**Raman spectroscopy of f-electron metals: an example of CeB$_6$**

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We performed an optical spectroscopy study of electronic and magnetic excitations for a rare-earth system with a single electron quasi-localized in the f-shell on an ion at high-symmetry crystallographic site in application to CeB$_6$ heavy-fermion metal. We carried out group-theoretical classification of the electronic crystal field (CF) transitions and assessed their coupling to light cross-sections for polarization resolved Raman scattering processes. We discuss applicability of symmetrized Raman susceptibility to studies of exotic charge and spin high multiplet ordering phases in f-electron systems. We study temperature effects on intra- and inter-multiplet CF transitions and also on the coupling between the CF excitations with the lattice vibrations. We acquired temperature dependence of the low-frequency polarization resolved Raman response and obtained the static Raman susceptibility for all Raman-allowed symmetry channels: A$_{1g}$, E$_g$, T$_{1g}$, and T$_{2g}$ of the cubic O$_h$ point group. We demonstrate that for CeB$_6$ system only T$_{1g}$-symmetry static Raman susceptibility shows an anomalous temperature dependence which is consistent with the magnetic susceptibility data measured by other techniques. This anomalous behavior in the T$_{1g}$-channel signifies the presence of long wavelength magnetic fluctuations, while the lack of susceptibility enhancement for all the remaining symmetry channels indicates that long wavelength charge quadrupole fluctuations at low-temperature are weak.

**I. INTRODUCTION**

Strongly correlated d- and f-electron systems support a rich variety of low-temperature phases, including magnetism and superconductivity [1–4]. Among these phases, long-range order of multipoles, namely high-rank electric or magnetic moments, has great interest [5–8]. For example, second-rank quadrupolar moments could lead to novel phenomena including the quadrupolar Kondo effect [9] and quadrupole-fluctuation-mediated superconductivity [10]. In d-electron systems, the orbital angular momentum is usually quenched by large crystal-field (CF) splitting, hindering multipolar moments. f-electron systems, on the other hand, are suitable choices to study multipolar interactions and ordering phenomena by virtue of the interplay of the spin and orbital degrees of freedom. Indeed, the actinide dioxides, in which 5f-electrons play an important role, serve as a paradigm for understanding the physics of multipolar interactions [6]. Quadrupolar orderings have also been discovered in a number of 4f-electron compounds [7, 11–15].

CeB$_6$, with its simple chemical composition, lattice structure, and electronic configuration, is considered a prototypical example of heavy-fermion metal with quadrupolar ordering. This material has a cubic structure (space group Pm3m, No. 221; point group O$_h$) composed of cerium ions and boron octahedrons [Fig. 1(a)]. Every Ce$^{3+}$ ion has only one electron in its 4f orbital and O$_h$ site symmetry. CeB$_6$ undergoes a second-order phase transition into a non-magnetic phase at T$_Q = 3.2$ K, before developing an antiferromagnetic (AFM) order below T$_N = 2.3$ K [16, 17]. The AFM phase has a double-Q commensurate magnetic structure with Q$_1$=(0.25, 0.25, 0) and Q$_2$=(0.25, 0.25, 0.5) [18, 19]. As for the non-magnetic phase, neutron scattering shows no structural transition at T$_Q$ [19]. Resonant X-ray diffraction determines that this non-magnetic phase involves an orbital ordering with wavevector (0.5, 0.5, 0.5) [20], and the C$_{44}$ elastic constant, related to $\epsilon_{xy}$-type strains, shows an anomaly at T$_Q$ [21]. Based on these results, it is generally believed that the non-magnetic phase is a two-sublattice arrangement of Ce$^{3+}$ O$_{xy}$-type electric quadrupole moments, with a wavevector (0.5, 0.5, 0.5) [7]. This proposed antiferroquadrupolar (AFQ) model is consistent with experimental data in the presence of magnetic field [22–26], but to our knowledge, up to now there is no direct evidence demonstrating the O$_{xy}$-type AFQ order in zero field. A sketch of field-temperature phase diagram

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for CeB$_6$ is shown in Fig. 1(b).

Experimental results in recent years have revealed the importance of unexpected ferromagnetic (FM) correlations in the low-temperature ordering phenomena of CeB$_6$. In the AFQ phase with finite magnetic field, electron spin resonance (ESR) with narrow linewidth was uncovered, pointing to existence of FM correlations [27]. Theoretical study suggested that such FM correlations result from AFQ ordering [26]. A zone-center excitation at the (110) point, following the energy of ESR, was found by inelastic neutron scattering (INS) [28]. In the AFQ phase at zero magnetic field, this finite-energy mode collapses into a quasi-elastic peak [29]. Moreover, intense FM fluctuations were uncovered in the AFM phase, suggesting propensity to FM instability [29].

Both the AFQ and AFM phases are closely related to the CF ground state [7]. In CeB$_6$, 6-fold degenerate $^2$F$_{5/2}$ is the ground multiplet, and 8-fold $^2$F$_{7/2}$ is the lowest-energy excited multiplet [Fig. 2]. These two multiplets were identified in photoemission spectroscopy studies [30, 31] because of self-energy effects [32]. From group theory analysis [33], the cubic CF potential splits the $^2$F$_{5/2}$ multiplet into quartet $\Gamma_8$ and doublet $\Gamma_7$ states, and it splits the $^2$F$_{7/2}$ multiplet into doublet $\Gamma_6$, doublet $\Gamma_7$, and quartet $\Gamma_8$ states [34]. For the $^2$F$_{5/2}$ multiplet, the $\Gamma_8$ state is the ground state [35–38] and the $\Gamma_7$ state has an energy of 372 cm$^{-1}$ at room temperature [36, 39]. For the $^2$F$_{7/2}$ multiplet, the energy of the CF levels were not determined experimentally.

