Orbital Dynamics of the 4f Shell in DyB_2C_2

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For the first time, fluctuations in the Dy quadrupole (orbital) moment have been observed in DyB_2C_2 using inelastic neutron scattering. The observed quasielastic response is decomposed into two components, one reflecting transitions within the doublets (narrow) and the other transitions between the doublets (broad) of the effective Dy quartet ground state. The widths of the narrow and broad components are shown to arise from fluctuations in the magnetic dipole and the electric quadrupole moments, respectively.

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Orbital degrees of freedom have attracted significant interest in recent years, as they are believed to be important for the occurrence or suppression of the colossal magnetoresistance in manganites [1]. Orbital ordering can also play an important role in f-electron materials. Orbitals (quadrupoles or higher multipoles) may order independently of the magnetic dipoles, which causes discussions about the order parameter involved in the phase transition as, e.g., in NpO_2 [2,3]. Since recently, it is possible to access such ordering phenomena in f-electron materials by means of resonant [2–5] and nonresonant [6] x-ray scattering. These measurements give important details on the spatial orientation of the orbitals in the ordered state. Very little is known about the dynamics of the orbitals due to restrictions of suitable techniques to observe excitations caused by the interactions between the orbitals.

Inelastic neutron scattering (INS) is a technique that accesses the multipole dynamics through its influence on the dipole magnetic excitations of the f states, as has been shown by extensive calculations on CeB_6 [7]. However, corresponding transitions in zero field have not been observed so far, and it has been proven to be extremely difficult to observe all the predicted details in applied magnetic fields [8]. The energy scale of these effects are directly related to the quadrupole order temperature T_Q, which is rather small (3.2 K) for CeB_6. Moreover, in CeB_6 the Kondo effect leads to additional broadening of the INS response, further complicating a distinction between the proposed excitations.

The system DyB_2C_2 is the better candidate to study multipole dynamics because it exhibits the highest antiferroquadrupole (AFQ) transition with $T_Q = 24.7$ K [9], which is significantly higher than the magnetic dipole transition occurring at $T_N = 14.7$ K. Such a high T_Q indicates that the energies of the quadrupole-quadrupole interaction are in the range of a few meV and the effects should be more easily observable than in CeB_6. The static ordering of the quadrupoles in DyB_2C_2 has been studied intensively with resonant x-ray scattering [4,5,10,11], neutron diffraction in applied magnetic fields [12,13], and theory [14,15]. Recently, an INS study has shown [16] that the ground state is an effective quartet in the paramagnetic state as it has been predicted from the evaluation of specific heat measurements [9]. The ground state without the f-f interactions has been determined to be a doublet followed by the first excited doublet at 1.4 meV [16]. Therefore, it is the quadrupole-quadrupole interaction that is responsible for these two doublet states to form an effective quartet. Only when the AFQ interaction overcomes the energy separation between the two doublets does orbital order occur. This is similar to magnetic order induced in a singlet ground state of a non-Kramers f ion [17].

Here, we present detailed INS data on the temperature dependence of the quasielastic response in DyB_2C_2. The observed spectra are described by two components, which reflect the dipole and quadrupole dynamics of the f shell. The results indicate that both fluctuation time scales are significantly slowing down at T_Q. For the first time, the temperature-dependent fluctuations of the quadrupoles are determined in a rather direct way. The quadrupole fluctuations are found to be significantly faster over the whole temperature range compared to the dipole fluctuations.

The polycrystalline sample was isotope ^{11}B enriched $Dy^{11}B_2C_2$ as in Ref. [16]. The INS experiments were performed at the time-of-flight spectrometer FOCUS at the spallation neutron source SINQ of the Paul Scherrer Institut. An incident neutron energy of 7 meV was used. The sample was filled into a hollow cylinder with 15 mm outer and 14 mm inner diameter in order to reduce the effect of the strong absorption of Dy. The sample was mounted on a closed cycle refrigerator reaching temperatures between 16 and 200 K. The spectra of all detectors without Bragg contributions were summed. For the difference spectra, the monitor normalized data were subtracted

in the time window, then corrected for the detector efficiency and transformed to the energy axis by standard procedures.

