Polarized light scattering investigation of UBe_{13}

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The results of a Raman scattering study of single-crystal UBe_{13} are presented and discussed. These results are compared with spectra from the isostructural compounds MBe_{13} (M = La, Ce, Th), within the temperature range $3 \leq T \leq 350$ K. Ten phonons are observed in UBe_{13}, displaying symmetries $2A_{1g}+4E_g+4T_{2g}$, consistent with predictions using the space- and site-group symmetries previously determined for this compound [space group O_h^6 ($Fm3c$)]. In addition, electronic scattering is evident in our spectra, exhibiting the symmetry of the purely antisymmetric representation, T_{1g}. Evidence suggests that this scattering results from localized excitations of the $5f$ electrons. Various interpretations of this scattering are discussed.

I. INTRODUCTION

The preconception that "heavy" electrons have a proclivity towards localization and magnetization has seemingly been defied by the discovery of heavy-electron superconductivity in such systems as $CeCu_2Si_2$,[1] UBe_{13},[2] and UPt_3.[3] Participation of these heavy electrons in the superconducting state is principally suggested by the large specific-heat jumps at T_c noted in these compounds.[4] Furthermore, evidence that these electrons form a narrow band at the Fermi energy has been inferred from the enormous electronic specific-heat coefficients that these materials exhibit. As the magnetic atom separations (U-U and Ce-Ce) are too large in heavy-electron systems for direct f-orbital overlap, the formation of bands must proceed instead via hybridization of the f electrons with non-f ligands from neighboring atoms. One manifestation of such hybridization, and the resulting heavy-electron itineracy, is expected to be local moment instabilities, giving rise to strong magnetic fluctuations in the excitation spectrum. The observation of such fluctuations has been reported, for example, in $CeCu_2Si_2$,[5] which exhibits quasielastic neutron scattering with a half-width (HWHM) of 1 meV.

Neutron and light scattering from magnetic excitations have also been reported in UBe_{13},[6,7] although the presumed quasielastic response displays a half-width (HWHM) which is much larger than that expected from specific-heat measurements. This apparent incongruity has fueled speculation that the magnetic response in UBe_{13} might instead result from inelastic transitions between crystal-field-split levels.[8,9] Evidence for such crystal-field excitations has in fact been suggested by recent specific-heat measurements, in which a Schottky anomaly at 70 K has been observed.[8]

In this paper we present the results of a polarized Raman scattering investigation of the electronic and vibrational excitation spectrum of UBe_{13}. This high-resolution technique allows close scrutiny of both the line-shape and the temperature dependence of an observed excitation, while the use of polarized light and single crystals afford symmetry information. Although these details do not resolve the origin of the magnetic response in UBe_{13}, they nevertheless place stringent constraints on its interpretation.

II. EXPERIMENTAL DETAILS

Our experiments were conducted on single-crystal samples of MBe_{13} with M=U, Th, La, Ce. All samples were cut so as to expose the (100) lattice plane, and the surfaces were mechanically polished with diamond paste. Proper orientation was confirmed through Laue x-ray diffraction. The effects of polish-induced surface strain on our Raman spectra were determined by observing selected spectra from unpolished samples. No differences were noted between spectra from polished and unpolished samples.

All data was obtained using a polarized 4765- or 5145-Å line of an argon laser as an excitation source. Measurements were made in a near-backscattering geometry, with the incident light polarized along various crystalline directions. This allowed us to couple to different components of the Raman tensor, and thereby identify each excitation's symmetry. Table I delineates the allowed symmetries for the various scattering geometries used in our experiment. Due to the imperfect backscattering

TABLE I. Allowed excitation symmetries for various scattering geometries in UBe_{13}. $\mathbf{x}=(1,0,0)$, $\mathbf{y}=(0,1,0)$; $\mathbf{x}'=(1/\sqrt{2})(1,1,0)$, $\mathbf{y}'=(1/\sqrt{2})(1,-1,0)$.

Geometry (ϵ_i,ϵ_s)	Allowed symmetries
$(\mathbf{x},\mathbf{x})$	$A_{1g}+E_g$
$(\mathbf{x},\mathbf{y})$	$T_{2g}+T_{1g}+E_g$ "leakage"
$(\mathbf{x}',\mathbf{x}')$	$A_{1g}+\frac{1}{4}E_g+T_{2g}$
$(\mathbf{x}',\mathbf{y}')$	$\frac{3}{4}E_g+T_{1g}$

geometry used, however, small contributions from otherwise forbidden symmetries were observed in certain spectra. This "leakage" of symmetry is noted in Table I where expected.

