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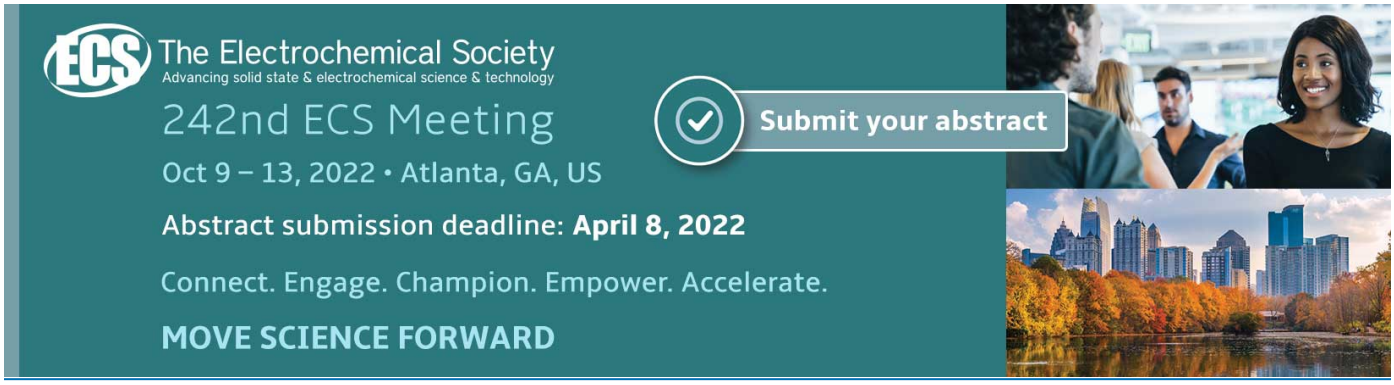

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Crystal-field excitations and quadrupolar fluctuations of $4f$-electron systems studied by polarized light scattering

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Abstract. We present Raman-scattering results for three materials, CeB_6, $TbInO_3$, and $YbRu_2Ge_2$, to illustrate the essential aspects of crystal-field (CF) excitations and quadrupolar fluctuations of $4f$-electron systems. For CF excitations, we illustrate how the $4f$ orbits are split by spin-orbit coupling and CF potential by presenting spectra for inter- and intra-multiplet excitations over a large energy range. We discuss identification of the CF ground state and establishment of low-energy CF level scheme from the symmetry and energy of measured CF excitations. In addition, we demonstrate that the CF linewidth is a sensitive probe of electron correlation by virtue of self-energy effect. For quadrupolar fluctuations, we discuss both ferroquadrupolar (FQ) and antiferroquadrupolar (AFQ) cases. Long-wavelength quadrupolar fluctuations of the same symmetry as the FQ order parameter persists well above the transition temperature, from which the strength of electronic intersite quadrupolar interaction can be evaluated. The tendency towards AFQ ordering induces ferromagnetic correlation between neighboring $4f$-ion sites, leading to long-wavelength magnetic fluctuations.

1. Introduction

Because of the heaviness of f elements and the compactness of f orbits, the energy scale of crystal-field (CF) effect is much weaker than that of spin-orbit coupling (SOC) for $4f$-electron systems. As a result, CF interaction plays an important role in the low-temperature physics of these materials [1, 2, 3, 4]. In particular, if the CF ground state possesses orbital degeneracy, it supports multipole moments, with quadrupole moments being the most common one. Although the field of CF analysis is well established with a long history, predictive understanding of structure-property relationships is still in its infancy for f-electron systems, and new questions continuously emerge with advances in material synthesis and characterization.

For investigation of the new questions related to CF and quadrupolar physics of $4f$-electron systems, polarization-resolved Raman spectroscopy is a well suited experimental technique.

Besides supreme spectral resolution, this method offers the ability to disentangle the long-wavelength excitation spectra into individual symmetry channels. By controlling the polarization of the incident and scattered light, we can identify the symmetry of different CF levels and separate quadrupolar excitations from other signals.

Here we first examine the CF excitations of CeB_6 and $TbInO_3$ to illustrate the relationship between CF linewidth and electron correlation effects. We show that Kondo effect in heavy-fermion metal CeB_6 leads to consistent temperature dependence of CF linewidth and electric resistivity data from Ref. [5]. Ferroelectric insulator $TbInO_3$ is a spin-liquid (SL) candidate, but the symmetry of the proposed SL ground state remains unclear [4, 6]. We demonstrate that the ground state of Tb^{3+} ions is a non-Kramers doublet, which suggests a triangular-lattice spin liquid. We further relate the enhanced linewidth of its CF modes to the magnetic fluctuations near the SL ground state. Then, we examine the quasi-elastic fluctuations of CeB_6 and $YbRu_2Ge_2$. CeB_6 has an antiferroquadrupolar (AFQ) phase below 3.2 K [7]. Above the transition temperature, the tendency towards AFQ ordering induces magnetic fluctuations. The corresponding Raman susceptibility, and magnetic susceptibility data from Ref. [8] show consistent temperature dependence. $YbRu_2Ge_2$ has a ferroquadrupolar (FQ) phase below 10 K [9]. We present the quadrupolar fluctuations, and evaluate the electronic intersite quadrupolar coupling by analyzing the corresponding Raman susceptibility whose temperature dependence is consistent with that of quadrupole-strain susceptibility derived from elastoresistivity data of Ref. [9].

