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Influence of stress and magnetic field on the orbital orientations in CeB_6

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Abstract

Non-resonant x-ray scattering experiments on CeB_6 under applied uniaxial pressure and magnetic field have been performed. Measurements of different orbital superlattice reflections show different temperature dependences. The changes in the scattered x-ray intensity as a function of applied pressure and field can be interpreted as being due to the change in the orientation of the 4f orbitals.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Orbital degrees of freedom have attracted significant interest in recent years, as they are believed to be important for the occurrence/suppression of the colossal magneto-resistance in manganites and the occurrence of metal–insulator transitions in many transition metal oxides [1]. Orbital ordering can also play an important role in f-electron materials. In 4f electron materials, orbitals (quadrupoles or higher multipoles) may order independently of the magnetic dipoles, which has provoked discussions about the order parameter for the phase transitions, as for example in NpO_2 [2, 3]. Recently, it has also become possible to access such ordering phenomena for f-electron materials more directly by resonant x-ray scattering [2, 4–7], and quantitatively even for multipoles with non-resonant x-ray scattering [8, 9]. These measurements can give important details of the spatial orientation of the orbitals in the ordered state. At this stage, little is known on the influence of pressure and magnetic field on the orbital orientations.

CeB_6 is one of the classical materials exhibiting orbital (antiferroquadrupole, AFQ) ordering at $T_Q = 3.2$ K (phase II), significantly higher than the antiferromagnetic dipole transition at $T_N = 2.4$ K (phase III [10]). At ambient temperatures, the material is cubic

with $a = 4.1412$ Å and space group $Pm\bar{3}m$ [11]. The symmetry of the possible order parameters has been studied in detail by theory [12]. The magnetic phase is characterized by ordering wavevectors $k_{1,2} = (1/4\ \pm 1/4\ 0)$ and $k_{3,4} = (1/4\ \pm 1/4\ 1/2)$, with magnetic moments pointing along the [110] and [1$\bar{1}$0] directions [10]. A recent neutron diffraction study found that the magnetic moments are small and large within alternating sheets along the c axis, respectively [13]. In phase II, neutron diffraction in the presence of an external magnetic field found antiferromagnetic reflections with ordering wavevector $k_0 = (1/2\ 1/2\ 1/2)$, indicative of doubling of the unit cell due to the AFQ order [10]. This has been confirmed by resonant x-ray scattering, which observed superlattice reflections of this type at the Ce L_3 edge [14]. More recently, we have performed non-resonant x-ray diffraction [8, 9], to quantitatively determine these superlattice reflections. The Q-dependence of these reflections clearly indicated that the origin of the scattering is a mixture of quadrupole and hexadecapole moments, as has been predicted theoretically [15]. It has also been shown that the application of a weak magnetic field (0.2 T) perpendicular to the scattering wavevector suppresses the $(h/2\ h/2\ h/2)$ type of reflections. This phenomenon can be understood in terms of rotation of the 4f charge density in an applied field due to the interaction between the quadrupoles and induced octupoles, so that the projection of scattering leads to a zero structure factor. Moreover, by applying a magnetic field along the [111] direction and collecting the $(h/2\ h/2\ h/2)$ reflections, the scattered intensity is significantly increased [16], which reflects the rotation of the 4f charge density as predicted [17].

In this study we concentrate on the influence of uniaxial pressure and magnetic field on the orbital (reflected by the 4f charge density). We show that, when applying uniaxial pressure within the scattering plane perpendicular to the momentum transfer, the intensity of the $(h/2\ h/2\ h/2)$ reflections increases significantly in phase II. This is an indication that the application of uniaxial pressure does rotate the 4f charge density (orbitals), similar to the application of a magnetic field. This shows that we can rotate the orbitals and remove the domains by applying uniaxial pressure and magnetic fields.

2. Experiments

Single crystals were grown by a floating zone method. A plate-like crystal of size $5 \times 3 \times 0.5$ mm^3 was cut with the largest surface perpendicular to the [111] direction. This crystal was clamped using a copper beryllium clamp and mounted in an 8 T superconducting magnet from Oxford Instruments. The uniaxial pressure was applied along the [$\bar{1}$10] direction and its strength was estimated by the size of the surface and the force applied to it. A second crystal of similar dimension cut along the [110] direction was also used. The x-ray diffraction experiments were performed at BL19LXU at SPring-8 using the diffractometer of the experimental station at the end of the beamline [18]. An incident energy of 30 keV was selected by the double-crystal monochromator and a Pt-coated mirror was used to suppress higher harmonics. Copper absorber plates were used to reduce the effect of beam heating on the sample.

