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Magnetic excitations and phonon anomalies in URu_2Si_2

S. L. Cooper and M. V. Klein
Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801

M. B. Maple and M. S. Torikachvili
Department of Physics and Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92093

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The results of a polarized light scattering study of URu_2Si_2 are presented and discussed for the temperature range $5 \leq T \leq 350$ K. Two of the Raman-active phonons allowed by the space- and site-group symmetries of URu_2Si_2 (D_{4h}^{17}-$I4/mmm$) are observed, displaying symmetries A_{1g} and B_{1g}. The A_{1g} phonon demonstrates a large integrated intensity increase with decreasing temperature, suggesting a low-temperature increase in the strong electron-phonon coupling. Additionally, quasielastic scattering from spin fluctuations is noted, displaying the symmetry of the antisymmetric representation A_{2g}. The spin-fluctuation linewidth is seen to decrease rapidly near T_N, alluding to the formation of a gap over much of the Fermi surface.

Heavy-electron materials, distinguished by their enormous low-temperature specific-heat coefficients and Pauli susceptibilities, have until recently fallen exclusively into one of three categories: (1) those which have a superconducting ground state [e.g., $CeCu_2Si_2$,[1] UPt_3,[2] and UBe_{13} (Ref. 3)], (2) those which magnetically order [e.g., UCd_{11} (Ref. 4) and U_2Zn_{17} (Ref. 5)], and finally (3) those in which no ordering is manifest to the lowest temperatures observed [e.g., $CeAl_3$ (Ref. 6) and $CeCu_6$ (Ref. 7)]. Recently, however, the coexistence of magnetic ordering and superconductivity in a heavy-electron system has been demonstrated in the compound URu_2Si_2, which displays an antiferromagnetic transition below 17.5 K, and bulk superconductivity below 1.5 K.[8-10] The coexistence of these two ordered states in URu_2Si_2 is to be distinguished from that found in other "magnetic superconductors",[11] insofar as the same type of "heavy" electrons are thought responsible for both transitions in the former material. Studies of URu_2Si_2, including specific-heat[8-10] and neutron scattering measurements,[12] have further suggested that the magnetic transition involves the opening of an energy gap over a portion of the Fermi surface, possibly driven by a charge- or spin-density wave.

Such diversity in the excitation spectrum of URu_2Si_2 naturally lends itself to study by light scattering techniques. Light scattering offers a means of studying the effects of a gap-opening transition on both the lattice and magnetic properties of URu_2Si_2, and potentially affords insight into the nature of such a transition. We elucidate these points in this paper, which details the results of a Raman-scattering investigation of URu_2Si_2.

Our study was conducted on oriented, single-crystal facets in polycrystalline samples of URu_2Si_2, as confirmed through Laue x-ray diffraction. Light scattering experiments included an argon laser as an excitation source, with the incident light polarized along different crystalline directions in order to isolate the symmetries of the various excitations. The scattered light was dispersed and collected using a standard triple-stage monochromator and a cooled photomultiplier tube detector.

URu_2Si_2 crystallizes in the tetragonal $ThCr_2Si_2$ structure, with space group D_{4h}^{17}-$I4/mmm$.[13] The Raman-allowed phonons associated with this structure are $A_{1g}+B_{1g}+2E_g$, with the A_{1g} mode involving only Si atoms, the B_{1g} phonon involving solely Ru atoms, and the E_g phonons involving both Si and Ru. Since the wave vector of light used as an excitation source is only a fraction of the Brillouin zone, the excitations probed in this study are essentially at the zone center ($\mathbf{q}=0$).