2. Crystal-field excitations

CeB_6 has a simple $4f^1$ Ce^{3+} electronic configuration; the $4f$ orbits of Ce^{3+} ions are split into sixfold $^2F_{5/2}$ and eightfold $^2F_{7/2}$ multiplets. The electronic configuration for $TbInO_3$ is $4f^8$; the lowest-lying ^7F term of Tb^{3+} ions is split into 7 multiplets, with J=6 having the lowest energy and J=0 having the highest energy. In Fig. 1 we show the inter-multiplet excitations for CeB_6 and $TbInO_3$. It is clear that SOC becomes larger with atomic number: for Ce^{3+} ion (Z=58) the energy difference between $^2F_{5/2}$ and $^2F_{7/2}$ multiplets is around 0.3 eV; for Tb^{3+} ion (Z=65) the energy separation between $^7F_6$ and $^7F_0$ is around 0.7 eV.

The CF potential leads to fine structure within each multiplet, and the CF level scheme of the lowest-energy multiplet is most relevant to the low-temperature physics of the system. For CeB_6, the $^2F_{5/2}$ multiplet is split into Γ_8 ground state and Γ_7 excited state, and one intra-multiplet CF excitation within $^2F_{5/2}$ multiplet is observed [Fig. 1(a)] (As the linewidth of this excitation is around 4 meV, the previously proposed 2.5 meV splitting of the Γ_8 ground state [10] does not contradict our data). For $TbInO_3$, the $^7F_6$ multiplet is split into 5 singlets and 4 doublets, resulting in a total of 9 CF transitions within $^7F_6$ multiplet [Fig. 1(c)]. Multiple scattering geometries need to be employed to identify the symmetry of the CF transitions and in turn that of the CF states; only a doublet ground state is consistent with the experimental results [11].

Although only the energy and symmetry of the CF excitations are required for determining the low-energy CF level scheme, the spectral linewidth of these excitations provides further information relevant to scattering and fluctuation effects. In CeB_6, the CF linewidth is observed to increase on cooling below the temperature at which the resistivity data from Ref. [5] show local minimum [Fig. 1(a) Inset]. Such behavior is a manifestation of Kondo effect, which shortens the lifetime of the excited CF states [12]. In $TbInO_3$, the enhanced linewidth of the CF transitions within the $^7F_6$ multiplet is associated with the the magnetic fluctuations near the spin-liquid ground state: the dynamics of the correlated yet nonordered magnetic moments manifests itself through the width of CF excitations.

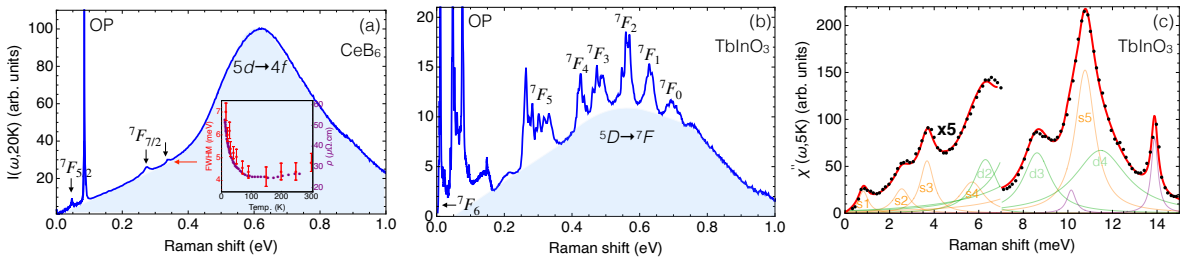

Figure 1. The inter- and intra-multiplet excitations for CeB_6 (a) and $TbInO_3$ (b-c). The Raman features are superposed on a broad photoluminescence continuum (PL, shaded with blue). For metallic CeB_6 the PL originates from the transition from broad $5d$ band bottom to narrow $4f$ band; for insulating $TbInO_3$ the PL results from the transition from ^5D term to ^7F term. The strong, sharp modes at low energy are optical phonons (OP). The inset of (a) compares the linewidth of the 0.34 eV CF excitation, and the electric resistivity taken from Ref. [5]. (c) The intra-multiplet CF transitions within the $^7F_6$ multiplet for $TbInO_3$. The Raman data are represented by black dots. The red lines represent the fits by Lorentzian lineshapes. The orange lines show doublet-to-singlet CF modes labeled by the final singlet state, and the green lines show doublet-to-doublet CF modes; the phonon modes are shown in purple. The Raman data and fitting curves below 7 meV are multiplied by a factor of 5 for clarity.