Figure 1 shows the difference between INS spectra taken at various temperatures and a spectrum taken at 16 K, just above T_N. This is the best way to get intrinsic information from the raw data as strong absorption makes the background correction of individual spectra inaccurate. This has the advantage that the nonmagnetic contribution, e.g., the incoherent elastic intensity, does not appear as it is at most very weakly temperature dependent. Therefore, the observed negative as well as positive contributions to the difference spectra are both of magnetic origin. For increasing temperatures, the width of the quasielastic response is increasing, leading to an increase of both the positive broad and the negative narrow contribution. The magnetic quasielastic neutron cross section of a polycrystalline material is a direct measure of the local susceptibility in the paramagnetic state of the $4f$ ion (moment averaged) similar to that obtained by NMR or EPR. The width of the quasielastic peak is commonly related to the time scale of the dipole fluctuations; however, here the situation is more complex.

The 200–16 K spectrum has been fitted with positive (200 K) and negative (16 K) Lorentz functions convoluted with the instrumental resolution function of Gaussian type resulting in Voigt functions. This fit led to accurate values of the integrated intensity of the magnetic cross section within this energy window, which is temperature independent as the integral of the difference spectra is approximately zero for all temperatures. For positive intensities of difference spectra (30 K) a single Voigt does not give satisfactory agreement with the data. Therefore, the difference spectra were described by one negative component, and two positive components labeled A and B, with individual widths and intensities. Because the negative components are temperature independent, four independent parameters are fitted. Such a fit to the 28–16 K spectrum is shown in Fig. 2. The detailed balance factor has been neglected as the energy k_BT is always larger than the width.

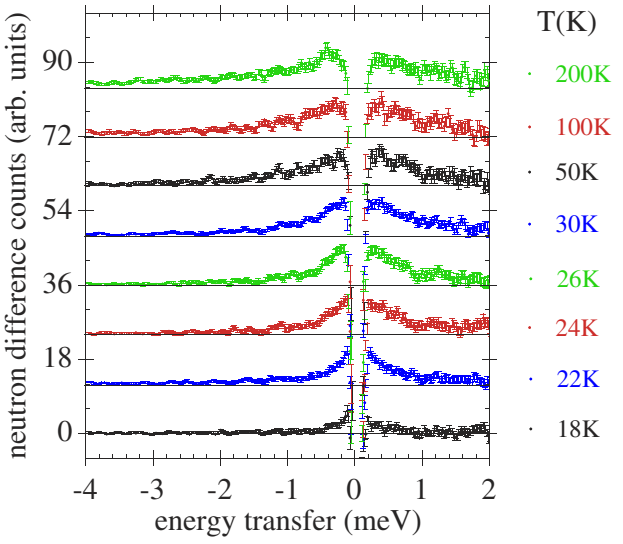

FIG. 1 (color online). Selected neutron difference spectra of the quasielastic region in $Dy^{11}B_2C_2$ between temperature T and 16 K.

The temperature dependence of the widths Γ_A and Γ_B and integrated intensities I_A and I_B are shown in Fig. 3. At 16 K, I_B is zero and I_A reflects the total magnetic scattering within the quasiquartet. For increasing temperatures, I_A decreases (I_B increases) steeply with a significant change in slope at T_Q. Above T_Q, I_A decreases (I_B increases) with a much smaller slope. The temperature dependence of Γ_A does also exhibit a change in slope at T_Q. The ratio Γ_B/Γ_A is constant over the whole temperature range.