In order to better understand the low-temperature ordering phenomena in CeB$_6$, a more detailed study of the interplay of CF excitations, lattice dynamics and the FM correlations is required. Raman spectroscopy is a suitable technique providing symmetry-resolved excitation spectra of electronic, magnetic, and phononic degrees of freedom. As a photon-in-photon-out inelastic scattering process, polarization-resolved Raman scattering has the unique advantage of high energy-resolution and the ability to disentangle the excitation spectra into individual symmetry channels. The symmetry of a particular excitation can be identified by controlling the polarization of the incident and scattered light [1]. This experimental method has been successfully used to study CF excitations [41, 42]; it is a well-fitted choice of investigating the intra- and inter-multiplet CF excitations of CeB$_6$. Moreover, Raman scattering makes it possible to study the excitations in the magnetic dipolar ($T_{1g}$ of $O_h$ group) and electric quadrupolar ($E_g$ and $T_{2g}$ of $O_h$ group) channels separately. Thus, the relationship between the quadrupolar correlations and FM correlations can be clarified. Notice that quadrupolar excitations involve a change of the component of angular momentum along the quantization axis by two quantum units. Among conventional experimental probes, only photons can induce quadrupolar excitations.

In this paper, we present a comprehensive study of CeB$_6$ using secondary-emission spectroscopy. We identify an intense photo-luminescence feature corresponding to 5$d$ – 4$f$ recombination process. We analyze the temperature-dependence of both intra- and inter-multiplet CF excitations, and illustrate the interaction between light and CF states by a model Hamiltonian calculation. We draw information about the electron-phonon interaction by studying lattice dynamics. We observe dynamical magnetic fluctuations related to the ordered broken-symmetry states. Especially, we demonstrate two virtues of Raman scattering which have not been generally appreciated: 1, temperature dependence of the parameters of CF excitations reveals the interaction between $f$-electrons and itinerant electrons; 2, low-energy Raman response probes dynamical fluctuations related to exotic multipolar ordering.

The rest of this paper is organized as follows. In Sec. II we describe the sample preparation and experimental setup. In Sec. III we present and discuss the experimental results; in this section, we first show an overview of the main spectral features in SubSec. III A and then discuss them separately in the following subsections. In SubSec. III B we show the high-energy photoluminescence (CF) feature. In SubSec. III C we discuss the CF excitations. Specifically, in III C 1 we present the four lowest-energy CF excitations of Ce$^{3+}$ ions, and identify the symmetry of the CF states; in III C 2, we analyze the temperature dependence of the CF parameters, and explain the observed anomaly on the basis of Kondo effect; in III C 3, we build a single-ion Hamiltonian, and fit the measured CF energies with this Hamiltonian to evaluate the SOC and CF strength, and to obtain the wavefunctions of eigenstates. In SubSec. III D we discuss lattice dynamics. The asymmetric lineshape, and large temperature-independent contribution to the full-width-at-half-maximum (FWHM) of the optical phonon modes point to electron-phonon interaction. In SubSec. III E we discuss quasi-elastic excitations. We find that quasi-
elastically magnetic fluctuations develops below 20K, and the corresponding Raman susceptibility follows a Curie-type behavior. Finally, in Sec. IV we provide a summary of our significant observations and their implications.

II. EXPERIMENTAL

Single crystals of CeB$_6$ were grown in Al flux by slow cooling from 1450 °C. The crystals were removed from the Al flux by leaching in NaOH solution [43, 44]. The sample measured in this study was cleaved in ambient condition to expose its (001) crystallographic plane; the cleaved surface was then examined under a Nomarski microscope to find a strain-free area.

Raman-scattering measurements were performed in a quasi-back scattering geometry. A set of lines from a Kr$^+$ ion laser, 476, 531, 647, 676 and 752 nm, were used for excitation. Incident light with less than 10 mW power was focused into a 50×100 μm$^2$ spot. The temperature points reported in this paper were corrected for laser heating, which was estimated to be 0.5 K/mW.

Six polarization configurations were employed to probe excitations in different symmetry channels. The relationship between the scattering geometries and the symmetry channels [1] is given in Table I. The algebra used to decompose measured spectra into four symmetry channels is shown in Table II.

We used a custom triple-grating spectrometer with a liquid-nitrogen-cooled charge-coupled device (CCD) detector for analysis and collection of the scattered light. Low-resolution gratings with 150 lines per mm were used to measure the broad PL feature, while high-resolution gratings with 1800 lines per mm were used for measurements of the sharp Raman features. The data were corrected for the spectral response of the system.

For first-order scattering processes, the measured secondary-emission intensity $I(\omega, T)$ is related to the Raman response $\chi''(\omega, T)$ by $I(\omega, T) = [1 + n(\omega, T)]\chi''(\omega, T) + L(\omega, T)$, where $n$ is the Bose factor, $\omega$ is excitation energy, $T$ with temperature, and $L(\omega, T)$ represents photo-luminescence [45]. For the second-order acoustic-phonon scattering process to be discussed in SubSec. III D, assuming the two constitute excitations have the same energy, $I(\omega, T)$ and $\chi''(\omega, T)$ are related by $I(\omega, T) = [1 + n(\omega/2, T)]^2\chi''(\omega, T) + L(\omega, T)$ [46].

III. RESULTS AND DISCUSSION

A. Overview

In Fig. 3 we present a typical secondary-emission spectrum from 5 cm$^{-1}$ to 4000 cm$^{-1}$, containing Raman features of distinct origins. Among the Raman features, quasi-elastic excitations have the lowest-energy. Second-order acoustic phonon excitations are at around 200 cm$^{-1}$, while first-order optical phonon excitations are near 1000 cm$^{-1}$. The energy of the intra-multiplet CF excitation is around 400 cm$^{-1}$, while that of the inter-multiplet CF excitations is more than 2000 cm$^{-1}$. The PL continuum arises from a broad PL peak at around 16000 cm$^{-1}$. We will discuss these spectral features in detail in the following subsections.

B. Photo-Luminescence

In Fig. 4(a) we show the excitation dependence of the PL feature at room temperature. The PL peak has 2.0 eV excitation threshold, and excitations below 2.0 eV threshold show predominantly Raman features. The PL feature is centered at 1.95 eV, just below the threshold energy, and has about 0.4 eV full width at half maximum (FWHM). Upon cooling the peak shifts slightly to higher energy [Fig. 4(b)].

