Quadrupolar and dipolar magnetic order in DyPd_3S_4 : A neutron scattering and muon spin rotation and relaxation investigation

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The quadrupolar and dipolar magnetic phases in polycrystalline DyPd_3S_4 have been investigated by neutron scattering and muon spin rotation/relaxation (μSR) technique. The transition from paramagnetic to antiferro-quadrupolar state at $T_Q=3.4$ K as well as two successive dipolar magnetic phase transitions at $T_{N1}\approx 1$ K and $T_{N2}\approx 0.8$ K are evidenced by anomalies in the observed relaxation rates in the zero-field μSR measurements. In addition, measurements in longitudinal external magnetic field showed clear evidence for field-induced dipolar magnetic moments below T_Q . In inelastic neutron scattering measurements the transition to an ordered lattice of the Dy quadrupole moments at T_Q is observed by a temperature dependent splitting of the ground-state crystal-field multiplet below T_Q . Neutron diffraction revealed the induced magnetic structure in the quadrupolar phase of DyPd_3S_4 to be of the canted antiferromagnetic type with a canting angle close to perpendicular, similar to the spontaneous zero-field magnetic structures below 1 K.

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Multipolar or orbital ordering in f -electron compounds leads to a rich variety of interesting phenomena.^{1–5} In such a case the higher order interactions, which are usually small, should be comparable with or overcome the dipolar one. Some examples of compounds exhibiting quadrupolar ordering are CeB_6 ,⁶ $\text{Ce}_3\text{Pd}_{20}\text{Ge}_6$,⁷ and DyB_2C_2 .⁸ For DyPd_3S_4 macroscopic measurements on polycrystalline samples showed evidence for three phase transitions which were interpreted as quadrupolar order at $T_Q=3.4$ K followed by two magnetic phase transitions of presumably ferromagnetic type below $T_{N1}=1$ K and $T_{N2}=0.7$ K, respectively.⁹ External magnetic fields shift T_Q to higher temperatures up to the saturation value 4.7 K at 3 T. A recent single crystal study,¹⁰ also by macroscopic methods, showed comparable results but with somewhat lower critical temperatures for the ordering phenomena. In the single crystal the quadrupolar order was found below $T_Q=2.7$ K, and the two presumed ferromagnetic phase transitions occur at 0.84 and 0.55 K. All these results are consistent with quadrupolar order below T_Q and it is now widely accepted that polycrystalline DyPd_3S_4 undergoes a phase transition to an ordered quadrupolar, most likely antiferroquadrupolar, state at 3.4 K.

Macroscopic measurements are a valuable tool for the investigation of such ordering phenomena but are somewhat limited to characterize the nature of the observed phases. As local and microscopic methods neutron scattering and muon spin rotation/relaxation (μSR) are the methods of choice for the investigation of magnetic ordering phenomena and local magnetic field dynamics.

We report on a μSR investigation of the quadrupolar and magnetic phase transitions in DyPd_3S_4 , first inelastic neutron scattering results on the crystal field in the quadrupolar phase and the first low-temperature neutron diffraction measurements of the field-induced and spontaneous magnetic structures in DyPd_3S_4 .

The polycrystalline sample of DyPd_3S_4 was synthesized at the Paul Scherrer Institute (PSI) in Villigen, Switzerland, as described, e.g., in Ref. 9. The μSR experiments in the

temperature range of 0.4–10 K were performed at the Swiss muon source $\text{S}\mu\text{S}$ of PSI using the low-temperature instrument LTF and the Dolly instrument. The neutron scattering experiments were performed at the Swiss spallation neutron source SINQ of PSI. The magnetic structures were measured on the cold neutron powder diffractometer DMC. For the zero-field measurements sample temperatures down to 130 mK were available, for the measurements with external magnetic field the lowest temperature was 1.7 K. High resolution neutron diffraction data were obtained on the thermal neutron diffractometer HRPT. The neutron spectroscopic measurements were performed on the time-of-flight spectrometer FOCUS. The refinement of the neutron diffraction data was done using the Rietveld method and the program FULLPROF,¹¹ using its internal tables of scattering lengths and magnetic form factors.

