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Crystal-field excitations in CeB_6 studied by Raman and neutron spectroscopy

E. Zirngiebl, B. Hillebrands, S. Blumenröder, and G. Güntherodt
II. Physikalisches Institut, Universität Köln, 5000 Köln 41, Federal Republic of Germany

M. Loewenhaupt
Institut für Festkörperforschung, Kernforschungsanlage Jülich, 5170 Jülich 1, Federal Republic of Germany

J. M. Carpenter
Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, Illinois 60439

K. Winzer
I. Physikalisches Institut, Universität Göttingen, 3400 Göttingen, Federal Republic of Germany

Z. Fisk
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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The Γ_8-Γ_7 crystalline-electric-field (CEF) transition of CeB_6 has been identified near 530 K (46 meV, 372 cm^{-1}) with use of inelastic neutron and polarized Raman scattering. From the anomalous temperature behavior of the transition energy observed in Raman scattering we deduce a Γ_8 ground state split by 20 cm^{-1} (30 K). The novel CEF level scheme yields a consistent and unified interpretation of so far seemingly unrelated thermal, elastic, and magnetic data.

In spite of the large body of thermal, magnetic, and elastic data of CeB_6 accumulated over the past years[1-9] various diverging speculations have entered the literature concerning the crystalline-electric-field (CEF) excitations.[2-11] Their absence in direct spectroscopic measurements[4] has been puzzling ever since. This led to a wide variety of proposed CEF splittings ranging from 10 K (Ref. 3) to more than 400 K (Ref. 4) and gave rise to conjectures about anomalous broadening or splitting effects.[4,5,11]

Since the key point to the underlying physics of CeB_6 turned out to be the direct observation of the CEF excitations, we have performed inelastic magnetic neutron scattering experiments using high-energy incident neutrons up to 185 meV. We found an inelastic magnetic transition near 530 K,[12] which has also been investigated by Raman spectroscopy, taking advantage of the high resolution as compared to neutron spectroscopy. Our data yield a completely new CEF level scheme: The ground state has Γ_8 symmetry and is split by about 30 K, whereas the Γ_7 state is at 545 K. On this basis we show that a straightforward, consistent interpretation of the different experimental data is achieved. Moreover, this is the first time that a CEF excitation has been observed in a metal by means of Raman scattering.

CeB_6 crystallizes in the cubic CaB_6 structure (space group O_h^1).[13] The sample preparation is described elsewhere.[1,14] The sixfold degenerate ground state $4f^1(J=\frac{5}{2})$ of Ce^{3+} is expected to split into a Γ_7 doublet and a Γ_8 quartet. This excitation has been investigated by inelastic neutron scattering experiments on a powder of 35 g CeB_6 (enriched to 99% with the low-absorption ^{11}B isotope; parts of the same sample were taken for the neutron experiments of Ref. 4) using the chopper instrument LRMECS (low-resolution medium energy chopper spectrometer) of the Intense Pulsed Neutron Source at Argonne Laboratory. The measurements were carried out at 18 and 300 K, with incident neutron energies of $E_0=185$ and 145 meV, respectively. The spectra were corrected for transmission-dependent background and calibrated by a vanadium standard. Figure 1 shows the scattering law for CeB_6 obtained from the forward detectors between scattering angles of 3°–7°, corresponding to a momentum transfer of 1.5 $Å^{-1}$ at 46-meV energy transfer. An inelastic peak at $\Delta=46$ meV (530 K) is clearly identified as magnetic scattering by its Q dependence and is indicated by the dashed guide line. The absolute intensity of this inelastic magnetic transition corresponds to the value for a Γ_8-Γ_7 crystal-field transition of Ce^{3+}. The phonon background in the spectrum, as indicated by the dotted line, is usually observed in experiments with high incident neutron energies due to multiple phonon scattering.

Moreover, we have carried out Raman measurements on

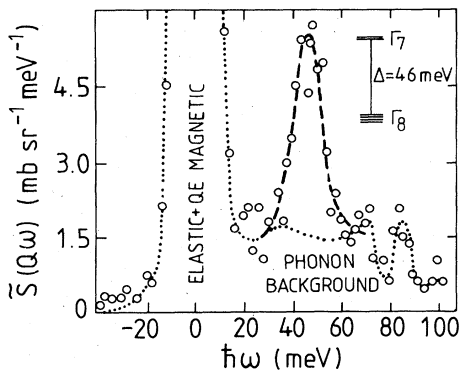

FIG. 1. Neutron-scattering law for CeB_6 at 18 K with an incident neutron energy of 185 meV ($Q_{inel}=1.5$ $Å^{-1}$ at 46 meV).