We note that the optical conductivity shows a step at around 2.0 eV [47–49], suggesting an optical gap. Band-structure calculations further indicate a 2.0 eV gap between the Ce dispersive 5d-band bottom and flat 4f-band [50–52]. We therefore attribute the PL peak to the recombination of the electron-hole excitations between the 5d- and 4f-bands. Transitions between d- and f-states are dipole allowed, and the energy separation of the 5d-bands bottom and the 4f-bands is consistent with the energy of this PL peak.

| Scattering Geometry | Symmetry Channel |
|---------------------|------------------|
| XX                  | $A_{1g} + 4E_g$  |
| XY                  | $T_{1g} + T_{2g}$|
| X’X’                | $A_{1g} + E_g + T_{2g}$ |
| X’Y’                | $3E_g + T_{1g}$  |
| RR                  | $A_{1g} + E_g + T_{1g}$ |
| RL                  | $3E_g + T_{2g}$  |

| Symmetry Channel | Expression |
|------------------|------------|
| $A_{1g}$         | $(1/3) (XX + X’X’ + RR – X’Y’ – RL)$ |
| $E_g$            | $(1/6) (XY + RL – XY)$ |
| $T_{1g}$         | $(1/2) (XY + RR – X’X’)$ |
| $T_{2g}$         | $(1/2) (XY + RL – XY’)$ |

TABLE II. The algebra used in this study to decompose the data into four symmetry channels.
C. Crystal-Field Excitations

1. Identification

In total, there are four CF excitations from the $\Gamma_8$ ground state to the higher states within the $^2F_{5/2}$ and $^2F_{7/2}$ multiplets: one intra-multiplet excitation and three inter-multiplet excitations [Fig. 2]. In Fig. 5 we present the spectrum of the four CF excitations measured at 15 K. Four peaks at 380 cm$^{-1}$, 2060 cm$^{-1}$, 2200 cm$^{-1}$ and 2720 cm$^{-1}$ are observed. The 380 cm$^{-1}$ excitation is the inter-multiplet $\Gamma_8 \rightarrow \Gamma_7$ transition. Among the three inter-multiplet excitations, only the $\Gamma_8 \rightarrow \Gamma_6^*$ transition can have a finite $A_{1g}$ component [33]. In the inset of Fig. 5 we show that among the inter-multiplet excitations only the one at 2200 cm$^{-1}$ contains an $A_{1g}$ component. The 2200 cm$^{-1}$ excitation is therefore assigned to the $\Gamma_8 \rightarrow \Gamma_6^*$ transition. The CF excitation at 2720 cm$^{-1}$, in turn, can only be a transition between the $\Gamma_8$ ground state and the $\Gamma_6^*$ or $\Gamma_7^*$ states. Raman scattering cannot distinguish between $\Gamma_8 \rightarrow \Gamma_6^*$ and $\Gamma_8 \rightarrow \Gamma_7^*$ transitions because they both contain the same irreducible representations [33]: $\Gamma_8 \otimes \Gamma_6^* = \Gamma_8 \otimes \Gamma_7^* = E_g \oplus T_{2g} \oplus T_{2g}$. However, we will show in III C 3 that the electron-cloud distribution of the $\Gamma_6^*$ state has the smallest overlap with the boron octahedrons, the $\Gamma_8^*$ state has intermediate overlap, and the $\Gamma_7^*$ state has the largest overlap. Because of the Coulomb repulsion between cerium and boron electrons, the $\Gamma_7^*$ state has the highest energy while the $\Gamma_6^*$ state has the lowest energy. Indeed, within the $^2F_{5/2}$ multiplet because the $\Gamma_7$ state has more overlap with the boron octahedrons it has a higher energy than the $\Gamma_8$ state. Therefore, the 2720 cm$^{-1}$ excitation is assigned to the $\Gamma_8 \rightarrow \Gamma_7^*$ transition, and the 2060 cm$^{-1}$ excitation is assigned to the $\Gamma_8 \rightarrow \Gamma_6^*$ transition.

2. Temperature Dependence

In Fig. 6 we present the temperature dependence of the energy and FWHM of three CF excitations. The spectral parameters of the CF excitations were obtained by fitting the measured spectral peaks with a Lorentzian lineshape.

The energy of the $\Gamma_8 \rightarrow \Gamma_7$, $\Gamma_8 \rightarrow \Gamma_8^*$, and $\Gamma_8 \rightarrow \Gamma_7^*$ transitions increases by 7 cm$^{-1}$, 5 cm$^{-1}$, and 18 cm$^{-1}$, respectively on cooling from 304 K to 15 K [53]. On cooling, the lattice contraction strengthens the electrostatic potential at the Ce sites. Discussion of the change of the

FIG. 3. The low-temperature secondary-emission intensity $I(\omega)$, measured in XY geometry at 20 K with 476 nm excitation, plot in log-log scale. Raman features are superposed on a photo-luminescence continuum. The top scale is the energy of the secondary-emission photons; the bottom scale is the scattered-photon energy minus the laser-photon energy, namely Raman shift. Red: quasi-elastic (QE) excitation. Green: second-order acoustic-phonon (AP) excitation and first-order optical-phonon (OP) excitation. Purple: crystal-field (CF) excitation. Blue: photo-luminescence.

FIG. 4. (a) Excitation dependence of the secondary-emission intensity $I(\omega)$ measured in XY geometry at 300 K. For clarity, each spectrum is shifted by a factor proportional to the excitation energy. The broad peak which does not change in energy with excitations is a photo-luminescence feature, while the sharp modes which follow in energy with excitation are Raman features. (b) Temperature dependence of the photo-luminescence feature measured in XY geometry with 476 nm excitation.
FIG. 5. Raman response $\chi''(\omega)$ of the CF excitations measured in XY scattering geometry $(T_{1g} + T_{2g})$ with 476 nm excitation at 15 K. Three axis breakers are used on the horizontal axis in order to show the four excitations together. The spectral resolution is 3.5 cm$^{-1}$. Inset: $\chi''(\omega)$ measured in XX scattering geometry $(A_{1g} + 4E_{g})$ at 15 K. The spectral resolution of the inset is about 30 cm$^{-1}$.

The energy of the CF states with increasing CF potential will be given in III C 3.

