The quartet ground state in CeB\textsubscript{6}: An inelastic x-ray scattering study

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Abstract – We investigated the ground-state symmetry of the cubic hidden order compound CeB\textsubscript{6} by means of core level non-resonant inelastic x-ray scattering (NIXS). The information is obtained from the directional dependence of the scattering function that arises from higher than dipole transitions. Our new method confirms that the ground state is well described using a localized crystal-field model assuming a Γ\textsubscript{8} quartet ground state.

Introduction. – The material class of rare-earth hexaborides has attracted considerable attention over the years. It comprises a variety of different fascinating ground states (see ref. [1] and references therein) which include exotic magnetically ordered phases, heavy-fermion behavior, as well as Kondo insulating ground states. CeB\textsubscript{6} is an important member of this material class, well known for its so-called hidden magnetic order. The very recent theoretical suggestion that SmB\textsubscript{6} could be a strongly correlated topological insulator [2,3] even caused a flurry of new investigations (see ref. [4] and references therein), thereby raising speculations that also YbB\textsubscript{6} under pressure could be topological. The standard and at the same time pressing question in all these studies concerns the symmetry of the ground-state wave function of the crystal-electric field split 4\textit{f} multiplet. Here we explore the feasibility of using a recently developed experimental method, namely core-level non-resonant inelastic x-ray scattering (NIXS), to determine the ground-state wave function of CeB\textsubscript{6}, a system which crystallizes in the cubic CsCl structure. Figure 1 displays how the crystal-electric field splits the sixfold degenerate \( j = 5/2 \) multiplet state of the Ce\textit{4f}\textsuperscript{1} into a Γ\textsubscript{8} quartet and Γ\textsubscript{7} doublet. CeB\textsubscript{6} is a heavy-fermion compound that has been intensively studied for its rich magnetic phase diagram [5].
and $\Gamma^7$ are not distinguishable between the $\Gamma^7$ quartet and the $\Gamma^7$ doublet state (see fig. 1). We have therefore performed an experiment that probes the symmetry with higher multipole transitions. This can be realized in a core level non-resonant inelastic x-ray scattering (NIXS) experiment with large momentum transfers $|q|$. For large enough $|q|$ the expansion of the transition operator $e^{iqr}$ in the scattering function $S(q, \omega)$ can no longer be truncated after the first term and, as a result, higher multipole terms contribute to $S(q, \omega)$. These extra multipole contributions then give information that is not accessible in a dipole experiment [26–36].

Bradley et al. [33] and Gordon et al. [34] were the first to observe higher multipole transitions in rare-earth materials at the $N_{4.5}$ core level excitation for large momentum transfers $|q|$ and the data were well described with a local many-body approach by Haverkort et al. [27]. Already the early papers suggested that vector-\(q\)-dependent NIXS experiments on a single crystal should give insight into the ground-state symmetry in analogy to an XAS experiment with linear polarized light [27,28,33,34], and indeed, an experiment on cubic single crystals of MnO and CeO$_2$ at the Mn $M_{2,3}$ and Ce $N_{4.5}$ edges revealed direction dependences in the higher multipole scattering function [29]. Very recently, NIXS has been successfully used to determine the ground-state symmetry and/or determine the rotation of the \(f\)-orbitals in fourfold symmetry in Ce single crystals [37–39].

**Experimental.** – The single-crystal samples of CeB$_6$ were grown by the Al-flux method. Typically 0.7 g of CeB$_6$ (as the elements) are heated with 60 g of high-purity Al (59) to 1450°C, held there for 8 h and then cooled to 1000°C at 2°C/h, when the furnace is shut off. The crystals are leached from the Al in NaOH solution.