The μSR signal, i.e., the time evolution of the μ^+ spin polarization $P(t)$, was measured in zero applied field (ZF) and in a longitudinal field (LF), i.e., a field applied parallel to the initial μ^+ polarization $P(0)$, of 0.1 T. $P(t)$ displayed distinctive differences between the various phases, clearly monitoring the transition temperatures. Above T_{N1} in ZF $P(t)$ is found to be composed of two exponentially relaxing components (relaxation rates λ_1, λ_2 , see Fig. 1). Above T_Q up to 10 K, λ_1 and λ_2 are essentially temperature independent but start to rise strongly below T_Q . Apparently the μ^+ are exposed to fluctuating local fields arising from the fluctuating Dy $4f$ moments which start to slow down below T_Q in parallel with the onset of antiferroquadrupolar order. Then below T_{N1} $P(t)$ is composed of three components, a Gaussian damped (damping constant σ) and two exponentially damped (relaxation rates λ_2, λ_3 , see Fig. 1). The Gaussian component accounts for 2/3 of the implanted μ^+ . This component reflects the development of a wide distribution of static fields at the μ^+ positions below T_{N1} . The fraction 2/3 is expected for a polycrystalline sample in which the spontaneous internal fields are randomly oriented with respect to $P(0)$. On average 1/3 of the μ^+ will experience internal fields parallel

FIG. 1. Temperature dependencies of the muon spin relaxation rates. The zero (ZF) and longitudinal field (LF) experiments are shown by open and filled symbols, respectively. Anomalies at T_Q , T_{N1} , and T_{N2} are signatures of the quadrupolar and the magnetic ordering phenomena.

to their spins and hence will not precess, but may relax in the presence of randomly fluctuating local fields, as obviously observed in the present case. The appearance of two differently relaxing components, also above T_Q , may point to the occupation of two different sites. In any case the data imply that below T_{N1} a considerable part of the Dy 4f moments does not freeze out. λ_3 is quite small between T_{N2} and T_{N1} but rises strongly on approaching T_{N2} from below. λ_2 shows jumps at T_{N1} and T_{N2} .

In LF of 0.1 T we still find two exponentially decaying components with unchanged amplitudes above T_Q (relaxation rates λ'_1 , λ'_2 , see Fig. 1), but below T_Q the λ'_1 component changes to a Gaussian behavior (damping rate σ^* , see Fig. 1). σ^* approaches the σ found below T_{N2} . This behavior pointed to the appearance of a field-induced magnetic phase below T_Q and motivated the neutron diffraction measurements reported below. Between T_{N1} and T_{N2} $P(t)$ in LF is also composed of three components, like in ZF, with $\lambda'_2 = \lambda_2$ and $\lambda'_3 = \lambda_3$, implying fluctuation rates $\nu > 10^8 \text{ s}^{-1}$. Note that $\lambda'_2 > \lambda_2$ in the range $T_{N1} < T < T_Q$, indicating that the fluctuation rates must have been slightly reduced by the applied field. The temperature dependence of λ'_2 above T_{N1} does not give any hint for a critical slowing down and hence suggest that the phase transition at T_{N1} in the presence of an applied field is of first order.

The determination of the crystalline electric field (CEF) may act as a sensitive probe for quadrupolar interactions and the onset of quadrupolar order,¹² since in the ordered quadrupolar state the lowered local symmetry of the rare earth ion will be reflected in a splitting of CEF levels. Therefore we applied neutron spectroscopy on DyPd_3S_4 above and below the phase transition at 3.4 K. The inelastic neutron spectra showed distinct differences that are not consistent with regular temperature behavior of the crystal field. The most prominent effect is the appearance of an additional transition at low temperatures, as best seen in the high-resolution spectra shown in Fig. 2. From specific heat measurements⁹ it was deduced that the CEF ground state is either a quartet or a pseudoquartet, i.e., two Kramers doublets close to each other.

FIG. 2. Inelastic neutron scattering spectra of DyPd_3S_4 at (a) $T > T_Q$ and (b) $T < T_Q$.

