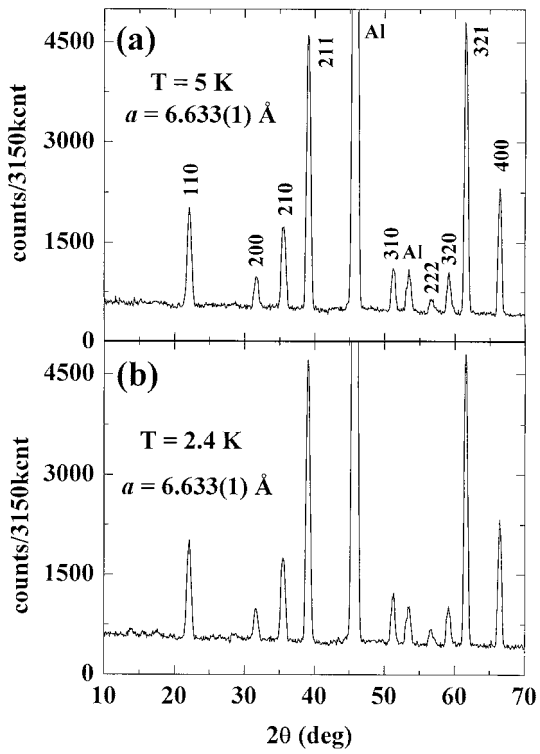

Figure 4. Neutron powder diffraction patterns measured at 5 K (a) and 2.4 K (b).

From the results for the specific heat and the magnetization measured in several magnetic fields, we can construct an H–T phase diagram as shown in figure 5. T_Q rises from 3.4 K in zero magnetic field as the magnetic field increases, but the rate of the increase is rather small below

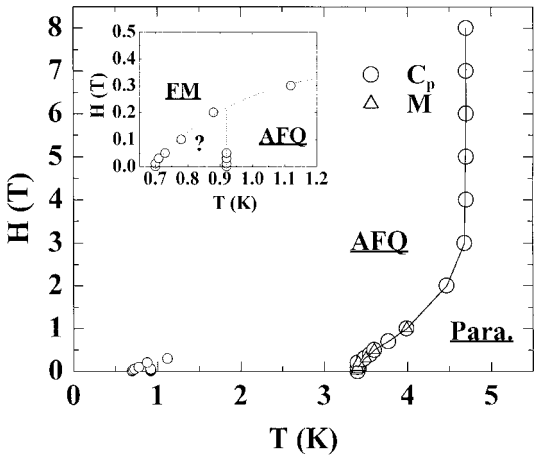

Figure 5. The H–T phase diagram of $DyPd_3S_4$ deduced from the specific heat (C_p) and the magnetization (M). The inset shows the low-temperature and the low-magnetic-field part of the phase diagram.

$H = 0.5$ T. Above 0.5 T, T_Q increases more rapidly with the magnetic field but apparently saturates at 4.7 K for fields above 3 T. However, this saturating behaviour of T_Q may simply be a result of an anisotropy. This point will be studied by employing a single crystal. The inset of figure 5 shows the low-temperature part below 1 K, which was drawn by merely plotting the peak temperatures found in the specific heat measurements. We do not know at present whether the phase boundaries drawn in the inset really exist or not. When the CEF ground state is a Γ_8 quartet, the increase of T_Q and its anisotropic behaviour were theoretically predicted and the H–T phase diagrams of CeB_6 and TmTe were qualitatively explained [11, 12]. In order to compare the H–T phase diagram of $DyPd_3S_4$ with these theories, we have to know the precise CEF ground state of $DyPd_3S_4$.

We briefly note here the symmetry of the CEF potential in $DyPd_3S_4$. In this compound, the Dy^{3+} ion is subjected to a cubic CEF potential represented by the point group, T_h. Although the splitting pattern of the J-manifold and the degeneracy of each energy level of T_h are the same as those for the O, T_d, and O_h CEFs, the irreducible representations of each of the eigenstates are different from those tabulated by Lea *et al* for the latter group [13]. This difference between T_h and the latter set of point groups arises from the lack of Umklappung and fourfold symmetry axis in the case of the T_h CEF [14]. So far, all of the cubic compounds that were reported to show quadrupolar ordering have O_h or T_d CEFs and $DyPd_3S_4$ would be the first compound with a T_h CEF to show quadrupolar ordering.

4. Summary

In this paper, we have reported that new samples of $DyPd_3S_4$ synthesized by an improved method exhibit a new phase transition at $T_Q = 3.4$ K besides the two magnetic transitions around 1 K. The neutron powder diffraction experiment demonstrated neither new magnetic reflections nor evidence of a change of the crystal structure below T_Q. It was furthermore found that the quartet CEF ground state is consistent with the result for the magnetic entropy deduced from the specific heat and that T_Q increases with the external magnetic field. These results strongly suggest that the new phase transition at T_Q is due to AFQ ordering. On the

other hand, the magnetic transitions found below 1 K may imply a rather complex magnetic structure, which may be disclosed by low-temperature neutron diffraction or magnetization experiments.

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