Figure 1 illustrates the excitation spectra in the various scattering geometries used to isolate the different symmetries. The $A_{2g}+B_{1g}$ spectra in Fig. 1(a) show the temperature dependence of the B_{1g} mode at 163 cm^{-1}, while the totally symmetric A_{1g} breathing mode is evident at 431 cm^{-1} in the $A_{1g}+B_{1g}$ spectra shown in Fig. 1(b). An anomalous intensity increase with decreasing temperature is clearly evident in the A_{1g} phonon, the implications of which will be discussed later. Also observed in the $A_{2g}+B_{1g}$ spectra is weak quasielastic scattering from spin fluctuations below 300 cm^{-1}, showing a decreasing linewidth between 350 and 40 K. By varying the scattering geometry, we have determined the symmetry of these excitations to be that of the totally antisymmetric representation of the URu_2Si_2 space group A_{2g} characteristic of magnetic scattering.

Figure 2 exemplifies the spin-fluctuation scattering for various temperatures, again indicating a steadily decreasing linewidth with decreasing temperature. As expected, the quasielastic scattering (hatched region) is well described by a simple relaxational model, which we have illustrated in Fig. 2 by fitting to the power spectrum:

$$S(\omega) \propto [1+n(\omega)] \frac{\omega\Gamma}{\Gamma/2^2+\omega^2} .$$

Here $n(\omega)$ is the Bose factor, and $\Gamma/2$ is the temperature dependent half width at half maximum (HWHM). Also

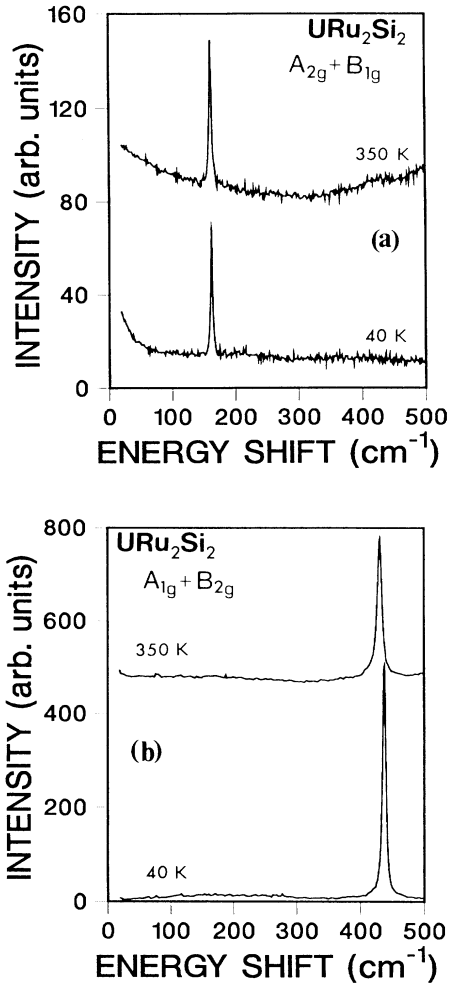

FIG. 1. (a) $A_{2g}+B_{1g}$ spectra and (b) $A_{1g}+B_{2g}$ spectra for URu_2Si_2 at 350 and 40 K. Resolution: 4 cm^{-1}. The spectra have been offset for clarity.