For the interpretation of these observations, it is necessary to take into account various interactions present in the material. In the mean-field approximation, a Hamiltonian describing these interactions is

$$H = H_{\mathrm{CEF}} + J_Q^{\alpha}\langle \mathbf{Q}^{\alpha}\rangle \mathbf{Q}^{\alpha} + J_M\langle \mathbf{J}\rangle \mathbf{J}. \qquad (1)$$

Here the first term is the crystalline-electric field (CEF) term. The second and the third terms describe the quadrupole-quadrupole and magnetic exchange interactions, respectively, with J_Q^{α} and J_M being the corresponding exchange integrals. $\mathbf{Q}^{\alpha}$ represent the quadrupole operators (with, e.g., $\alpha = xy$ [10]). We discuss four possible regimes: the pure single ion case (I), where the Dy^{3+} ions are dilute with nonmagnetic Y, and for nondiluted DyB_2C_2 the ranges $T_N < T_Q < T$ (II), $T_N < T < T_Q$ (III), and $T < T_N < T_Q$ (IV). Note that for (III) and (IV), H_{CEF} will also be slightly changed by different local structure (Jahn-Teller distortion); however, this effect is expected to be small as the distortions are tiny. These regimes are schematically shown in Fig. 4. For case (I), the ground state is built by two

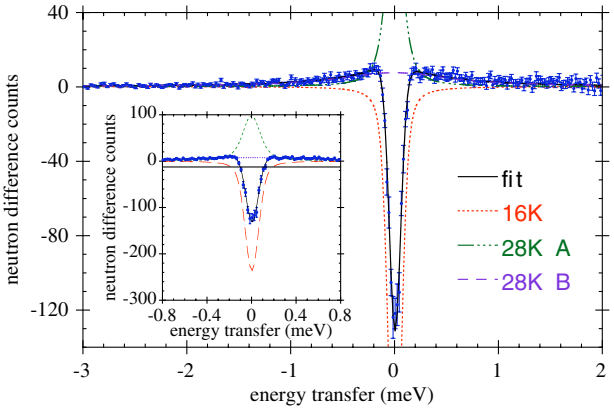

FIG. 2 (color online). Neutron difference spectra of 28–16 K (filled circles), together with a fit (full line is total) of a negative Voigt (broken lines) and two positive Voigts (dotted lines). The inset shows the spectra rescaled.

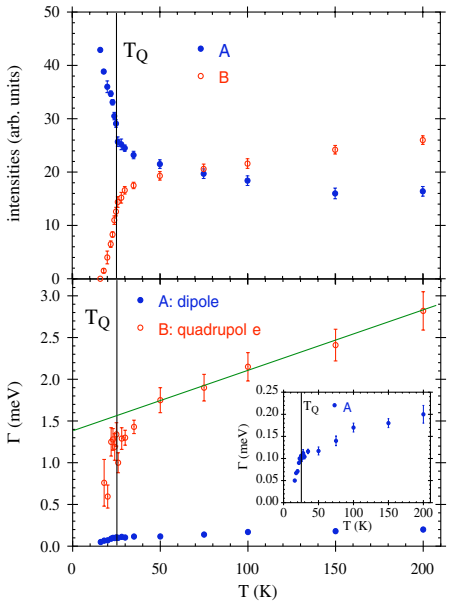

FIG. 3 (color online). Temperature dependence of the intensity (upper part) and the full width at half maximum Γ (lower part) of the two components. The vertical line represents T_Q and the solid line through the points reflects Eq. (2). The inset shows Γ_A in the enlarged scale.