At room temperature, the CF spectral lines of CeB$_6$ are broader than those measured from Ce$^{3+}$ ions embedded in insulators, e.g. Ce-doped Y$_2$O$_3$ [54] or Ce-doped LuPO$_4$ [55]. The broadening is caused by two factors: first, a lattice of Ce$^{3+}$ ions leads to small dispersion of the narrow $4f$-bands; second, hopping of conduction electrons among the boron sites induces fluctuations of the electrostatic potential at the cerium sites, which leads to a larger FWHM.

On cooling, the FWHM of the $\Gamma_8 \rightarrow \Gamma_7$ and $\Gamma_8 \rightarrow \Gamma^*_7$ CF transitions decreases from 300 K to 80 K, but anomalously increases below 80 K [Fig. 6 (d) and (f)]. The decrease of FWHM is expected because lattice vibrations, causing fluctuations of the electrostatic potential at Ce sites, diminish with decreasing temperature. In order to understand the anomalous increase of FWHM below 80 K, it is important to notice that the electrical resistivity of CeB$_6$ has its local minimum at 80 K, and the upturn of the resistivity below 80 K results from the Kondo effect [16]; the increased conduction-electron scattering rate off the local moments at Ce sites as temperature decreases [56, 57]. The scattering shortens the lifetime of the $\Gamma_7$ and $\Gamma^*_7$ CF states, so the FWHM of the $\Gamma_8 \rightarrow \Gamma_7$ and $\Gamma_8 \rightarrow \Gamma^*_7$ CF transitions increases below 80 K. Nevertheless, the FWHM of the $\Gamma_8 \rightarrow \Gamma^*_8$ CF transition does not show the upturn below 80 K [Fig. 6 (e)]. This is because the $\Gamma^*_8$ state has smaller overlap with the boron octahedrons than the $\Gamma_7$ and $\Gamma^*_7$ states, and in turn is less influenced by the increased conduction-electron scattering rate.

Our data do not directly support a splitting of the $\Gamma_8$ CF ground state. However, the minimum FWHM of the $\Gamma_8 \rightarrow \Gamma_7$ is around 33 cm$^{-1}$ [Fig. 6 (d)]. If the splitting of the CF ground state is smaller than 33 cm$^{-1}$, it cannot be resolved. Previous studies suggest a splitting of 20 cm$^{-1}$ [36, 58], which does not contradict our results.

3. Model Hamiltonian Calculation

To shed light on the nature of the CF transitions, we perform a model Hamiltonian calculation. We use the following single-ion Hamiltonian

$$H = E_0 + H_{SOC} + H_{CF}.$$  

(1)

The first term $E_0$ represents the energy of unperturbed $4f$ shell. The value $E_0$ is chosen to put the $\Gamma_8$ ground
state at zero energy.

The second term

$$H_{SOC} = \xi \mathbf{L} \cdot \hat{\sigma} \quad (2)$$

describes the effect of SOC. $\xi$ is the SOC coefficient, $\mathbf{L}$ is the orbital angular momentum operator and $\hat{\sigma}$ are Pauli matrices.

The third term

$$H_{CF} = B_4 (\hat{O}_4^0 + 5\hat{O}_4^2) + B_6 (\hat{O}_6^0 - 21\hat{O}_6^2) \quad (3)$$

is the general expression for a CF potential of cubic site symmetry \[59\]. $\hat{O}_4^0$, $\hat{O}_4^2$, $\hat{O}_6^0$ and $\hat{O}_6^2$ are Stevens operators \[60\]. $B_4$ and $B_6$ are the CF coefficients \[61\]:

$$B_4 = A_4 < r^4 > \beta \quad , \quad B_6 = A_6 < r^6 > \gamma \quad . \quad (5)$$

$A_4$ and $A_6$ are the geometrical coordination factors determined by the charge configuration around Ce sites. Regardless of the specific configuration, $A_4 \sim a^{-5}$ and $A_6 \sim a^{-7}$, where $a$ is the lattice constant. $< r^4 >$ and $< r^6 >$ are the mean fourth and sixth powers of the radii of the Ce$^{3+}$ 4f-electron. $\beta$ and $\gamma$ are the Stevens multiplicative factors \[60\].

The effect of SOC and CF potential on the energy and angular electron-cloud distribution of the CF levels is illustrated in Fig. 7. In the absence of SOC, the CF eigenfunctions could be classified by the irreducible representations (IRs) of $O_h$ double group. The relevant IRs are the one-dimensional $A_{2u}$, three-dimensional $T_{2u}$, and...
three-dimensional $T_{1u}$ for the orbital part of the wavefunction, and two-dimensional $\Gamma_6$ for the spin part. The 14-fold degenerate 4f orbital would be split into two $A_{2u} \otimes \Gamma_6$, 6-fold $T_{2u} \otimes \Gamma_6$, and 6-fold $T_{1u} \otimes \Gamma_6$ orbitals. Finite SOC splits these orbitals and results in mixing of wavefunctions derived from different orbitals. The symmetry of the split states is given by the decomposition of the direct products into direct sums of IRs of $O_h$ double group [33]: $A_{2u} \otimes \Gamma_6 = \Gamma_7$, $T_{2u} \otimes \Gamma_6 = \Gamma_8 \oplus \Gamma_7$, and $T_{1u} \otimes \Gamma_6 = \Gamma_6 \oplus \Gamma_8$.

On the other hand, if cubic CF were absent, the 4f orbital would be split into 8-fold $^2F_{7/2}$ ($J = L + S$) and 6-fold $^2F_{5/2}$ ($J = L - S$) multiplets. Finite CF potential splits the two multiplets and induces mixing of wavefunctions derived from different multiplets [62]. The symmetry of the split states is given by the compatibility table showing the mapping of IRs of the full rotational group into IRs of $O_h$ double group [33]: $^2F_{7/2} = \Gamma_8 \oplus \Gamma_7 \oplus \Gamma_6$, and $^2F_{5/2} = \Gamma_8 \oplus \Gamma_7$. With both SOC and CF present, the CF eigenfunctions should be classified by the IRs of the double group, namely two-dimensional $\Gamma_6$, two-dimensional $\Gamma_7$, and four-dimensional $\Gamma_8$.