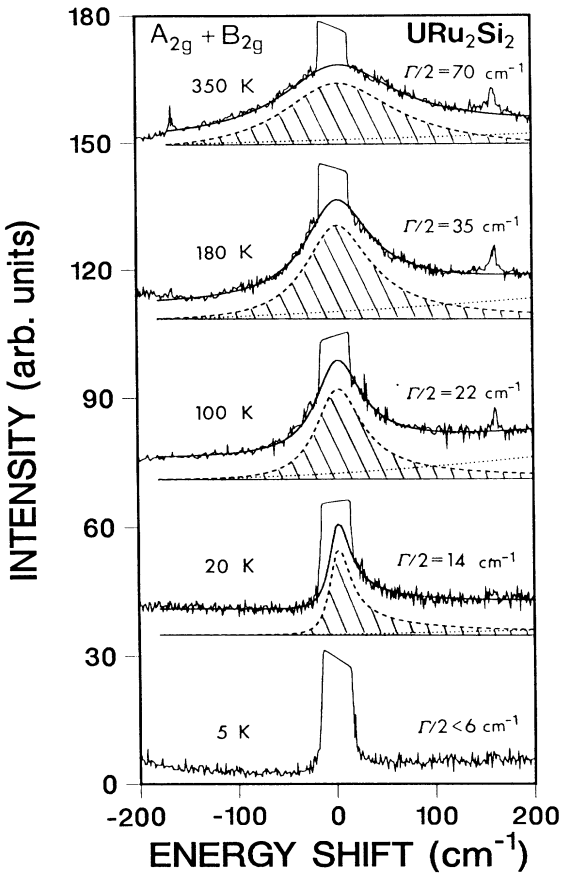

FIG. 2. Spin-fluctuation scattering in URu_2Si_2 at various temperatures. The hatched area shows the quasielastic contribution, the dotted line gives the linear (inelastic) contribution, and the solid line is the sum of these contributions with a small offset. The small feature near 150 cm^{-1} is slight leakage of the B_{1g} phonon into this spectra. All spectra have been offset.

observed in the spectral response is a small inelastic linear term, $\propto[1+n(\omega)]\omega$, which is illustrated in Fig. 2 by a dotted line. The fit to the full spectra (solid line) is given as the sum of this term and the quasielastic contribution, plus a small offset. The small inelastic contribution is presumed due to crystal-field excitations centered at much higher energies (>1000 cm^{-1}).

The temperature dependence of the observed quasielastic linewidths (HWHM) is shown in Fig. 3. The linewidths and temperatures for all quasielastic spectra were extracted from a least-squares fit to the full spectra (-200–200 cm^{-1}). For all cases, the best fits were obtained only within a narrow range of linewidths (± 3 cm^{-1}) centered at the points displayed in Fig. 3.

As illustrated in Fig. 3, several distinct regimes are clearly observed in $\Gamma(T)/2$ vs T. Above roughly 70 K, for example, the quasielastic linewidth exhibits a linear dependence on temperature, $\Gamma/2=\alpha k_B T$. For single-ion f electron systems without crystal fields, $\alpha=4\pi[n(E_F)\times(g_J-1)J_{sf}]^2$, where $n(E_F)$ is the conduction-band density of states at the Fermi energy, g_j is the Landé g factor for the ground state, and J_{sf} is the s-f exchange coupling.[14] A linear temperature dependence suggests that, above 70 K, the $5f$ electrons in URu_2Si_2 relax via a Korringa process, wherein damping of the $5f$ electrons occurs through the creation of electron-hole pairs within the conduction band. From the slope of the linear region in Fig. 3, we can estimate $\alpha=0.27$, which is an order of magnitude larger than that found for systems in which the Kondo coupling is weak.[14,15] This suggests, not surprisingly, that such coupling is rather strong in URu_2Si_2, although an exact determination of the coupling strength $[\sim n(E_F)J_{sf}]$ from our data demands a calculation of the Korringa coefficient α appropriate to noncubic U compounds with crystal fields.

Between 70 and 23 K, the linewidth is observed to approach a residual value of roughly 19 cm^{-1} ($\simeq 27$ K). A temperature-independent linewidth is expected as further thermal (Korringa) decreases in the linewidth are interrupted at low temperatures by the U moment–conduction-electron exchange channel. Due to the importance of