The NIXS measurements on the CeB$_6$ Ce $N_{4.5}$ core level were performed at the beamline P01 of PETRA-III. The incident energy was selected with a Si(311) double monochromator. The P01 NIXS end station has a vertical geometry with twelve Si(660) 1 m radius spherically bent crystal analyzers that are arranged in a 3 x 4 array (see fig. 2). The fixed final energy was 9690 eV. The analyzers were positioned at scattering angles of $2\theta \approx 150^\circ$.
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155°, and 160°, which corresponds at elastic scattering to an averaged momentum transfer of \(|q| = (9.6 \pm 0.1) \text{ Å}^{-1}\). The scattered beam was detected by a position-sensitive custom-made Lambda detector, based on a Medipix3 chip detector. The elastic line was regularly measured and pixelwise calibration yields an instrumental energy resolution of FWHM ≈ 0.7 eV. A sketch of the scattering geometry, showing the incoming and outgoing photons as well as the transferred momentum \(\mathbf{q}\), is given in fig. 2 for a scan with \(|\mathbf{q}| = 100\) in specular geometry. In order to realize another crystallographic direction, e.g., \(|\mathbf{q}| = 110\), the sample can be turned with respect to the scattering triangle, or a different sample with another polished surface may be mounted in specular geometry.

Two crystals with (100) and (110) surfaces were mounted in a vacuum cryostat with Kapton windows. The measurements were performed with a pressure in the 10⁻⁶ mbar range. The two samples were oriented such that for \(|\mathbf{q}| = 100\) and \(|\mathbf{q}| = 110\) a specular scattering geometry was realized, i.e., with the surface normal parallel to the momentum transfer (\(\phi = \phi_0 = \theta\)). In order to check the reliability, the \(|\mathbf{q}| = 110\) measurement was repeated on the (100) crystal but with the surface normal being rotated 45° away from \(\mathbf{q}\) (\(\phi = \phi_0 - 45°\)). The data were fully consistent. The \(|\mathbf{q}| = 111\) situation was realized by turning the (110) crystal to \(\phi = \phi_0 - 35°\).

**Results and discussion.** – Figure 3 shows the NIXS spectrum across the Ce N₄,₅, N₂,₃, and N₁ edges, the B K edge as well as the Compton signal. The direction of the momentum transfer is \(|\mathbf{q}| = 9.6 \text{ Å}^{-1}\). (a) CeB₆ CeN₄,₅ NIXS spectra \(|\mathbf{q}| = 9.6 \text{ Å}^{-1}\) \(\Gamma_7\) \(\Gamma_8\) \(T = 17K\) \(T = 295K\)

Fig. 3: Experimental NIXS spectra of CeB₆: a wide scan covering the Ce O₅, N₄,₅, N₂,₃, and N₁ edges, the B K edge as well as the Compton signal. The direction of the momentum transfer is \(|\mathbf{q}| = 100\).

N₄,₅ NIXS is an extremely suitable experimental method for the study of the local electronic structure of CeB₆, and for that matter, the class of rare-earth hexaborides. The top panel (a) of fig. 4 shows the Ce N₄,₅ NIXS spectra of CeB₆ (dots) taken at 17 K, for the three momentum directions \(|\mathbf{q}| = 100\), \(|\mathbf{q}| = 110\), and \(|\mathbf{q}| = 111\). The temperature of 17 K is low enough to assure that only the ground state is populated. We recall that the excited crystal-field state is 46 meV above the ground state [16,17]. Here only a constant background has been subtracted to account for the (weak) Compton signal (about 12% of the signal peak) (see fig. 3). The size of the dots resembles the statistical error bar.

There is a clear direction dependence that shows up strongest in the energy interval of 103 to 106 eV. Espe-

Fig. 4: (Colour online) Top panel (a): calculated and experimental NIXS spectra of the Ce N₄,₅ edge for the three transferred momentum directions \(|\mathbf{q}| = 100\), \(|\mathbf{q}| = 110\), and \(|\mathbf{q}| = 111\). Bottom panel: difference spectra \(I(\mathbf{q}| = 100\) – \(I(\mathbf{q}| = 110\) (black dots) at low \(T\) and (c) at room temperature and respective simulations (see text).
cially the $\mathbf{q} \parallel [100]$ direction differs from the $\mathbf{q} \parallel [110]$ and [111]. We can obtain a more detailed view at the directional dependence by constructing the difference spectra $I_{\mathbf{q} \parallel [100]} - I_{\mathbf{q} \parallel [110]}$ that is displayed as dichroism in the bottom panel (b) of fig. 4 (black dots).