We interpret our experimental results as the splitting of this ground-state multiplet due to quadrupolar order. The splitting sets in at T_Q and increases with decreasing temperature up to $\Delta E = 0.75 \text{ meV}$ at $T = 1.5 \text{ K}$. This is still well above the critical temperature for dipolar magnetic order and Zeeman splitting can be excluded as the origin of this effect. These findings strongly support that quadrupolar order in DyPd_3S_4 is caused by lifting the orbital degeneracy of the CEF ground state, as previously suggested.⁹ A comparable behavior was observed in DyB_2C_2 , a compound exhibiting antiferroquadrupolar order.⁸ Our inelastic neutron scattering experiments did not detect the full set of CEF levels. Therefore it is not possible to find a unique solution for the CEF of DyPd_3S_4 and to unambiguously determine the character of the CEF ground state. Since not only quadrupolar order but also structural distortions can cause the observed level splitting, we performed high-resolution neutron diffraction on our polycrystalline DyPd_3S_4 sample. Within the available resolution, $(\delta d/d)_{\min} \approx 0.001$, no evidence was found for a distortion of the cubic crystal symmetry below T_Q , which is in agreement with previous results.⁹ We can exclude a pure structural origin of the observed CEF behavior. Ferroquadrupolar order, as, e.g., in HoB_6 ,^{13,14} is always accompanied by a lattice distortion and can therefore be excluded for DyPd_3S_4 .

μSR evidenced the appearance of field-induced magnetic moments in the quadrupolar phase of DyPd_3S_4 . To solve the magnetic structure we have employed neutron diffraction technique under external magnetic field on polycrystalline DyPd_3S_4 . At $T = 1.7 \text{ K}$, in the quadrupolar phase, any external field even as low as 0.1 T leads to the appearance of additional Bragg peaks in the neutron diffraction patterns (Fig. 3). The analysis of the data revealed that ferromagnetism as well as simple collinear antiferromagnetism can be excluded. The field-induced magnetic structure is of the canted antiferromagnetic type. Due to the cubic structure it was not possible to determine the absolute moment directions, but it was possible to determine the relative moment direction, i.e., the canting angle of the magnetic moments in the two antiferromagnetic sublattices as well as the magnitude of the ordered magnetic moment. The refinement of the

FIG. 3. Refinement of the neutron diffraction patterns of DyPd_3S_4 at $T=1.7$ K in (a) zero field and (b) $H=0.5$ T in the magnetically ordered state.

diffraction patterns at $T=1.7$ K in the paramagnetic state (zero field) and in the magnetically ordered state are shown in Fig. 3. The best fit was achieved with perpendicular moments as shown in the inset of Fig 3(b). The ordered Dy^{3+} moment at $H=0.5$ T turns out to be $3.4(1)\mu_B$. The temperature dependence of the ordered magnetic moment at $H=0.5$ T [Fig. 4(a)] shows the appearance of field-induced antiferromagnetic moments at T_Q . The field dependence at $T=1.7$ K [Fig. 4(b)] indicates that at this temperature the system is right at the edge of spontaneous magnetic order and even a small field of 0.1 T affects the magnetic transition. With higher fields the induced moment smoothly increases

FIG. 4. (a) Temperature dependence of the ordered magnetic Dy moment in DyPd_3S_4 for an external field of $H=0.5$ T, showing the onset of field-induced magnetic order at T_Q ; (b) field dependence of the induced magnetic Dy moment in DyPd_3S_4 at $T=1.7$ K.

FIG. 5. Refinement of the zero-field neutron diffraction patterns of DyPd_3S_4 at (a) $T_{N1} < T < T_Q$ and (b) $T < T_{N2}$.

without showing saturation up to $H=1$ T. Such a complex arrangement of induced magnetic moments in a simple cubic crystal lattice cannot be driven by only dipolar interactions. This is a sign of the underlying quadrupolar order, which now, in agreement with all the other experimental results presented here, can be identified as antiferroquadrupolar order.