3. Results and discussion

Rocking curves of the $(5/2\ 5/2\ 5/2)$ and $(4\ 4\ 4)$ reflections are shown (rescaled in θ and intensity) in figure 1. There is very little difference in the width of the rocking curve between the main and the orbital ordering superlattice reflections, indicating that both the crystal structure and the orbital ordering are similarly well ordered (also along Q, which is not shown), in contrast to the orbital ordering phenomena in the perovskite-based manganites [19]. There, the orbital reflection was found to be significantly broader than those of the lattice. Therefore,

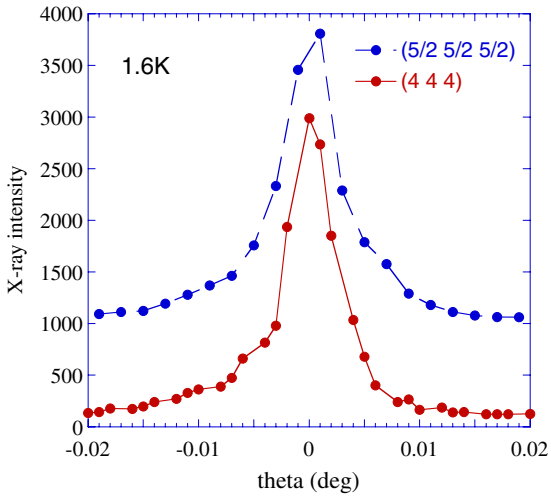

Figure 1. Rocking curve of the orbital (5/2 5/2 5/2) (top) and main structural (4 4 4) (bottom) reflections of CeB_6 taken at 1.6 K in zero magnetic fields.

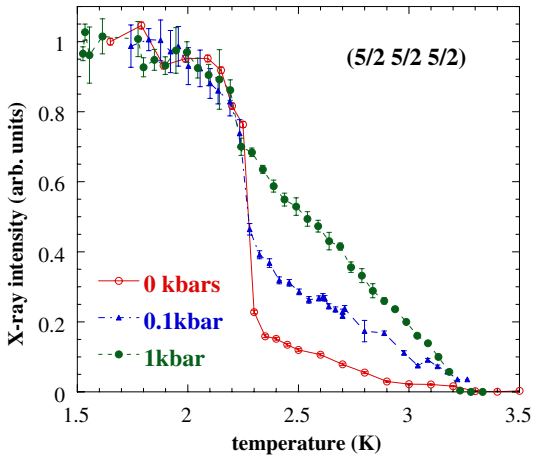

Figure 2. Temperature dependence of the (5/2 5/2 5/2) orbital reflection of CeB_6 for different applied uniaxial pressure along the $[\bar{1}10]$ direction.

in CeB_6, the orbitals are long-range ordered, with few imperfections. The temperature dependence of the (5/2 5/2 5/2) reflection is shown in figure 2 with zero applied pressure and with 0.1 and 1 kbar uniaxial applied pressure along the $[\bar{1}10]$ direction. This $[\bar{1}10]$ direction is lying in the scattering plane and is perpendicular to momentum transfer pointing along the [111] direction. The zero-pressure temperature dependence looks very similar to those presented previously [8], and exhibits a very sharp increase of intensity at T_N. This sharp increase does not originate from the increase of a regular order parameter, but is due to a reorientation of the orbital moments. Therefore, this jump is not caused by a first-order transition, as might be predicted from its discontinuity. The magnetic ordering transition is of second order [13]. This discontinuity at T_N is significantly smaller for 0.1 kbar pressure and almost vanishes at a pressure of 1 kbar, showing a clear trend as a function of applied pressure.

This behaviour can be understood in terms of order parameters (OPs) in phase II, the pure AFQ phase. The structure factor for non-resonant scattering of the multipolar $(h/2\ h/2\ h/2)$ reflections has previously been derived for CeB_6 to be [15]

$$F(\mathbf{q}) \propto \hat{q}_x \hat{q}_y \left\{ \langle j_2 \rangle \langle \mathbf{T}^2_{+2} \rangle + \frac{\sqrt{3}}{2} \langle j_4 \rangle \langle \mathbf{T}^4_{+2} \rangle (7\hat{q}_z^2 - 1) \right\}. \quad (1)$$