Our investigation employed both a three-stage spectrograph with a multichannel detection system and a triple-grating monochromator coupled to a cooled photomultiplier tube detector. These instruments provided resolutions of 10 and 3 cm^{-1}, respectively.

A variable-temperature liquid-He cryostat was used in our study for continuous adjustment of the temperature down to 2 K. Temperatures for all but the 3 K data were obtained from the Stokes–anti-Stokes ratios of the spectra, in order to account for the temperature rise of the sample due to laser heating. The 3 K data were obtained by immersion in superfluid helium, using low laser power to prevent boiling.

III. PHONONS

UBe_{13} maintains a face-centered-cubic lattice structure [space group O_h^6 ($Fm3c$)] consisting of two formula units per Bravais cell. Only 22 of the 81 optical phonons characteristic of this structure are Raman active, displaying the symmetries $2A_{1g}+4E_g+4T_{2g}(2\Gamma_1^+ +4\Gamma_3^+ +4\Gamma_5^+)$.[10] These phonons involve only those Be atoms which lie on the faces of a cube surrounding the U atom [$Be^{II}(24)$]. The U(2) and $Be^{I}(2)$ atoms both sit at sites of inversion symmetry in the crystal, and therefore do not participate in any Raman-active modes. Since the wavelengths of light used as an excitation source are a small fraction of the Brillouin zone, the excitations probed in this study are essentially at $\mathbf{q}=\mathbf{0}$.

Figure 1 displays the $A_{1g}+E_g$ spectrum at various temperatures. Five of the Raman-active phonons expected in this spectrum are observed,[11] exhibiting no temperature dependence beyond a slight hardening due to thermal variations in the lattice constant. The balance of the Raman-active phonons are illustrated in the $T_{1g}+T_{2g}$ spectrum of Fig. 2. Five phonons are observed in this spectrum above 300 cm^{-1}: the four T_{2g} modes expected in this geometry, and a fifth at 350 cm^{-1} resulting from a leakage of an E_g phonon into this spectra. The identification of the phonon symmetries is facilitated by the $A_{1g}+\frac{1}{4}E_g+T_{2g}$ and $\frac{3}{4}E_g+T_{1g}$ spectra shown in Fig. 3, observed by again altering the scattering geometry (see Table I). The resulting phonon symmetry and frequency assignments have been tabulated in Ref. 7.

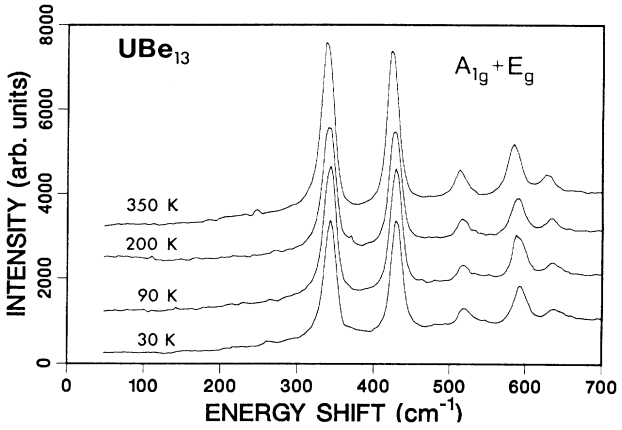

FIG. 1. $A_{1g}+E_g$ spectra for UBe_{13} at various temperatures. Resolution: 10 cm^{-1}. All spectra have been offset for clarity.

IV. ELECTRONIC SCATTERING

In addition to the vibrational excitations, a broad feature extending from 0 to nearly 380 cm^{-1} is evident in the $T_{1g}+T_{2g}$ spectrum of Fig. 2. This scattering is also conspicuous in the $\frac{3}{4}E_g+T_{1g}$ spectra of Fig. 3, confirming its symmetry to be that of the antisymmetric representation, T_{1g}. As the scattering tensor for ordinary vibrational scattering is symmetric, this T_{1g} excitation is characteristic of electronic scattering. Indeed, that the U $5f$ electrons contribute to the broad scattering in UBe_{13} is best illustrated in Fig. 4, which compares the $T_{1g}+T_{2g}$ spectrum of UBe_{13} with that of the nonmagnetic, isostructural compounds $LaBe_{13}$ and $ThBe_{13}$. The absence of an analogous feature in these latter materials further demonstrates that the broad excitation in UBe_{13} has an electronic rather than a structural origin. The $T_{1g}+T_{2g}$ spectrum of $CeBe_{13}$ has also been included in Fig. 4 for comparison. At all temperatures observed (30–350 K) this spectrum