We diagonalize $H$ in the basis of $|L, m_l\rangle|S, m_s\rangle$, where $L, m_l, S, m_s$ are quantum numbers corresponding to $L, L_2, S, S_z$, respectively. After diagonalization, the CF transition energies can be expressed in terms of $\xi, B_4$ and $B_6$. We obtain these three parameters by fitting the energy of three CF transitions (the weakest $\Gamma_8 \rightarrow \Gamma_6$ transition is not accounted in this procedure). The obtained set of parameters at 15 K is $\xi = 610 \text{ cm}^{-1}$, $B_4 = 0.758 \text{ cm}^{-1}$ and $B_6 = 0.0165 \text{ cm}^{-1}$. This set of parameters automatically renders the weakest transition at 2070 cm$^{-1}$, which is close to the measured value 2060 cm$^{-1}$. The value of $\xi$ ($610 \text{ cm}^{-1}$) is also consistent with the estimated value for Ce$^{3+}$ ions embedded in LuPO$_4$ (614 cm$^{-1}$) [55]. Such consistency demonstrates the reliability of this model.

We can use this single-ion model to calculate the temperature dependence of the CF excitation energy. We assume that $\xi$ is temperature-independent, and the temperature dependence of $B_4$ and $B_6$ comes from the temperature dependence of the lattice constant $a$. We therefore rewrite $B_4$ and $B_6$ as $B_4(T) = C_4 a(T)^{-5}$ and $B_6(T) = C_6 a(T)^{-7}$, where $C_4$ and $C_6$ are temperature-independent. Temperature dependence of the lattice constant is obtained from Refs. [19, 63]. Then, we determine the values of $\xi, C_4$ and $C_6$ by matching the calculated values with the measured data at 300 K. Finally, we use the determined $\xi, C_4$ and $C_6$ to calculate CF excitation energies below 300 K. The results are shown in Fig. 6 (a-e). The deviation of the measured data from the calculated values below 200 K results from missing terms in the model Hamiltonian [Eq. (1)]; for example hybridization between localized $f$-electrons and itinerant conduction electrons.

By virtue of the obtained eigenfunctions, the Raman intensity of the four CF transitions can be calculated. For non-resonant scattering, the Raman response $\chi''(\omega)$ has the following expression [64]:

$$\chi''(\omega) \sim \frac{1}{Z} \sum_{i,f} |\langle f | \hat{R}_{\mu\nu} | i \rangle|^2 e^{-E_i/kT} \delta(E_f - E_i - \hbar\omega),$$

where $Z$ is the partition function, $|i\rangle$, $|f\rangle$ are the initial and final state with energy $E_i$ and $E_f$, $\omega$ is the Raman shift, and $\hat{R}_{\mu\nu}$ is the effective Raman operator. In our case, $|i\rangle$ is the CF ground state and $|f\rangle$ is one of the excited CF states. For nonresonant Raman scattering, $\hat{R}_{\mu\nu}$ is a quadrupolar operator depending on the crystallographic symmetry and scattering geometry $\mu\nu$ [55, 65, 66]. For XY scattering geometry in a cubic crystal, $\hat{R}_{XY}$ transforms in the same way as quadrupole $xy$ under the symmetry operations of $O_h$ point group:

$$\hat{R}_{XY} = \frac{1}{2}(\hat{L}_x \hat{L}_y + \hat{L}_y \hat{L}_x) = \frac{1}{4i}(\hat{L}_+^2 - \hat{L}_-^2),$$

where $\hat{L}_+$ and $\hat{L}_-$ are the ladder operators of the orbital angular momentum. We note that because light only couples to the electron's orbital degree of freedom, the effective Raman operator should be written in terms of the orbital angular momentum operators, rather than the total angular momentum operators. Expression (7) should accordingly be evaluated in the basis of $|L, m_l\rangle|S, m_s\rangle$.

In Fig. 8 we compare the calculated and measured CF transition intensity. Because the 476 nm excitation is resonant with interband transitions (see SubSec. III B) but expression (7) is only valid for non-resonant scattering, we expect discrepancy between the calculated and measured results. Nevertheless, the relative intensity of the three inter-multiplet transitions is reproduced by this calculation.
D. Phononic Excitations

An overview of the phonon modes is presented in Fig. 9(a). From group-theory analysis, CeB$_6$ has three Raman-active optical phonon modes: $A_{1g}$, $E_g$ and $T_{2g}$. Their respective energies are 1272, 1144 and 681.7 cm$^{-1}$ at 300 K, consistent with previous results [67, 68]. Their lineshapes at 300 K and 4 K are presented in Fig. 9(b); no anomaly occurs on cooling. The asymmetric lineshape of the $E_g$ and $T_{2g}$ optical phonon modes could result from electron-phonon interaction.

The peak at 194 cm$^{-1}$ is not fully polarized. It originates from second-order scattering of acoustic branches at the Brillouin-zone boundary [68], where the flat dispersion gives rise to a large density of states [69]. Another feature at 373 cm$^{-1}$ shows larger $T_{2g}$ contribution and smaller $E_g$ contribution. It is the $\Gamma_8 \rightarrow \Gamma_7$ CF excitation discussed in SubSec. III.C. The peak at 1400 cm$^{-1}$ has strong $A_{1g}$ contribution and very weak $E_g$ contribution. It results from second-order scattering of the $T_{2g}$ phonon mode [68]. The symmetry-decomposed spectra further reveal an $A_{1g}$ peak at 1158 cm$^{-1}$, which was not reported previously. This peak might correspond to the summation mode of the $373$ cm$^{-1}$ CF excitation and the $T_{2g}$ phonon mode. Such coupling has been observed in another $f$-electron system UO$_2$ [70].

In Fig. 10 we show the temperature dependence of the energy and FWHM of the $A_{1g}$ contribution of the second-order acoustic mode, the $A_{1g}$ optical mode, and the $T_{2g}$ optical mode. The spectral parameters of the phonon modes were obtained by fitting the measured spectral peaks with a Lorentzian lineshape. We verified that the difference between Lorentzian fitting and Fano fitting is smaller than the error bars in Fig. 10.