Here, $\langle j_2 \rangle$ and $\langle j_4 \rangle$ are Bessel functions (form factors) reflecting the radial distribution of the 4f electrons, $\hat{q}_\alpha$ $\alpha = x, y, z$ is a unit vector and $\langle \mathbf{T}^2_{+2} \rangle$ and $\langle \mathbf{T}^4_{+2} \rangle$ the atomic tensors for the quadrupoles and hexadecapoles of the 4f shell. For the different experimental geometries, the structure factor for the $(h/2\ h/2\ h/2)$ type of reflections and the $(7/2\ 7/2\ 1/2)$ reflection factor can be expressed as

$$F(\mathbf{q}) \propto \hat{q}_x \hat{q}_y \{\langle j_2 \rangle + C\langle j_4 \rangle\} \langle \mathbf{Q}_{xy} \rangle, \tag{2}$$

where C is a constant, and one has $C = 10/3$ for the $(h/2\ h/2\ h/2)$-type reflections and $C = 230/99$ for the $(7/2\ 7/2\ 1/2)$. $\mathbf{Q}_{xy}$ is the order parameter, represented by a quadrupole operator. As the higher-multipole contributions are represented by $\langle j_4 \rangle$ (for the radial part of the electron density) the angular part is directly correlated to that of the $\mathbf{Q}_{xy}$. Therefore, we further consider in the discussion only the quadrupoles. Because of the cubic symmetry, the order parameter of type $\mathbf{Q}_{xy}$ can be any linear combination of $\mathbf{Q}_{xy}$, $\mathbf{Q}_{xz}$ and $\mathbf{Q}_{yz}$. It is therefore useful to describe the order parameter as a vector of type $\mu = (\mathbf{Q}_{yz}, \mathbf{Q}_{zx}, \mathbf{Q}_{xy})$ [17], which replaces the quadrupole moments in equation (2). For example, this replaces $\mathbf{Q}_{xy}$ by $\mathbf{Q}_{xy} + \mathbf{Q}_{xz} + \mathbf{Q}_{yz}$ in equation (2). Note that, in cubic systems, domains have to be considered; this will not affect the q-dependence of the $(h/2\ h/2\ h/2)$ reflections, but may change the ratio between $\langle j_2 \rangle$ and $\langle j_4 \rangle$ in equation (2).

In phase II, there is always some preferred orientation of the orbitals due to for example the surface strain or the strain induced by the glue to hold the sample. Therefore, the temperature dependence of the reflections $(5/2\ 5/2\ 5/2)$ and $(7/2\ 7/2\ 1/2)$ measured on two different crystals, cut along [110] and [111], respectively, are not necessarily the same, as can be seen from figures 2 and 4, respectively. As regards the $(7/2\ 7/2\ 1/2)$ intensity, the intensity increase is absent at T_N, and it even seems to decrease at T_N, in contrast to the $(5/2\ 5/2\ 5/2)$ reflection. A very similar temperature dependence on the $(h/2\ h/2\ l/2)$ reflection in this geometry has also been found by resonant x-ray scattering at the Ce L_3 edge [14]. The intensities in phase II for the two crystal orientations reflect different linear combinations of the order parameter $\boldsymbol{\mu}$. When entering phase III the orbital orientation is locked to the easy axis, introduced by the ordered dipole magnetic Ce moments. Therefore, in phase III the orbital orientation can be influenced only by significantly larger magnetic fields, which affect the magnetic ordering and the magnetic moment directions [8]. Correspondingly, the discontinuity at T_N is very different for the two crystal orientations, as it reflects for both phases a different projection of the different linear combinations of the $\mathbf{Q}_{\alpha\beta}$ in the $\boldsymbol{\mu}$ order parameter. The influence of magnetic fields on the orbital orientations has recently been studied quantitatively by non-resonant x-ray scattering in TbB_2C_2, where even a change of the quadrupole interaction was predicted, depending on the orientation of the orbitals [20]. Such a rotation can be obtained in strong magnetic fields; this also affects the magnetic ordering, as was observed by the field dependence of the antiferromagnetic transition temperature [10]. The reduction of the ordering temperature is clearly seen in figure 4. The discontinuity of the scattered intensity of the $(7/2\ 7/2\ \bar{1}/2)$ reflection at T_N is shifted to lower temperatures for increasing magnetic fields along the $[\bar{1}10]$ direction.

The almost first-order-like jump in the $(h/2\ h/2\ h/2)$-type superlattice reflections does not represent the change in the modulus of the expectation value of the quadrupole moment $\mathbf{Q}_{\alpha\beta}$, but only its linear combination (the rotation of the quadrupole). Alternatively, this could also be viewed as a redistribution of domains, from one type of orbital moment to another. This could not be distinguished in our experiment; however, for a given Ce moment in the domain, the one which disappears, it still reflects a reorientation of the orbital. Note that this applies also for the field and pressure influence on the orbital orientations. This enables us now to extract the true order parameter of the quadrupole $\mathbf{Q}_{\alpha\beta}$ by removing the anomalous