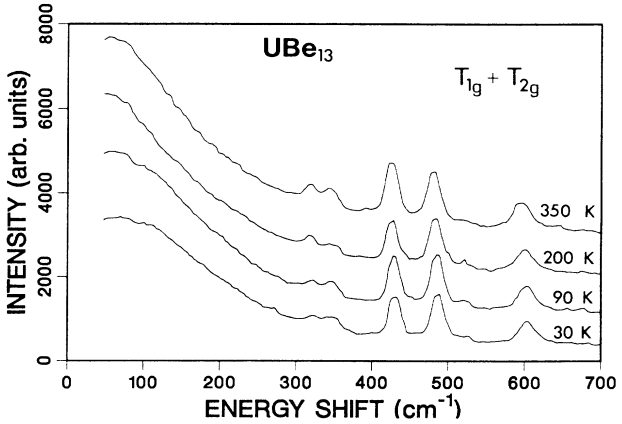

FIG. 2. $T_{1g}+T_{2g}$ spectra for UBe_{13} at various temperatures. Resolution: 10 cm^{-1}. The spectra have been offset for clarity.

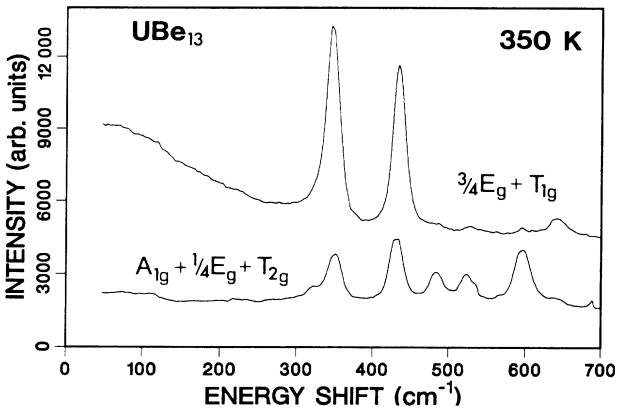

FIG. 3. $\frac{3}{4}E_g+T_{1g}$ (upper) vs $A_{1g}+\frac{1}{4}E_g+T_{2g}$ (lower) spectra for UBe_{13} at 350 K. Resolution: 10 cm^{-1}. The $\frac{3}{4}E_g+T_{1g}$ spectrum has been shifted upwards by 1000 a.u.

also lacks the broad feature apparent in UBe_{13}, although it does exhibit a rise due to luminescence above 150 cm^{-1}.

The line shape and symmetry of the broad scattering in UBe_{13} is suggestive of quasielastic scattering resulting from magnetic fluctuations. However, the credibility of such an interpretation is weakened by the absence in our spectra of quasielastic scattering in $CeBe_{13}$, as has been observed by neutron scattering.[12] Indeed, the large discrepancy between the T_{1g} scattering intensities in $CeBe_{13}$ and UBe_{13} appears to be inconsistent with the comparable coupling strengths expected between light and magnetic excitations in Ce and U compounds ($\sim\lambda_{s.o.}/\Delta E$ where $\lambda_{s.o.}$ is the spin-orbit interaction and ΔE is the level splitting). A more conclusive rejection of the magnetic fluctuation interpretation, however, demands consideration of the line shape and $\mathbf{q}$ dependence of the T_{1g} excitation.

In a light-scattering experiment, the scattering intensity is related by the fluctuation-dissipation theorem to the imaginary part of the susceptibility

$$S(\mathbf{q}=0,\omega)\propto[1+n(\omega)]\mathrm{Im}\chi(\mathbf{q}=0,\omega)\ ,$$

where $n(\omega)$ is the Bose factor. In Fig. 5, the thermal factor $[1+n(\omega)]$ has been divided from the T_{1g} spectra at various temperatures, thereby exposing the imaginary part of the response function due to this diffuse scattering. As illustrated by the dashed curve in Fig. 5, the observed line shape is not described well by a quasielastic response function

$$\mathrm{Im}\chi(\mathbf{q},\omega)\propto\frac{\Gamma\omega}{\omega^2+\Gamma^2}\ ,$$