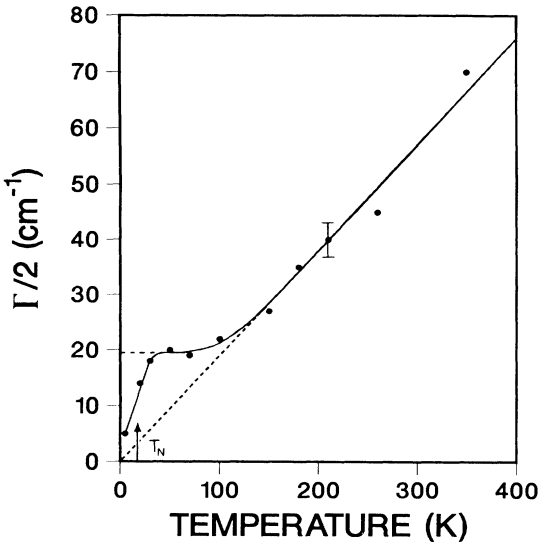

FIG. 3. Temperature dependence of the quasielastic half-width (HWHM). The estimated errors for all points reflect the range of linewidths for which the best fits were obtained (± 3 cm^{-1}). The solid line is a guide to the eye, while the dashed lines are extrapolations of the linear in T and the temperature independent regimes, as discussed in the text.

both the Kondo and Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions in URu_2Si_2, each is expected to contribute to the residual linewidth, and indeed, it has been suggested[16] that in such a case, $h\Gamma(\mathbf{q}) = |k_B T_K - J_{RKKY}(\mathbf{q})|$ is the relevant energy scale (where T_K is the single-ion Kondo temperature, and $J_{RKKY}(\mathbf{q})$ is the $\mathbf{q}$-dependent RKKY exchange parameter). Such a $\mathbf{q}$-dependent linewidth would account for the discrepancy noted between the residual linewidth [$\Gamma_0(\mathbf{q}=0) \sim 27$ K] observed in our experiment, and that reported at higher $\mathbf{q}$ by neutron scattering.[17]

Below 30 K (see Fig. 3), the spin fluctuation linewidth appears to exhibit an abrupt decrease, and by 5 K there is no observable spin-fluctuation scattering within our experimental resolution ($\Gamma/2 < 6$ cm^{-1}). It should be noted, however, that this rapid change in spin-fluctuation scattering may also result from a loss of quasielastic *intensity*. Indeed, due to the presence of the elastic line, it is difficult to precisely distinguish intensity and linewidth changes below 30 K. This disappearance of quasielastic scattering, within our experimental resolution, is believed to corroborate recent evidence[8-10,12] for the formation of an energy gap near $T_N = 17$ K.

As has been suggested and confirmed by a recent neutron scattering study, the gap-opening transition allows propagating magnetic states (spin waves) to exist within the gap.[17] These inelastic excitations, which have been found to be polarized along the c axis,[17] should transform like the E_g representation of the magnetic point group and thus can be coupled to by light only in the basal plane. As yet we have been unable to observe this mode in a polycrystalline sample, or to isolate a sufficiently large single crystal with basal orientation. A future search for this mode at $\mathbf{q}=0$ therefore necessitates larger single crystals.

As mentioned earlier, the $\mathbf{q}=0$ spin fluctuation linewidths observed in our Raman-scattering study are roughly half those reported at higher $\mathbf{q}$ by neutron scattering.[12,17] This discrepancy is much too large to be attributed solely to the lower resolution of neutron scattering, and instead suggests a real $\mathbf{q}$ dependence in Γ. Such large dispersion noted in Γ could arise from a strongly $\mathbf{q}$-dependent exchange coupling $J(\mathbf{q})$, indicating some spatial coherence of the spin fluctuations above T_N. In terms recently expressed by Aeppli,[16] the magnetic susceptibility

$$\chi(\mathbf{q},\omega) = \frac{\chi_0(\omega)}{1 - J(\mathbf{q})\chi_0(\omega)}$$

is subject to magnetic instability at values of $\mathbf{q}=\mathbf{q}_0$ for which $\chi_0 J(\mathbf{q}_0) = 1$. Here χ_0 is the $\mathbf{q}$-independent susceptibility, which for single-ion Kondo systems can be given as $\chi_0 \sim (k_B T_K)^{-1}$. Therefore, the narrow linewidths we observe near $\mathbf{q}=0$, compared to those seen at higher $\mathbf{q}$, by neutron scattering suggest that, in URu_2Si_2, $\mathbf{q}_0$ is near the zone center, and consequently the antiferromagnetic correlations in URu_2Si_2 have a long wavelength. A more thorough study of $\Gamma(\mathbf{q},T)$ by neutron scattering is necessary to confirm this point.