The energy $\hbar \omega(T)$ and FWHM $\Gamma(T)$ of the $T_{2g}$ optical mode are in accordance with the anharmonic decay model assuming decay into two phonon modes with identical frequencies and opposite momenta [72]:

$$\omega(T) = \omega_0 - \omega_2 [1 + \frac{2}{e^{\hbar \omega_0/2k_B T} - 1}], \quad (8)$$

$$\Gamma(T) = \Gamma_0 + \frac{2}{e^{\hbar \omega_0/2k_B T} - 1}. \quad (9)$$

The parameters of the $A_{1g}$ optical mode cannot be properly fitted by the above model, but the anharmonic decay model assuming decay into three phonon modes with identical frequencies [71] provides a reasonable fit to the $A_{1g}$ phonon mode:

$$\omega(T) = \omega_0 - \omega_3 [1 + \frac{3}{e^{\hbar \omega_0/3k_B T} - 1} + \frac{3}{(e^{\hbar \omega_0/3k_B T} - 1)^2}], \quad (10)$$

$$\Gamma(T) = \Gamma_0 + \frac{3}{e^{\hbar \omega_0/3k_B T} - 1} + \frac{3}{(e^{\hbar \omega_0/3k_B T} - 1)^2}. \quad (11)$$

The fitting results are summarized in Table III. The linewidth of the optical modes is dominated by the temperature-independent $\Gamma_0$, suggesting that electron-phonon interaction, rather than anharmonicity, plays the dominating role in lineshape broadening.

In contrast to the behavior of the optical modes, the second-order scattering of acoustic modes shows decreasing energy on cooling [Fig. 10(b)]. The 2% softening might be a prelude to the AFQ ordering.
E. Quasi-Elastic Excitations

In Fig. 11 we show the symmetry-decomposed Raman response measured with 752 nm excitation at 300 K and 16 K. The low-energy Raman response shows quasi-elastic features which can be described by a Drude line-shape:

$$\chi''(\omega) = \frac{a\omega}{\omega^2 + \gamma^2}. \quad (12)$$

Especially, the Raman response in the $T_{1g}$ symmetry channel changes qualitatively on cooling, and develops into a strong quasi-elastic feature at low temperature. The basis functions of the $T_{1g}$ representation in $O_h$ group transform as the three components of angular momentum, which behave as a pseudovector [33]. This transformation property indicates that the observed quasi-elastic peak in $T_{1g}$ symmetry channel has a magnetic origin.

We measured the temperature dependence of Raman response in the XY scattering geometry, in which $T_{1g} + T_{2g}$ symmetry components are probed. Since $T_{2g}$ signal at low-temperature is nearly constant [Fig. 11(b)], we fit the Raman response with the sum of Drude and constant terms, and then remove the constant part to obtain the desired $T_{1g}$ component [74]. The $T_{1g}$ Raman response obtained this way is shown in Fig. 12(a). The quasi-elastic excitation in $T_{1g}$ symmetry channel becomes significant below 20 K, and its intensity increases on further cooling. The static Raman susceptibility, $\chi(0)$, plotted in Fig. 12(b) is obtained from the Raman response by virtue of Kramers-Kronig relations:

$$\chi(0) = \frac{2}{\pi} \int_0^{50 \text{ cm}^{-1}} \frac{\chi''(\omega)}{\omega} d\omega.$$  

Drude function in Eq. (12) is used to extrapolate $\chi''(\omega)$ below 4 cm$^{-1}$. In Fig. 12(b)
of a magnetic field, the magnitude of the zone-center quasi-elastic peak decreases on warming above T_{Q} [29]. This observation is consistent with the temperature-dependence of the T_{1g} quasi-elastic peak in our Raman study. We note in passing that a first-principle calculation for CeB_{6} indicates that the expected values of both 4f-orbital occupancy and total angular momentum exhibit obvious anomalies around 20K [77]. This is the same temperature around which the T_{1g} quasi-elastic Raman response starts to develop.

The mechanism responsible for the FM correlations can be understood as follows [26]. Consider the two electrons at neighboring Ce^{3+} sites. In the staggered orbital-ordering phase, the orbital part of the total wavefunction of these two electrons is antisymmetric. Due to the resulting exchange interaction, the spins at neighboring Ce^{3+} sites are FM correlated.

Although it is proposed that the Ce^{3+} electric quadrupole moments are of T_{2g} symmetry in the AFQ phase, no noticeable quasi-elastic fluctuation in T_{2g} symmetry channel appears on cooling approaching T_{Q}. The absence of T_{2g} quasi-elastic response at low-temperature is probably because the AFQ ordering has a finite wavevector, and therefore the fluctuations at zero wavevector are too weak to be probed. However, we note that the \Gamma_{8} CF ground state of O_{h} group has zero quadrupole moment. Assume that the site symmetry is reduced from O_{h} group to D_{4h} group, and the \Gamma_{8} state of O_{h} group is split into the \Gamma_{6} and \Gamma_{7} states of D_{4h} group. The \Gamma_{6} and \Gamma_{7} states can only have quadrupole moments of z^{2} or y^{2}−z^{2} type, rather than the proposed xy, yz, and zx type. Only when the site symmetry is reduced to D_{2h} group, and the \Gamma_{8} state of O_{h} group is split into two \Gamma_{5} states of D_{2h} group, can quadrupolar operator of O_{xy} type have a non-vanishing expectation value. But in a continuous second-order phase transition, the symmetry of the system cannot be directly reduced from cubic to orthorhombic, which violates Landau theory [78]. Theories which claim an AFQ phase with O_{xy}-type moments using a localized picture must address this difficulty. Inconsistency of the AFQ description has also been suggested based on magnetic-susceptibility anisotropy and magnetostriction measurements [79].

IV. CONCLUSION

In summary, we employ optical secondary-emission spectroscopy to study the spin-orbital coupling (SOC), electronic crystal-field (CF) excitations, electron-phonon interaction and long-wavelength magnetic fluctuations in the heavy-fermion metal CeB_{6}.

Ce^{3+} ions have a single electron in the 4f-shell. SOC splits the degenerate 4f levels into a lower-energy \( ^{2}F_{5/2} \) multiplet and a higher-energy \( ^{2}F_{7/2} \) multiplet, with a separation of around 2000cm\(^{-1}\). We estimate the SOC strength \( \xi = 610\text{cm}^{-1} \).