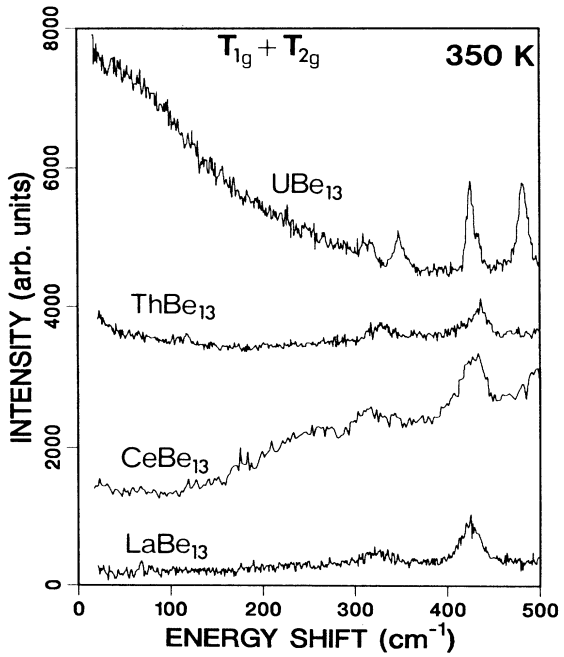

FIG. 4. $T_{1g}+T_{2g}$ spectra for MBe_{13} (M=U,Th,Ce,La) at 350 K. Resolution: 3 cm^{-1}. The spectra have been offset for clarity.

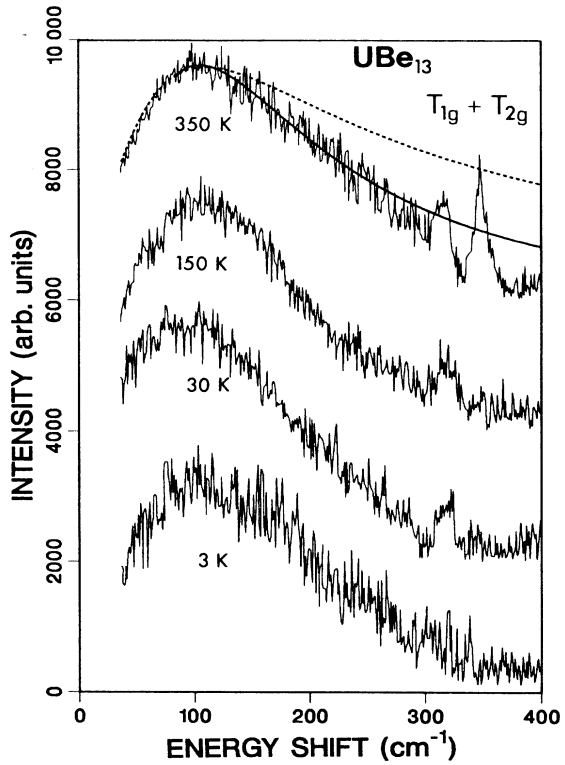

FIG. 5. $T_{1g}+T_{2g}$ spectra for UBe_{13} at various temperatures, shown with the thermal factor $[1+n(\omega)]$ divided out. The 3 K data have been multiplied by a factor of 10 to account for 90% less power used. The dashed line is a fit to a quasielastic Lorentzian, described in the text. The solid line is a fit to a $\sim 1/\omega^3$ falloff at high frequencies. Resolution: 3 cm^{-1}. All spectra have been offset for clarity.

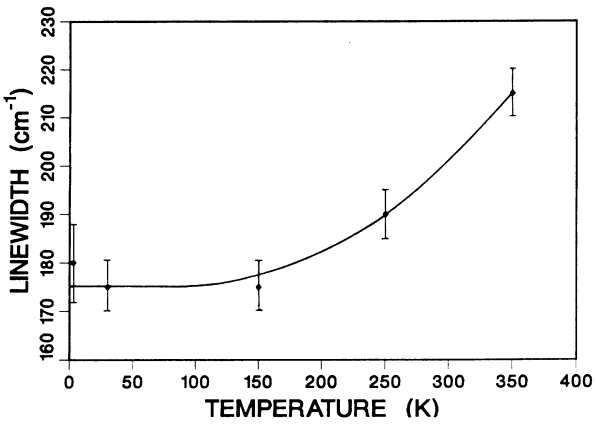

FIG. 6. Temperature dependence of the T_{1g} excitation linewidth (FWHM). The solid line is a guide to the eye.

which falls off too slowly at high frequencies ($\sim 1/\omega$). Rather, the high-frequency behavior suggests a more rapidly decreasing function of frequency, as illustrated, for example, by the fit to $\sim 1/\omega^3$ (solid curve in Fig. 5). Therefore, the broad scattering cannot be described by a simple relaxational process, as is typically applied to magnetic fluctuations.[12]