While many investigations have demonstrated the remarkable magnetic properties of URu_2Si_2, initial studies of the lattice have also yielded unusual results. Specifically, a recent thermal expansion study has observed a minimum in the c/a ratio at 60 K, suggesting anomalous elastic properties at low temperatures.[18] Furthermore, an electronic Grüneisen parameter of $\Omega_e = 25$ has been deduced at low temperatures by the thermal expansion data, which is an order of magnitude larger than that found in free-electron systems. Such a large value for Ω_e is typical in heavy-electron compounds, reflecting a heightened coupling of the lattice to the narrow heavy-electron band at low temperatures.

Evidence for elastic anomalies is also manifested in our study, where we observe a marked increase in the integrated intensity of a Raman-active phonon with de-

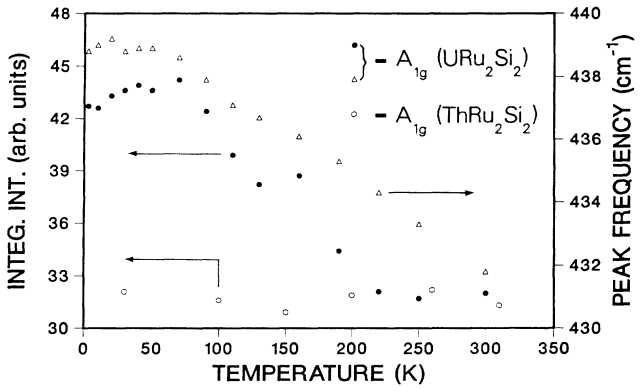

FIG. 4. Integrated intensity of the A_{1g} phonon vs temperature (dark circles) compared with the A_{1g} phonon peak position vs temperature (open triangles) in URu_2Si_2. Also shown is the integrated intensity of the A_{1g} phonon in reference sample $ThRu_2Si_2$ (open circles). The $ThRu_2Si_2$ data points have all been scaled by a factor of 2.45 for comparison with URu_2Si_2.

creasing temperature, alluding to an enhancement in the electron-phonon interaction at low temperatures. These results are exemplified in Fig. 4, which plots as a function of temperature the integrated intensity and peak position of the A_{1g} breathing mode of Si atoms around the U atom. A strong increase in the integrated intensity is observed below 220 K, reaching a weak maximum near 60 K. This is compared in the same plot to the integrated intensity of the A_{1g} phonon in isostructural $ThRu_2Si_2$, which demonstrates no anomalous behavior. One explanation for the A_{1g} integrated intensity increase is that there is a magnetoelastic coupling of the crystal-field-split f levels to the volume strain of $A_{1g}(\Gamma_1)$ symmetry ϵ_v, which is enhanced by the contraction of the unit cell. This interpretation is suggested in Fig. 4, in which the A_{1g} frequency shift (reflecting the thermal lattice contraction) is observed to track the A_{1g} integrated intensity. Such an explanation would also be consistent with evidence for magnetoelastic effects observed in neutron scattering and thermal expansion experiments.[17,18] A magnetoelastic coupling to the A_{1g} phonon would be particularly strong for crystal-field splittings on the order of the A_{1g} phonon energy ($\sim$430 cm^{-1}), and indeed, a crystal-field level near 395 cm^{-1} has been extracted from recent susceptibility data for URu_2Si_2.[18] The comparable energies of these two excited states provide further evidence that magnetoelastic effects may indeed be important in the observed phonon intensity enhancement. More conclusive evidence for this interpretation, however, is being sought through pressure studies.

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