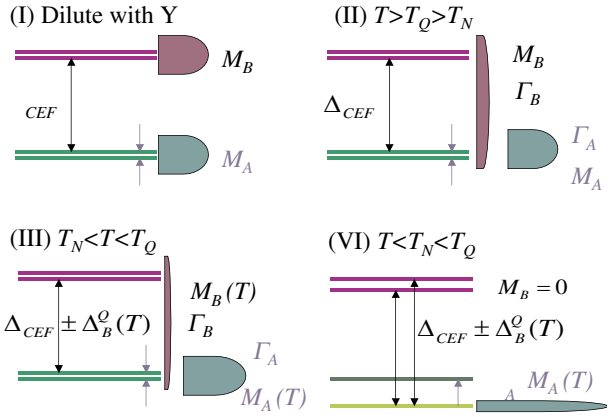

FIG. 4 (color online). Qualitative energy level diagram of the ground state of the Dy^{3+} ions in RB_2C_2 in four cases: I (top left) dilute Dy^{3+} ion; II (top right) paramagnetic state; III (bottom left) AFQ state; IV (bottom right) AFM + AFQ state. The broadening of the energy levels observed in the INS spectra is presented schematically at the right of every diagram and Δ_{CEF} reflects the CEF splitting.

doublets separated by $\Delta_{CEF} = 1.4$ meV [16] (Fig. 4). The neutron cross section exhibits two components: a quasielastic with transition probability M_A, reflecting the transition within the doublet, and an inelastic excitation with transition probability M_B between the two doublets.

In the paramagnetic state (II) (Fig. 4) an effective quartet is formed due to the exchange interactions. We observe still two components with transition matrix elements M_A and M_B, but not the CEF splitting. Γ_A reflects therefore the "dynamical splitting" within the doublets and Γ_B the dynamical splitting between the doublets. For elevated temperatures, additional excited states need to be taken into account, leading to a systematic uncertainty of the widths of less than 20%, and are causing the intensities I_A and I_B to be slightly temperature dependent. Physically, the width Γ_A directly relates to the fluctuation time of the dipole moments. The temperature-dependent broadening of this linewidth is either related to the interaction between the $4f$ electrons and conduction electrons (s-f) or phonons [18]. The first interaction dominates in good metals, whereas the second dominates in insulators. DyB_2C_2 is a good metal and therefore it is expected that the s-f interaction dominates. This leads to a linear temperature dependence above T_Q:

$$\Gamma_A = \Gamma_0 + 2J_{s\text{-}f}^2 M_{00}^2 k_B T N^2(E_F). \quad (2)$$

$J_{s\text{-}f}$ is equal to the exchange coupling between the $4f$ dipole moments and the conduction electrons, to M_{00}^2 the dipole matrix element of the transition within the ground state, $N(E_F)$ the density of states at the Fermi surface, and Γ_0 a residual temperature independent width.

The broadening Γ_B cannot be described by the magnetic interaction with the conduction electrons as $M_{00}^2 > M_{01}^2$ ($I_A > I_B$ see Fig. 3). The magnetic exchange interaction induces dispersion in the first excited doublet, but a finite gap would be expected at any temperature $T > T_N$. Moreover, the effect of spatial dispersion is decreasing for increasing temperature. Therefore, the origin of the broadening must be due to the interaction with the quadrupoles. This interaction overcomes the energy separation ($\Gamma_B > \Delta_{CEF}$) and transforms the two lowest lying doublets into an effective quartet.

For $T_N < T < T_Q$ (III), the additional quadrupole mean-field term is expected to split the quasiquartet into two doublets (Fig. 4). Interestingly, the transition between the two doublets is not observed in these experiments, indicating that even when the quadrupoles are partially ordered, fluctuations overwhelm the CEF splitting. In this regime a strong decrease of I_B is observed. This decrease suggests that the quadrupole mean field [Eq. (1)] causes a strong change in the $4f$ wave functions suppressing the dipole transition for neutrons between the two doublets. A similar effect has been observed due to magnetic ordering in lanthanides [19]. In addition, this interpretation is supported by the suppression of a CEF transition in the field induced AFQ phase of TbB_2C_2 [20]. In the regime $T < T_N < T_Q$ (IV) (Fig. 4), the mean-field magnetic term in Eq. (1) is expected to remove the remaining degeneracy.