(100) faces of CeB_6 between 300 and 4.2 K using 5309-Å Kr^+ laser excitation. At room temperature we have found an inelastic excitation at 372 cm^{-1} (530 K) as shown in Fig. 2. Below 20 K the peak shifts by about 10 cm^{-1} to higher energies. At 4.2 K it is much narrower and has an energy of 382 cm^{-1} (Fig. 2). The intensity of the peak does not change between 4.2 and 300 K because of the high excitation energy (530 K) compared to the sample temperature. Therefore, we cannot distinguish between a CEF excitation and a phonon by the intensity variation alone. However, the unusually large peak shift and its onset below 20 K rules out a phononic excitation since no lattice anomaly has been observed in this temperature range.[5] In addition, the nonmagnetic reference compound LaB_6 shows no excitation in that energy range at any temperature (see Fig. 2, e.g., 77 K). Hence, we conclude that the excitation near 372 cm^{-1} in CeB_6 corresponds to the Γ_8-Γ_7 CEF transition within the $4f^1$ configuration.

In order to further corroborate our CEF level assignment we have performed a symmetry analysis by polarized Raman measurements shown in Fig. 3. For comparison the well-known three Raman-active phonons appearing above 600 cm^{-1} have been included. The 372-cm^{-1} peak appears in the $\Gamma_3^+(E_g)$ and $\Gamma_5^+(T_{2g})$ symmetry components. This is consistent with a Γ_8-Γ_7 transition because the direct symmetry product of initial and final states $|\Gamma_8\rangle \otimes \langle\Gamma_7| = \Gamma_3^+ \oplus \Gamma_4^+ \oplus \Gamma_5^+$ contains the experimentally observed symmetries.

From our symmetry analysis it cannot be decided which is the electronic ground state. However, we can deduce this information from the anomalous shift of the 372 cm^{-1} peak in Fig. 2 for temperatures below 20 K. This behavior is explained by a non-Kramers ground state of Γ_8 symmetry, which is split into two doublets $\Gamma_{8,1}$ and $\Gamma_{8,2}$ with a separation of about 30 K. At temperatures well above 30 K, transitions from both $\Gamma_{8,i}$ doublets to the high-lying Γ_7 level are possible, yielding the measured mean transition energy of 372 cm^{-1} (530 K). A double peak structure could not be resolved even in Raman scattering (experimental resolution 3 cm^{-1}) because of the large inherent width of the peaks. Upon cooling well below 30 K the upper doublet $\Gamma_{8,2}$ becomes thermally depopulated and the scattering takes place between the lower $\Gamma_{8,1}$ doublet and the Γ_7 level. This yields a shift of the observed transition energy upon cooling by $(E_{8,2}-E_{8,1})/2 = 15$ K $= 10$ cm^{-1} towards higher energy. The new CEF level scheme derived from the Raman measurements is shown in the inset of Fig. 2. This is the first time that such a level scheme has been proposed for CeB_6. All previous schemes assumed a Γ_7 ground state and no splitting of the Γ_8 level.[1,3–8,10,12] The splitting of the Γ_8 level could not yet be observed directly by either neutron scattering[4] or Brillouin scattering, most likely owing to the $\Gamma_{8,1}$-$\Gamma_{8,2}$ matrix element which is about an order of magnitude smaller compared to the $\Gamma_{8,i}$-Γ_7 transitions.

The above introduced new level scheme provides a straightforward interpretation of the specific-heat data.[5] The change of the entropy from R ln2 at about 3 K to R ln4 at about 30 K is consistent with the 30-K splitting of the Γ_8 level into two doublets.

From the magnetization data in magnetic fields up to 150

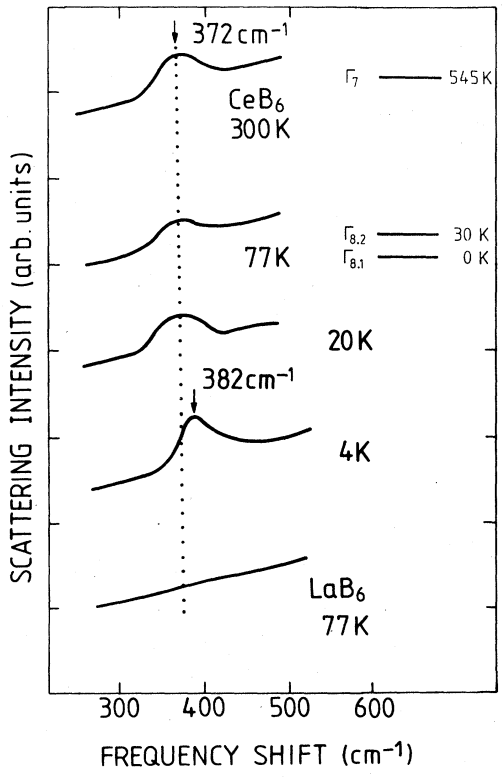

FIG. 2. Raman scattering intensities of CeB_6 and LaB_6 at different temperatures showing the Ce^{3+} Γ_8-Γ_7 CEF transition. Inset: Derived CEF level scheme of CeB_6.