The Ce$_{N_{4,5}}$ NIXS data are simulated by calculating the $4d^{10}4f^1 \rightarrow 4d^{9}4f^2$ transition using the full multiplet code Quanty [40] which includes Coulomb as well as spin-orbit interactions. A Gaussian and a Lorentzian broadening of FWHM = 0.7 eV and 0.4 eV, respectively, are used to account for the instrumental resolution and lifetime effects. The atomic Hartree-Fock values were adjusted via the peak positions, resulting in reductions of 30% and 22% for the 4f-4f and 4d-4f Coulomb interactions, respectively. The reduction accounts for configuration interaction effects not included in the Hartree-Fock scheme [41].

A momentum transfer of $|\mathbf{q}| = 9.2 \text{Å}^{-1}$ has been used for the simulations (and not the experimental value of $(9.6 \pm 0.1) \text{Å}^{-1}$) so that the experimental peak ratio of the two main features around 108 and 110 eV is reproduced best. This fine tuning optimizes the multipole contributions to the scattering functions to mimic for a minor adjustment of the calculated radial wave functions of the Ce$^{3+}$ atomic wave function (see, e.g., ref. [37]).

We now compare the measured spectra and the dichroism therein with the simulations for the two possible scenarios, namely one with the $\Gamma_8$ doublet as ground state and the other with the $\Gamma_8$ quartet. The results are plotted in fig. 4(a). The $\Gamma_8$ quartet scenario reproduces in great detail the experimental spectra for all three $\mathbf{q}$ directions. Actually, the match is excellent. In contrast, the simulation based on the $\Gamma_7$ doublet exhibits large discrepancies with respect to the experiment: the intensities of several features in the spectra are not correct. To make the difference between the two scenarios even more contrasting, we compare the experimental and calculated dichroic spectra, i.e., $I_{\mathbf{q} \parallel [100]} - I_{\mathbf{q} \parallel [110]}$, as displayed in the bottom panel (b). There is an excellent match for the $\Gamma_8$ quartet ground-state scenario but a large mismatch for the $\Gamma_7$ doublet. From these comparisons we can unambiguously conclude that the $\Gamma_8$ quartet forms the ground state in CeB$_6$.

In addition, we have taken spectra at $T = 295\text{K}$. The spectra look very similar to the low-temperature data but the dichroism is reduced by about 20%, see bottom panel (c) of fig. 4. We would like to note that thermal broadening effects are negligible with respect to the instrumental resolution and intrinsic lifetime. In agreement with ref. [21] the reduction in the dichroism is fully consistent with a partial population of the excited $\Gamma_7$ state at 46 meV. A simulation in which the Boltzmann weighted contributions of the $\Gamma_8$ and $\Gamma_7$ states are taken into account is represented by the magenta line in panel (c) of fig. 4. The excellent agreement provides yet another evidence for the thorough understanding we have obtained using NIXS on the Ce 4f symmetry and crystal-electric field effects in CeB$_6$.

**Summary.** – Using CeN$_{4,5}$ non-resonant inelastic x-ray scattering (NIXS) we were able to establish that the ground-state symmetry of the cubic hidden order compound CeB$_6$ is the $\Gamma_8$ quartet. The high signal-to-background ratio of the N$_{4,5}$ NIXS signal indicates that this bulk-sensitive and element-specific spectroscopic technique is a powerful method to study the local electronic structure of the rare-earth ions in rare-earth borides. With NIXS probing directly the charge distribution of the 4f electrons, it complements nicely neutron scattering based techniques which provide direct information on the spin distribution.