We employed a low-temperature neutron diffraction technique to measure and determine the spontaneous zero-field magnetic structures in DyPd_3S_4 below $T_{N1} \approx 1$ K and $T_{N2} \approx 0.8$ K. In Fig. 5 the diffraction patterns obtained at $T=1.3$ K and $T=0.13$ K are compared. At $T=0.13$ K we find additional Bragg peaks due to long-range dipolar magnetic order. The analysis of the peak positions immediately reveals that the previously proposed ferromagnetic structure can be excluded. We find a very similar pattern as in the field-induced magnetic phase below T_Q . The Dy ions form a body-centered lattice, and antiferromagnetic order separates the corner and center ions in two sublattices with a certain canting angle α between the moment directions in the two sublattices. In neutron diffraction experiments the intensity ratios of the magnetic peaks change with changing canting angle. The high quality of our diffraction data enables us to accurately determine the magnetic peak intensities. The temperature dependence of the integrated intensity of the magnetic (100) peak (Fig. 6) shows the onset of magnetic order around 1 K but also a clear anomaly around 0.8 K indicating the second magnetic phase transition at T_{N2} . We analyzed the neutron powder diffraction patterns below T_{N1} and T_{N2} by systematically varying the canting angle α from 0° (ferromagnetism) to 180° (collinear antiferromagnetism), as well as by refining the data with α as a free fit parameter. Both methods lead to the same unique solutions for the magnetic structures. We found two magnetic phases, both with canted antiferromagnetism, but distinguished by their canting angle

FIG. 6. Temperature dependence of the integrated intensity of the magnetic (100) peak, determined by neutron diffraction.

α . Below T_{N1} $\alpha=91(4)^\circ$, at T_{N2} we find a reorientation of the moments to $\alpha=99(4)^\circ$. The saturation value of the ordered Dy magnetic moment at $T=0.13$ K amounts to $5.2(1)\mu_B$. The magnetic structures at low temperatures are therefore of the same canted antiferromagnetic type as the field-induced one below T_Q , in both cases modulated by the underlying antiferroquadrupolar order.

As shown above, the onset of spontaneous magnetic order was also detected by zero-field μ SR measurements, evidenced by the appearance of a Gaussian component σ and a step-like increase in the relaxation rate below T_{N1} . This component signals the presence of static local fields. However, no Larmor precession signal is observed, which implies that the μ^+ must experience a broad local field distribution, rather than unique local fields. As also encountered in other compounds this may reflect short-range disorder of the magnetic structure, e.g., due to lattice imperfections or site disorder, while long-range order is preserved. The presence of two slowly relaxing components below T_{N1} implies that besides the static fields fluctuating fields also persist below T_{N1} .

In conclusion, we have presented new μ SR, inelastic, and elastic neutron scattering results on the quadrupolar and

magnetic phases in the rare-earth palladium sulphide DyPd_3S_4 . μ SR was able not only to detect the magnetic phase transitions at low temperatures but also the appearance of the antiferroquadrupolar phase. While these experimental results, in accordance with neutron diffraction, can exclude magnetic order at T_Q , the mechanism that actually leads to the pronounced changes in the μ^+ relaxation rates below T_Q remain subject to speculation, since the interaction of the quadrupole lattice with the muon can only be indirect, mediated by spin-orbit coupling. Other possible explanations like even higher multipolar effects¹⁵ are subject to future investigations.

The field-induced antiferromagnetic moments in the quadrupolar phase of DyPd_3S_4 were detected by both μ SR and neutron diffraction technique. The observed canted antiferromagnetic structure is a fingerprint of the underlying quadrupolar order, which can be identified being of the antiferroquadrupolar type.

The zero-field magnetic structures below T_{N1} and T_{N2} turned out to be of the canted antiferromagnetic type as well. We were able to refine the canting angles and the magnitude of the ordered magnetic moments and identify the phase transition at T_{N2} as a reorientation of the magnetic moments. In the canted antiferromagnetic structure the moments of the two magnetic sublattices do not cancel each other. The sum of the moments in the unit cell leads to a resulting ferromagnetic component, which in recent macroscopic investigations falsely lead to the assumption of ferromagnetic order. With neutron scattering as a microscopic method we were able to determine the origin of the macroscopically ferromagnetic behavior and deduce the correct antiferromagnetic structures of DyPd_3S_4 .

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