The two multiplets are further split into five Kramers-
degenerate CF states by the cubic CF potential. The \( ^2F_{5/2} \) multiplet is composed of one quartet \( \Gamma_8 \) ground state and one doublet \( \Gamma_7 \) excited state, and the \( ^2F_{7/2} \) multiplet consists of doublet \( \Gamma_6^0 \), doublet \( \Gamma_7^* \), and quartet \( \Gamma_8^* \) states. We resolve all four electronic CF transitions: \( 380 \text{ cm}^{-1} \) for the intra-multiplet excitation, and 2060, 2200 and 2720 cm\(^{-1}\) for the three inter-multiplet transitions.

On cooling, the FWHM for the \( \Gamma_8 \to \Gamma_7 \) and \( \Gamma_8 \to \Gamma_7^* \) transitions first decreases from 300 K to 80 K, but then increases below 80 K. We relate the decrease of the FWHM to lattice vibration driven fluctuations of the electrostatic potential at Ce sites, which diminish on cooling. The increase of the FWHM below 80 K results from the Kondo effect, an electron-correlation effect which increases the self-energy of the excited CF states.

We apply a single-ion Hamiltonian model to obtain the eigenvalues and eigenfunctions of the 4f-electron CF states. Using the Fermi Golden Rule, we also calculate the intensity of the four Raman active CF transitions and compare the calculation to the experimental data.

We study the lattice dynamics of CeB\(_6\) and analyze the temperature dependence of all Raman active phonon modes. We interpret the asymmetric lineshape of E\(_g\) and T\(_{2g}\) optical phonons as manifestation of electron-phonon interaction. We also identify a composite CF plus phonon excitation at 1158 cm\(^{-1}\).

We acquire temperature dependence of the low-energy Raman response for all Raman-allowed symmetry channels, and uncover the development of a quasi-elastic Raman response for all Raman-allowed symmetry channels below 20 K. The corresponding static Raman susceptibility shows similar temperature dependence as the magnetic susceptibility data, which supports the interpretation of its magnetic origin. By comparing the quasi-elastic Raman scattering data with electron spin resonance and inelastic neutron scattering results, we relate this T\(_{1g}\) spectral feature to ferromagnetic correlations. The lack of susceptibility enhancement for all the remaining Raman active symmetry channels, A\(_{1g}\), E\(_g\) and T\(_{2g}\), indicates that for CeB\(_6\) the long-wavelength charge-quadrupolar fluctuations at low-temperature are weak.

Additionally, we detect photo-luminescence emission at 2 eV. We relate this emission to recombination of the electron-hole excitations between the 5d- and 4f-bands.

The experimental methods, models, and analyses demonstrated in this study can be applied to a range of systems, especially for rare-earth materials containing localized f-electrons of Ce\(^{3+}\) or Yb\(^{3+}\) ions at high-symmetry crystallographic sites [80]. The approach enables to probe ferroquadrupolar (FQ) fluctuations in TmAg\(_2\) (T\(_{FQ}\) = 5.0 K) [11] or TmAu\(_2\) (T\(_{FQ}\) = 7.0 K) [12] systems, to name a few examples. Also, magnetic correlation induced by quadrupolar ordering could be probed in antiferroquadrupolar (AFQ) systems, for instance in UPd\(_3\) (multiple AFQ phases, with the highest T\(_{AFQ}\) = 7.6 K) [81], NpO\(_2\) (T\(_{AFQ}\) = 25.0 K) [14], or DyB\(_2\)C\(_2\) (T\(_{AFQ}\) = 24.7 K) [13].

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Supplemental Material for:
Raman spectroscopy of f-electron metals: an example of CeB$_6$

Appendix A: Analysis of Raman Spectra

1. Subtraction of Photo-Luminescence

The measured secondary-emission intensity $I(\omega,T)$ is related to the Raman response $\chi''(\omega,T)$ by $I(\omega,T) = [1 + n(\omega,T)]\chi''(\omega,T) + L(\omega,T)$, where $n$ is the Bose factor, $\omega$ is energy, $T$ is temperature, and $L(\omega,T)$ is a background coming from photo-luminescence. Spectra taken with 752 nm excitation are subtracted by a constant [Fig. S1 (a)], while those taken with 532 and 476 nm excitations are subtracted by a linear function of frequency [Fig. S1 (b) and (c)].

2. Thermal Factor for Second-Order Acoustic-Phonon Scattering

For first-order scattering processes, the scattering intensity is given by the expression $[1 + n(\omega,T)]\chi''(\omega,T)$ [1], where $n$ is the Bose factor, $\chi''$ is the response function, $\omega$ is excitation energy and $T$ is temperature. However, for the second-order acoustic-phonon scattering process observed in our study, assuming the two constitute acoustic phonons have the same energy, the expression should be modified to $[1 + n(\omega/2,T)]^2\chi''(\omega,T)$.

The reason for the modification is as follows. Second-order Raman scattering can result from either two successive first-order interactions, or one second-order interaction [2]. In the first case, the thermal factor $[1 + n(\omega/2,T)]$ should be used. However, it is essential that first-order scattering should be allowed for the two constituent excitations individually. Because the wavevector of visible light is much smaller than the Brillouin-zone size, first-order scattering of acoustic modes at the Brillouin-zone boundary is not allowed. The second-order Raman scattering of acoustic

![FIG. S1](image-url)

FIG. S1. Illustration of subtracting photo-luminescence (PL) for spectra taken with three different excitation energy at 300 K. Secondary-emission intensity $I(\omega)$ (red line) shown together with a constant PL (a) or a linear PL (b,c) to be subtracted. The resulting Raman response $\chi''(\omega)$ is shown in (d,e,f), respectively.
FIG. S2. Temperature dependence of the integrated intensity of the $A_{1g}$ component of the second-order acoustic phonon scattering peak. The intensity obtained with two different thermal factors is normalized to their respective value at 300 K.

FIG. S3. Comparison of the 16 K $T_{1g}$ spectra in Fig.12(b) (green color) and Fig.12(a) (orange color). The solid lines are Drude fits.

modes observed in our study, therefore, originates from the scattering process in which the light interacts with a pair of excitations in a single event. Wavevector conservation is effectively satisfied when the wavevectors of the constituent excitations are equal and opposite. In this case, assuming the two constituent excitations have the same energy, the thermal factor $[1 + n(\omega/2, T)]^2$ should be used [1, 3, 4]. Using thermal factor $[1 + n(\omega, T)]$ for the second-order acoustic-phonon scattering process in CeB$_6$ would lead to unreasonable decreasing intensity on cooling [Fig. S2]. The energy and FWHM of the peak, on the contrary, is insensitive to which thermal factor is used.

