Crystal-field excitations in CeB$_6$ studied by Raman and neutron spectroscopy

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The $\Gamma_8$-$\Gamma_7$ crystaline-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 $\Gamma_8$ 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 $\Gamma_8$ symmetry and is split by about 30 K, whereas the $\Gamma_7$ 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 $\Gamma_7$ doublet and a $\Gamma_8$ 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 LRMES (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 $\Gamma_8$-$\Gamma_7$ 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 ($Q_{\text{inc}} = 1.5$ Å$^{-1}$ at 46 meV).](image)

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(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. 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 $\Gamma_8$-$\Gamma_7$ CEF transition within the $4f^6$ 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 $\Gamma_1^+(E_g)$ and $\Gamma_2^+(T_{2g})$ symmetry components. This is consistent with a $\Gamma_3^-$-$\Gamma_7$ transition because the direct symmetry product of initial and final states $\Gamma_3^-(E_g) \otimes (\Gamma_7^-) = \Gamma_3^+ \oplus \Gamma_4^+ \oplus \Gamma_5^+$ 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 $\Gamma_5$ 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 $\Gamma_{8,1}$ doublets to the high-lying $\Gamma_7$ 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 $\Gamma_7$ level. This yields a shift of the observed transition energy upon cooling by $(E_{8,2} - E_{8,1})/2 = 15$ K $\sim 10$ 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 $\Gamma_7$ ground state and no splitting of the $\Gamma_8$ level. The splitting of the $\Gamma_8$ level could not yet be observed directly by either neutron scattering 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 $\Gamma_{8,1}$-$\Gamma_7$ transitions.

The above introduced new level scheme provides a straightforward interpretation of the specific-heat data. The change of the entropy from $R \ln 2$ at about 3 K to $R \ln 4$ at about 30 K is consistent with the 30-K splitting of the $\Gamma_8$ level into two doublets.

From the magnetization data in magnetic fields up to 150

![FIG. 2](image2.png)  
**FIG. 2.** Raman scattering intensities of CeB$_6$ and LaB$_6$ at different temperatures showing the Ce$^{3+} \Gamma_3^-$-$\Gamma_7$ CEF transition. Inset: Derived CEF level scheme of CeB$_6$.  

![FIG. 3](image3.png)  
**FIG. 3.** Symmetry analysis of the $\Gamma_3^+$-$\Gamma_7$ CEF transition and the Raman-active phonons of CeB$_6$. 
a magnetic moment of the ground state of about 1.0 $\mu_B$ can be deduced which exceeds 0.71$\mu_B$ for a pure $\Gamma_7$ ground state. This has previously been attributed to an admixture of the $\Gamma_8$ level into the $\Gamma_7$ ground state. 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 $\Gamma_7$ ground state, since the degenerate $\Gamma_8$ level gives a magnetic moment of 1.54$\mu_B$. The measured magnetic form factor is consistent with the split $\Gamma_8$ ground state. The previous interpretation involving a $\Gamma_8$ excited state less than 20 K above the $\Gamma_7$ ground state has to be rejected.

Measurements of the elastic constants as a function of temperature can be fitted more satisfactorily by supposing a $\Gamma_7$ ground state. This will be shown elsewhere. The fit presented by Goto et al., assuming a $\Gamma_7$ ground state and a $\Gamma_7$-$\Gamma_3$ 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 $\Gamma_7$ ground state is given by the magnetic field dependence of the elastic constants. These results also support the conjectured antiferroquadrupolar ordering at 3.3 K (Ref. 11) which necessarily involves a low-lying $\Gamma_8$ state.

The thermoelectric power data show a sharp maximum near 7 K, suggesting a CEF splitting of roughly 20 K which is in qualitative agreement with our $\Gamma_8$ splitting of about 30 K.

With our new CEF level scheme (inset of Fig. 2) the magnetic susceptibility data can be fitted between 3.3 and 700 K without any adjustable parameter, except a reduction factor of 1.29 for the total susceptibility. In a previous fit assuming a $\Gamma_7$ 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 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 $\Gamma_7$ 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 $\Delta a/a = 10^{-4}$. 

(b) A coupling of the $\Gamma_5^+$ optical phonon (672 cm$^{-1}$) to the $\Gamma_5^-$ CEF excitation (372 cm$^{-1}$) is too much off resonance in order to lift the $\Gamma_8$ degeneracy, contrary to the case of CeAl$_2$.

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

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

Cases (c) and (d) 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 $\Gamma_5^-$ CEF transition. The high resolution in Raman scattering allowed the identification of the $\Gamma_7$ 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 y-Ce-type Kondo compounds.

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References

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