3. Quadrupolar fluctuations

In Fig. 2 we show the quasi-elastic Raman response for CeB_6 and $YbRu_2Ge_2$, which can be well modelled by a Drude lineshape. The corresponding Raman susceptibility is obtained by virtue of Kramers-Kronig relation. Due to the short wavevector of photons compared to the size of Brillouin zone, inelastic light scattering can only probe quadrupolar excitations at the Brillouin zone center. Thus for quadrupolar ordering at finite wavevector, including the case of AFQ order, the quadrupolar fluctuations are not observed in the corresponding symmetry channel. However, on cooling towards the AFQ transition temperature, long-wavelength fluctuations in the magnetic channel are observed for CeB_6 [Fig. 2(a)], suggesting development of ferromagnetic (FM) correlations. The FM correlations are induced by the tendency towards AFQ ordering: as the orbits at neighboring Ce sites are quasi-degenerate, the intra-atomic Hund's rule favors the spins to be aligned[12].

For $YbRu_2Ge_2$, the FQ phase is a realization of electronic nematic states since the electronic properties spontaneously break the fourfold rotational symmetry of the tetragonal crystal. Above the FQ transition temperature, fluctuations in the quadrupolar channel are enhanced on cooling [Fig. 2(c)]. A Curie-Weiss fit to the corresponding Raman susceptibility renders a Weiss temperature of -2±3 K [Fig. 2(d)], indicating that the susceptibility essentially follows Curie law, and the electronic intersite quadrupolar coupling is weak. It is the relatively strong coupling between the quadrupole moments and lattice strain fields, analogous to cooperative Jahn-Teller effect, that is essential for the FQ transition at finite temperature [13].

4. Conclusion

In summary, we use three $4f$-electron systems, CeB_6, $TbInO_3$, and $YbRu_2Ge_2$, as examples to show the key features and underlying physics of CF excitations and quadrupolar fluctuations. The symmetry and energy of low-energy CF transitions are crucial for establishing the CF level scheme of the lowest-lying multiplet; the linewidth of CF excitations provides information on electron correlation. At low temperature, the charge quadrupoles of $4f$ electrons tend to order in a uniform arrangement (FQ order) or a staggered arrangement (AFQ order). The quadrupolar

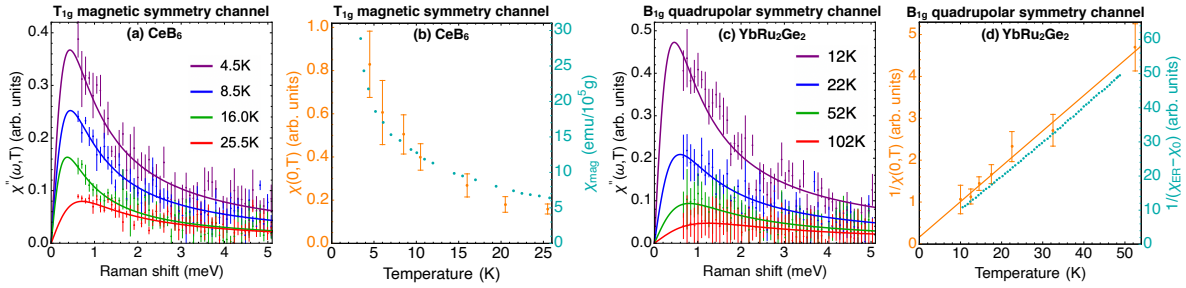

Figure 2. The quasi-elastic Raman response and the corresponding Raman susceptibility for CeB_6 and $YbRu_2Ge_2$. (a) Fluctuations in the magnetic symmetry channel for CeB_6. (b) The Raman susceptibility derived from the Raman response shown in (a) [left axis], compared with the magnetic susceptibility taken from Ref.[8] [right axis]. (c) Fluctuations in the quadrupolar symmetry channel for $YbRu_2Ge_2$. (d) The inverse Raman susceptibility derived from the Raman response shown in (c) [left axis], compared with the inverse quadrupole-strain susceptibility derived from elastoresistivity of Ref.[9] [right axis]. For (a) and (c), the curves represent Drude fits; in (d), the line represents Curie-Weiss fit.

fluctuations above the FQ transition temperature can be directly probed by inelastic light scattering, and the corresponding susceptibility provides the strength of the electronic intersite quadrupolar interactions. The AFQ fluctuations at finite wavevector are not directly accessible to Raman scattering, but the induced long-wavelength magnetic fluctuations can be probed.

Acknowledgments

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