3. Measurement of $T_{1g}$ Quasi-Elastic Excitations

The $T_{1g}$ Raman response shown in Fig.12 of the Main Text is extracted from Raman response in the XY scattering geometry. We fit the Raman response with the sum of Drude and constant terms, and then remove the constant part to obtain the desired $T_{1g}$ component. To justify this procedure, Fig. S3 compares the 16 K $T_{1g}$ spectra in Fig.12(b) (decomposed from the spectra measured in the XY, X'Y' and RL scattering geometries) and Fig.12(a) (obtained solely from the spectra measured in the XY scattering geometry). It is clear that they match well.

Appendix B: Crystal-Field Eigenfunctions

The calculated eigenfunctions are given in Table S1. Because of Kramers degeneracy, every eigenfunction $\sum_i c_i |L, m_l, S, m_s\rangle$ has a partner $\sum_i c_i |L, -m_l, S, -m_s\rangle$. Usually, $H_{CF}$ is solved within a particular multiplet in the basis of $|J, m_J\rangle$ [5]. This treatment assumes that SOC is much larger than CF potential, and inter-multiplet mixing can therefore be ignored. Without inter-multiplet mixing,
TABLE S1. The eigenfunctions of the best-fit single-ion Hamiltonian for Ce$^{3+}$ in CeB$_6$. The coefficients of $|m_l, m_s\rangle$ are given; a blank entry means a zero coefficient.

| $m_s$ | $-3$ | $-2$ | $-1$ | $0$ | $1$ | $2$ | $3$ | $-3$ | $-2$ | $-1$ | $0$ | $1$ | $2$ | $3$ | $\frac{1}{2}$ | $0$ | $1$ | $2$ | $3$ |
|-------|------|------|------|-----|-----|-----|-----|------|------|------|-----|-----|-----|-----|--------|-----|-----|-----|-----|
| $\Gamma_{8(1)}$ | -0.033 | 0 | -0.737 | +0.675 | -0.737 | +0.675 | -0.033 |
| $\Gamma_{8(2)}$ | -0.325 | +0.675 | -0.325 | +0.853 | +0.325 | -0.250 |
| $\Gamma_{8(3)}$ | +0.250 | +0.723 | +0.853 | +0.423 | -0.325 | -0.546 |
| $\Gamma_{8(4)}$ | -0.325 | -0.737 | +0.853 | +0.423 | +0.723 | -0.033 |
| $\Gamma_{7(1)}$ | -0.816 | +0.380 | -0.267 | +0.345 | +0.345 | +0.845 |
| $\Gamma_{7(2)}$ | -0.488 | +0.772 | +0.378 | +0.772 | -0.345 | -0.488 |
| $\Gamma_{7(3)}$ | +0.218 | +0.845 | +0.345 | -0.345 | -0.488 | -0.345 |
| $\Gamma_{7(4)}$ | -0.345 | -0.267 | +0.380 | +0.345 | -0.763 | +0.459 |
| $\Gamma_{6(1)}$ | +0.465 | +0.500 | +0.500 | +0.500 | +0.465 |
| $\Gamma_{6(2)}$ | +0.577 | +0.500 | +0.500 | +0.500 | +0.577 |

TABLE S2. The eigenfunctions obtained by separately diagonalizing $H_{CF}$ in the $J = 5/2$ and $J = 7/2$ multiplets. The coefficients of $|m_l, m_s\rangle$ are given; a blank entry means a zero coefficient.

| $m_s$ | $-3$ | $-2$ | $-1$ | $0$ | $1$ | $2$ | $3$ | $-3$ | $-2$ | $-1$ | $0$ | $1$ | $2$ | $3$ | $\frac{1}{2}$ | $0$ | $1$ | $2$ | $3$ |
|-------|------|------|------|-----|-----|-----|-----|------|------|------|-----|-----|-----|-----|--------|-----|-----|-----|-----|
| $\Gamma_s$ | -0.756 | +0.655 | -0.756 | +0.655 | +0.655 |
| $\Gamma_s$ | 0.345 | -0.345 | 0.345 | -0.345 | -0.345 |
| $\Gamma_s$ | -0.816 | +0.380 | -0.267 | +0.345 | +0.345 |
| $\Gamma_s$ | -0.463 | +0.423 | -0.327 | +0.423 | +0.423 |
| $\Gamma_s$ | +0.463 | +0.423 | -0.327 | +0.423 | +0.423 |
| $\Gamma_s$ | +0.345 | +0.423 | -0.327 | +0.423 | +0.423 |
| $\Gamma_s$ | +0.577 | +0.500 | +0.500 | +0.500 | +0.577 |

the eigenfunctions are independent of the parameters $B_4$ and $B_6$. However, Ce has the smallest SOC among the 4f lanthanides. Thus comparing the exact results with the approximate results helps to illustrate the limitations of the approximate treatment. The eigenfunctions obtained by separately diagonalizing $H_{CF}$ in the $J = 5/2$ and $J = 7/2$ multiplets are presented in Table S2. For convenient comparison with Table S1, the results have been converted into $|L, m_L\rangle|S, m_s\rangle$ basis. Inter-multiplet mixing occurs between $\Gamma_{8(i)}$ and $\Gamma_{8(i)}^\ast$, and between $\Gamma_{7(j)}$ and $\Gamma_{7(j)}^\ast$, where $i = 1, 2, 3, 4$ and $j = 1, 2$. The absolute change of coefficients are larger for $\Gamma_7$ and $\Gamma_8$ states than for $\Gamma_{8}$ and $\Gamma_{8}^\ast$ states. $\Gamma_6^\ast$ state derived from the $J = 7/2$ multiplet has no corresponding state in the $J = 5/2$ multiplet; hence it has no inter-multiplet mixing, and the coefficients for $\Gamma_6^\ast$ state are the same in Table S1 and S2. Notice that the approximate treatment not only changes the magnitude of various coefficients, but also makes some finite coefficients vanish.

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