The influence of the AFQ transition on the neutron cross section can be evaluated from wave functions deduced by the analysis of resonant x-ray scattering data [10]. Minimal wave functions for the two Dy doublets labeled 0 and 1

forming the ground state are

$$|\psi_0^{\pm}\rangle = i\sin\theta\sin\varphi|\pm 5/2\rangle \pm \cos\theta|\pm 1/2\rangle + i\sin\theta\cos\varphi|\mp 3/2\rangle$$

$$|\psi_1^{\pm}\rangle = \pm i\cos\theta\sin\varphi|\pm 5/2\rangle + i\sin\theta|\pm 1/2\rangle \pm \cos\theta\cos\varphi|\mp 3/2\rangle$$

with mixing angles $\theta = 47^\circ$ and $\varphi = -42^\circ$ in the AFQ phase with $2/m$ symmetry, and $\theta = 0^\circ$ and $\varphi = -42^\circ$ in the paraquadrupole phase with $4/m$ symmetry. The neutron cross section for polycrystalline materials is proportional to $M_{ij}^2 = 2/3\sum_{\alpha=x,y,z}|\langle i|J^\alpha|j\rangle|^2$. For case (III) we obtain $M_{00}^2 \approx 32$ and $M_{01}^2 = 0.07$, in excellent agreement with data gathered at 16 K for I_A and I_B, respectively. In the paraquadrupole phase (II) we calculate $M_{00}^2 \approx 21$, $M_{01}^2 \approx 11$, and $M_{11}^2 \approx 20$, leading to a predicted ratio I_A/I_B of 1.9, again in very good agreement with the experimentally observed 1.7 at 25 K (Fig. 3). These findings imply that our interpretation agrees with results derived from resonant x-ray scattering.

In analogy with the quasielastic broadening of the doublets reflecting the dynamics of the magnetic dipoles, the broadening due to the transition between the two doublets reflects the dynamics of the quadrupoles. To our knowledge this is the first time that the fluctuation times of the quadrupoles (orbitals) have been directly determined. There are many techniques able to determine dipole fluctuation time scales (muon-spin spectroscopies, Mössbauer, etc.), yet little is known at this time of quadrupole fluctuations. It is interesting to see that the fluctuation time of the quadrupoles is significantly faster at all temperatures than those of the dipoles by approximately one order of magnitude. Considering Eq. (2) to be valid for the dipoles, it is intriguing to propose an equivalent interaction for the quadrupoles, by replacing $J_{s\text{-}f}$ by the analogue exchange integral of the quadrupoles and the conduction electrons $Q_{s\text{-}f}$. From $M_{00}^2/M_{10}^2 \approx 2$ we estimate a value $Q_{s\text{-}f}/J_{s\text{-}f} \approx 4$. The linear temperature dependence Γ_B indicates that for DyB_2C_2 the RKKY interaction is the dominating interaction for AFQ. This is similar as proposed for CeB_6 [21]. The larger Coulomb type of interaction between the conduction electron and the orbital compared to that between the magnetic moment and the conduction electrons is also well represented by $T_Q > T_N$.

Interestingly, even at temperatures below T_Q, where there is a nonzero expectation value for the ordered quadrupoles, there is still quite fast dynamics in the range of 10^{-11} s. This dynamics maybe also responsible for the different behavior of reflections sensitive to different contributions in the orbital ordered manganites as observed by resonant x-ray scattering [22]. A different temperature dependence of the charge order and structural order parameters have also been suggested to be due to the different time scales of the corresponding fluctuations [23].

In conclusion, we have measured the temperature dependence of the quasielastic response of the Dy^{3+} ions in DyB_2C_2. Two components are observed that are related to the scattering within the doublets and between the doublets in the effective quartet ground state. The broadening of these two components reflects the fluctuation time of the dipoles and the quadrupoles allowing us, for the first time, to determine a temperature dependence of the quadrupole dynamics of the f shell. It is shown that the AFQ interaction is mediated by the conduction electrons. Our results and previous data on Dy multipole moments obtained by resonant x-ray diffraction are unified by an atomic model for the Dy ground state. In addition, these results indicate that INS might be a good tool to study orbital liquids.

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