**REFERENCES**

[1] Sun L. and Wu Q., *Rep. Prog. Phys.*, **79** (2016) 084503.

[2] Dzero M., Sun K., Galitski V. and Coleman P., *Phys. Rev. Lett.*, **104** (2010) 106408.

[3] Takimoto T., *J. Phys. Soc. Jpn.*, **80** (2011) 123710.

[4] Dzero M., Xia J., Galitski V. and Coleman P., *Anna. Rev. Condens. Matter Phys.*, **7** (2016) 249.

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

[6] Erkelenk W., Egnaught L. P., Burlet P., Rossat-Mignod J., Kunii S. and Kasuya T., *J. Magn. & Magn. Mater.*, **63-64** (1987) 61.

[7] Shina R., Shiba H. and Thalmeier, *J. Phys. Soc. Jpn.*, **66** (1997) 1741.

[8] Matsumura T., Yonemura T., Kunimori K., Sera M. and Iga F., *Phys. Rev. Lett.*, **103** (2009) 017203.

[9] Lovesey S. W., *J. Phys.: Condens. Matter*, **14** (2002) 4415.

[10] Friemel G., Li Y., Dukhnenko A., Shitsevalova N., Sluchanko N., Ivanov A., Filipov V., Kedzierski B. and Inosov D., *Nat. Commun.*, **3** (2012) 830.

[11] Portnichenko P. Y., Demishev S. V., Semen A. V., Ohta H., Cameron A. S., Surmach M. A., Jang H., Friemel G., Dukhnenko A. V., Shitsevalova N. Y., Filipov V. B., Schneidewind A., Ollivier J., Podlesnyak A. and Inosov D. S., *Phys. Rev. B*, **94** (2016) 035114.
The quartet ground state in CeB$_6$: An inelastic x-ray scattering study

[12] Cameron A. S., Friemel G. and Inosov D. S., Rep. Prog. Phys., 79 (2016) 066502.

[13] Akbari A., Neupane M., Alidoust N., Belopolski I., Bian G., Xu S.-Y., Kim D.-J., Shihayev P. P., Sanchez D. S., Zheng H., Chang T.-R., Jeng H.-T., Riseborough P. S., Lin H., Bansil A., Durakiewicz T., Fisk Z. and Hasan M. Z., Phys. Rev. B, 92 (2015) 104420.

[14] Koitzsch A., Heming N., Knupfer M., Bühchner B., Portnichenko P. Y., Dukhnenko A. V., Shitsevalova N. Y., Filipov V. B., Lev L. L., Strocov V. N., Ollivier J. and Inosov D. S., Nat. Commun., 7 (2016) 10876.

[15] Zirngibl E., Hillebrands B., Blumenröder S., Güntherodt G., Loewenhaupt M., Carpenter J. M., Winzer K. and Fisk Z., Phys. Rev. B, 30 (1984) 4052.

[16] Loewenhaupt M., Carpenter J. M. and Loong C.-K., J. Magn. & Magn. Mater., 52 (1985) 245.

[17] Terzioğlu C., Browne D. A., Goodrich R. G., Hassan A. and Fisk Z., Phys. Rev. B, 63 (2001) 235110.

[18] Sato N., Kunii S., Oguro I., Komatsubara T. and Kasuya T., J. Phys. Soc. Jpn., 53 (1984) 3067.

[19] Givord F., Bouchierle J.-X., Burlet P., Gibson B. and Kunii S., J. Phys.: Condens. Matter, 15 (2003) 3095.

[20] Tanaka K. and Onuki Y., Acta Crystallogr. B, 58 (2002) 423.

[21] Makita R., Tanaka K., Onuki Y. and Tatewaki H., Acta Crystallogr. B, 63 (2007) 683.