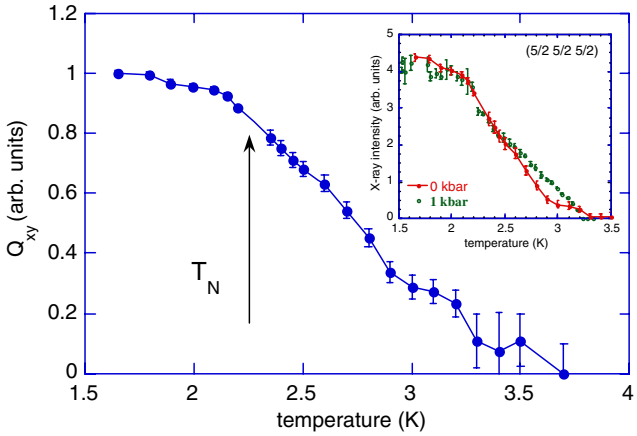

Figure 3. Temperature dependence of the quadrupole moment $\mathbf{Q}_{xy}$ in CeB_6 (order parameter) extracted from the orbital (5/2 5/2 5/2) reflection. Inset: temperature dependence of the integrated x-ray intensity of the (5/2 5/2 5/2) reflection, corrected for the jump at T_N and compared with the intensities taken with 1 kbar applied uniaxial pressure along the $[\bar{1}10]$ direction.

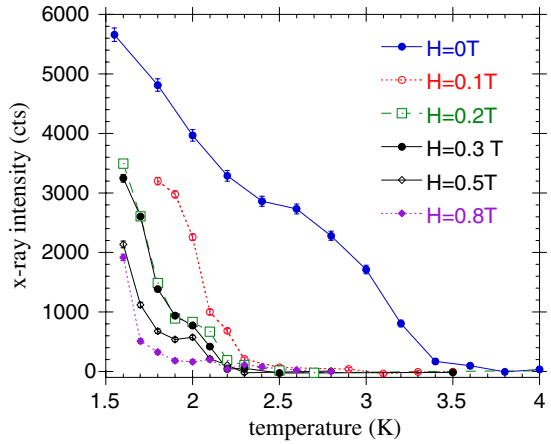

Figure 4. Temperature dependence of the (7/2 7/2 1/2) reflection for different applied magnetic fields along the $[\bar{1}10]$ direction of CeB_6.

part associated with the phase transition from the data obtained at zero pressure. Figure 3 (inset) shows the corresponding temperature dependence of the integrated intensity extracted from the (5/2 5/2 5/2) reflection compared with the data under 1 kbar uniaxial pressure. They both look very similar and mainly reflect the order parameter behaviour. The corresponding temperature dependence of the quadrupole moment $\mathbf{Q}_{\alpha\beta}$, which is proportional to the structure factor, is then easily extracted by rescaling of the x-ray intensities below T_N. The two x-ray intensities, which lie below and above the discontinuity, are removed and the square roots of the intensities, reflecting the quadrupole moment, are shown in figure 3. This shows a gradual temperature dependence, as expected from the order parameter of the AFQ transition down to low temperatures. In similarity with a magnetic order parameter, it resembles a Brillouin function. It is interesting to compare these results with those of the AFQ in DyB_2C_2, where no discontinuity in the temperature dependence was observed in the orbital (0 0 1/2) reflection

at T_N [21]. This reflects that there is no locking of the orbital at T_N, indicative for a stronger orbital–orbital or orbital–lattice interaction. Surprisingly, the temperature dependence of the reflection under 1 kbar uniaxial pressure has a linear dependence below the phase transition, indicative for a critical exponent close to 0.5, which reflects a mean-field-type behaviour. This is in contrast to that observed for DyB_2C_2 [22] with a smaller critical exponent, possibly caused by the anisotropy of the Dy susceptibility, leading to a tendency to be more Ising like. We note that also a smaller coefficient was found in zero fields and zero pressure for the (5/2 3/2 3/2) reflection in CeB_6, consistent with our zero-field data [14].

In summary, we have performed non-resonant x-ray scattering experiments CeB_6 to study the field and stress dependence of the antiferroquadrupolar ordering of the Ce 4f moments. The application of moderate uniaxial pressure along the $[\bar{1}10]$ direction enhances the intensity of the $(h/2\ h/2\ h/2)$ reflection in the AFQ phase significantly. This does not reflect a significant increase in order parameter, but rather a rotation of the 4f charge density (orbitals), as also observed by the application of a magnetic field in the same direction. A magnetic field perpendicular to the scattering wavevector reduces the intensities very strongly. These results show that the orbital orientation can relatively easy be manipulated by magnetic fields and uniaxial applied pressure due to the cubic symmetry of CeB_6.

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