Additionally, the position of the peak (~ 100 cm^{-1}) in the broad response is consistent with that seen by neutron scattering at much higher $\mathbf{q}$.[6] The apparent $\mathbf{q}$ independence associated with $\mathrm{Im}\chi(\mathbf{q},\omega)$ suggests that the broad scattering we observe results from localized excitations. This alludes to two principal interpretations of the electronic scattering. The broad response might be due to quasielastic scattering from magnetic fluctuations, with the participating electrons remaining localized, even down to 3 K where the highly correlated electronic state is believed to be developing. However, a more credible interpretation, as suggested by recent specific-heat results,[8] is that these localized excitations result from crystal-field transitions. Firstly, the observed T_{1g} symmetry of this excitation is consistent with either the Γ_6-Γ_8 or the Γ_7-Γ_8 transition suggested by this earlier work, as can be illustrated by decomposing the direct product of these states:

$$\Gamma_{6,7}\otimes\Gamma_8=\Gamma_3^+\oplus\Gamma_4^+\oplus\Gamma_5^+(E_g\oplus T_{1g}\oplus T_{2g})\ .$$

Furthermore, the absence of broad scattering in $CeBe_{13}$ corroborates the crystal-field interpretation. Finally, the observed temperature dependence of the excitation linewidth [full width at half-maximum (FWHM)] shown in Fig. 6 is consistent with relaxation processes expected in materials with crystal-field-split levels.[13] Namely, above about 150 K one notes a roughly linear dependence on temperature, as expected of the usual Korringa broadening at high temperatures. Below 150 K, the linewidth is observed to saturate, as is expected at low temperatures when excitations between crystal-field levels become the principal relaxational channel. However, it should be remarked that similar temperature dependences have also been noted in quasielastic linewidths of some Kondo systems,[14] obscuring a definitive interpretation of the electronic scattering we observe.

V. CONCLUSION

Using Raman scattering, we have observed electronic excitations of the $5f$ electrons in UBe_{13} displaying a characteristic energy of about 100 cm^{-1} (144 K). A comparison of our $\mathbf{q}=\mathbf{0}$ data with neutron scattering data at much higher $\mathbf{q}$ demonstrates no evidence for any $\mathbf{q}$ dependence associated with this electronic response, suggesting that the excitations remain spatially localized down to 3 K. Furthermore, the strength of the observed response provides evidence that a large part of the magnetic susceptibility is exhausted by these localized excitations, even for temperatures at which the highly correlated electronic state is thought to be evolving. This electronic response is attributed to inelastic scattering from crystal-field excitations, although the possibility that it is instead quasielastic scattering from localized magnetic fluctuations cannot be excluded.

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[1]F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and J. Schafer, Phys. Rev. Lett. **43**, 1982 (1979).
[2]H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith, Phys. Rev. Lett. **50**, 1595 (1983).
[3]G. R. Stewart, Z. Fisk, J. O. Willis, and J. L. Smith, Phys. Rev. Lett. **52**, 679 (1984).
[4]For a general review, see G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).
[5]S. Horn, E. Holland-Moritz, M. Loewenhaupt, F. Steglich, H. Scheuer, A. Benoit, and J. Floquet, Phys. Rev. B **23**, 3171 (1981).
[6]A. I. Goldman, S. M. Shapiro, G. Shirane, J. L. Smith, and Z. Fisk, Phys. Rev. B **33**, 1627 (1986).
[7]S. L. Cooper, R. T. Demers, M. V. Klein, Z. Fisk, and J. L. Smith, Physica B **135**, 49 (1985).
[8]R. Felten, F. Steglich, G. Weber, H. Rietschel, F. Gompf, B. Renker, and J. Beuers, Europhys. Lett. **2**, 323 (1986).
[9]D. Cox (private communication).
[10]See also L. J. Sham and J. W. Wilkins, Phys. Rev. B **30**, 3062 (1984).
[11]A sixth phonon at 539 cm^{-1} and displaying E_g symmetry cannot be discerned in Fig. 1 due to the low resolution. This phonon is evident in higher resolution spectra (see Ref. 7).
[12]M. Loewenhaupt and E. Holland-Moritz, J. Appl. Phys. **50**, 7456 (1979).
[13]See, for example, L. C. Lopes and B. Coqblin, Phys. Rev. B **33**, 1804 (1986).
[14]R. M. Galera, A. P. Murani, and J. Pierre, J. Phys. (Paris) **46**, 303 (1985).