[22] Hansmann P., Severing A., Hu Z., Haverkort M. W., Chang C. F., Klein S., Tanaka A., Hsieh H. H., Lin H.-J., Chen C. T., Fäk B., Lejay P. and Tjeng L. H., Phys. Rev. Lett., 100 (2008) 066405.

[23] Strigari F., Willers T., Muro Y., Yutani K., Takabatake T., Hu Z., Chin Y.-Y., Agrestini S., Lin H.-J., Chen C. T., Tanaka A., Haverkort M. W., Tjeng L. H. and Severing A., Phys. Rev. B, 86 (2012) 081105(R).

[24] Willers T., Strigari F., Hu Z., Sessi V., Brookes N., Bauer E., Sarrao J., Thompson J., Tanaka A., Wirth T., Tjeng L. and Severing A., Proc. Natl. Acad. Sci. U.S.A., 112 (2015) 2384.

[25] Larson B. C., Ku W., Tischler J. Z., Lee C.-C., Restrepo O. D., Eguíluz A. G., Zschack P. and Finkelstein K. D., Phys. Rev. Lett., 99 (2007) 026401.

[26] Haverkort M. W., Tanaka A., Tjeng L. H. and Sawatzky G. A., Phys. Rev. Lett., 99 (2007) 257401.

[27] Gordon R. A., Seidler G. T., Fister T. T., Haverkort M. W., Sawatzky G. A., Tanaka A. and Shams T. K., EPL, 81 (2008) 26004.

[28] Gordon R. A., Haverkort M. W., Sen Gupta S. and Sawatzky G. A., J. Phys.: Conf. Ser., 190 (2009).

[29] Bradley J. A., Sen Gupta S., Seidler G. T., Moore K. T., Haverkort M. W., Sawatzky G. A., Conradson S. D., Clark D. L., Kozimor S. A. and Boland K. S., Phys. Rev. B, 81 (2010) 193104.

[30] Cacciuffo R., van der Laan G., Simonelli L., Vitova T., Mazzoli C., Denecke M. A. and Lander G. H., Phys. Rev. B, 81 (2010) 195104.

[31] Sen Gupta S., Bradley J. A., Haverkort M. W., Seidler G. T., Tanaka A. and Sawatzky G. A., Phys. Rev. B, 84 (2011) 075134.

[32] Bradley J. A., Moore K. T., van der Laan G., Bradley J. P. and Gordon R. A., Phys. Rev. B, 84 (2011) 205105.

[33] Gordon R. A., Seidler G. T., Fister T. T. and Nagle K. P., J. Electron Spectrosc. Relat. Phenom., 184 (2011) 220.

[34] Hiraoka N., Suzuki M., Cai Y. Q., Haverkort M. W., Lee C. C. and Ku K., Phys. Rev. Lett., 96 (2006) 37007.

[35] van der Laan G., Phys. Rev. Lett., 108 (2012) 077401.

[36] Willers T., Strigari F., Hiraoka N., Cai Y. Q., Haverkort M. W., Tsuei K.-D., Liu Y. F., Seibo S., Geibel C., Steglich F., Tjeng L. H. and Severing A., Phys. Rev. Lett., 109 (2012) 046401.

[37] Rudef J.-P., Ablett J. M., Strigari F., Deppe M., Haverkort M. W., Tjeng L. H. and Severing A., Phys. Rev. B, 91 (2015) 201108.

[38] Sundermann M., Strigari F., Willers T., Winkler H., Prokofiev A., Ablett J. M., Rudef J.-P., Schmitz D., Weshke E., Moretti Sala M., Al-Zein A., Tanaka A., Haverkort M. W., Kasinathan D., Tjeng L. H., Paschen S. and Severing A., Sci. Rep., 5 (2015) 17937.

[39] Haverkort M. W., J. Phys.: Conf. Ser., 712 (2016) 012001.

[40] Tanaka A. and Jo T., J. Phys. Soc. Jpn., 63 (1994) 2788.