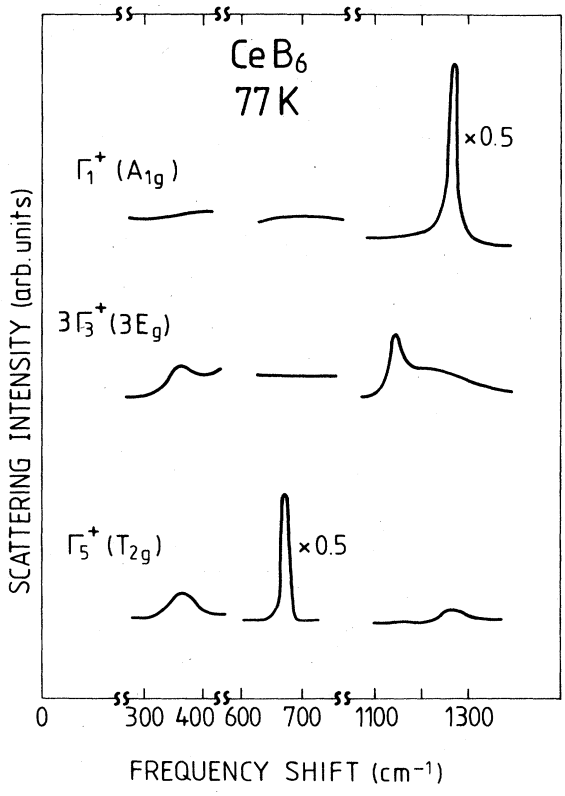

FIG. 3. Symmetry analysis of the Γ_8-Γ_7 CEF transition and the Raman-active phonons of CeB_6.

kG[2,4,8] a magnetic moment of the ground state of about 1.0 μ_B can be deduced which exceeds $0.71\mu_B$ for a pure Γ_7 ground state. This has previously been attributed to an admixture of the Γ_8 level into the Γ_7 ground state.[8] In view of the new findings of a high-lying CEF level near 545 K, this explanation has to be ruled out. The magnetization data, in fact, suggest a splitting of the Γ_8 ground state, since the degenerate Γ_8 level gives a magnetic moment of $1.54\mu_B$. The measured magnetic form factor[9] is consistent with the split Γ_8 ground state. The previous interpretation involving a Γ_8 excited state less than 20 K above the Γ_7 ground state has to be rejected.

Measurements of the elastic constants as a function of temperature[3] can be fitted more satisfactory by supposing a Γ_8 ground state. This will be shown elsewhere.[15,16] The fit presented by Goto *et al.*,[3] assuming a Γ_7 ground state and a Γ_7-Γ_8 splitting of 10 K, is inappropriate because it yields a minimum near 5 K and a sharp increase below this temperature. More direct evidence for a Γ_8 ground state is given by the magnetic field dependence of the elastic constants.[16] These results also support the conjectured antiferroquadrupolar ordering at 3.3 K (Ref. 11) which necessarily involves a low-lying Γ_8 state.

The thermoelectric power data[17] show a sharp maximum near 7 K, suggesting a CEF splitting of roughly 20 K which is in qualitative agreement with our Γ_8 splitting of abut 30 K.

With our new CEF level scheme (inset of Fig. 2) the magnetic susceptibility data[8] can be fitted between 3.3 and 700 K without any adjustable parameter, except a reduction factor of 1.29 for the total susceptibility.[18] In a previous fit[4] assuming a Γ_7 ground state, a phenomenological treatment of the temperature-dependent exchange interactions has been used involving four adjustable parameters. The magnetic susceptibility between 5 and 600 K could be fitted by Kawakami, Kunii, Komatsubara, and Kasuya[8] only for two different temperature intervals, using the same phenomenological exchange treatment and up to three parameters.

The experimental evidence for the splitting of the Γ_8 ground state has to be attributed to a distortion of the cubic symmetry. Four mechanisms have to be considered.

(a) A static distortion has to be ruled out on the basis of x-ray analysis between 300 and 4.2 K with an accuracy $\Delta a/a \simeq 10^{-4}$.[19]

(b) A coupling of the Γ_5^+ optical phonon (672 cm^{-1}) to the Γ_8-Γ_7 CEF excitation (372 cm^{-1}) is too much off resonance in order to lift the Γ_8 degeneracy, contrary to the case of $CeAl_2$.[20,21]

(c) A dynamic Jahn-Teller effect, involving low-energy acoustic phonons of appropriate energy and symmety, appears in principle possible.

(d) A hybridization-mediated anisotropic coupling of the $4f$ wave functions to the p-like boron or $5d$-type cerium wave functions[2] could yield a reduction of the cubic symmetry for the electronic system, analogously to the cerium monopnictides.[22]

Cases (c)[23] and (d)[22] could account for the reduction of the magnetic susceptibility as compared to the free-ion effective moment.

In conclusion, we have provided direct spectroscopic evidence that the inelastic excitation in Raman and neutron scattering in CeB_6 near 372 cm^{-1} is the Γ_8-Γ_7 CEF transition. The high resolution in Raman scattering allowed the identification of the Γ_8 ground-state splitting of about 30 K. The versatility of this high-resolution spectroscopic tool could be emphasized by the first observation of CEF excitations in a metal. The derived new CEF level scheme so far provides the most simple interpretation of the measured thermal, elastic, and magnetic data. However, the reduced magnetic moment of CeB_6 appears to evolve as a common feature of many γ-Ce-type Kondo compounds.

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