Raman scattering study of the electronic and vibrational excitations in $CeCu_2Si_2$

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The vibrational and crystal-field excitation spectrum is examined in $CeCu_2Si_2$ using polarized Raman scattering. These results are compared to spectra from the isostructural compounds RCu_2Si_2 (R=La,Gd,Yb) in the temperature range $2 \leq T \leq 390$ K. The observed vibrational spectrum of $CeCu_2Si_2$ consists partly of a B_{1g} and an A_{1g} mode involving only Cu and Si atoms, respectively. Two E_g modes, involving both Cu and Si atoms, are also seen. An additional A_{1g} phonon peak is observed, in defiance of the phonon spectrum allowed by the space-group symmetry of $CeCu_2Si_2$. This peak is believed due to disorder and is attributed to an A_{1g} breathing mode of Cu atoms sitting at Si sites. Electronic crystal-field excitations are also evident in our spectra, displaying a broad peak centered roughly at 290 cm^{-1}. This excitation is observed only in the purely antisymmetric A_{2g} (depolarized) spectrum, and is seen to narrow and intensify with decreasing temperature. No other crystal-field transition is observed. The temperature dependence of the crystal-field excitation linewidth is discussed.

I. INTRODUCTION

A great deal of attention has been recently afforded a group of intermetallic compounds which behave like local moment systems at high temperatures, yet display many features of a simple metal at low temperatures.[1] These compounds are particularly notable in that their electronic specific-heat coefficients are often quite large, alluding to a substantial electronic density of states at E_F. Of special interest are four such materials, $CeCu_2Si_2$,[2] UBe_{13},[3] UPt_3,[4] and U_6Fe,[5] which have been shown to possess a superconducting ground state in which the heavier electrons are thought to participate. This contradicts the expectation that such electrons should be predisposed towards localization and magnetization.

This incongruous behavior is perhaps best understood in $CeCu_2Si_2$, for which much of the experimental evidence suggests a "Kondo lattice" description.[6] In this model the conduction electrons, by compensating the magnetic moment, aid in the formation of a narrow resonance at E_F. From this resonance derives both the strength of the electronic specific-heat coefficient and the "heavy" electrons responsible for pairing in the superconducting state.

Given its evident importance, the electronic excitation spectrum of $CeCu_2Si_2$ has been scrutinized by neutron scattering[7-10] in an effort to characterize the magnetic fluctuations of the f electrons and the effects of the crystal field on the Ce multiplet. However, both the dependence of T_c on atomic volume[6] and the evidence for elastic anomalies[11] discovered in $CeCu_2Si_2$ illustrate that the lattice is also important to the novel properties of this system.

In view of such rich activity in the excitation spectrum of $CeCu_2Si_2$, polarized Raman scattering promises to be a useful means of probing both the lattice anomalies and the crystal-field effects inherent in this material. The intrinsic high resolution of this technique is well suited to the study of temperature or compositional effects on the various excitations, particularly those manifested in changes in linewidth or energy. The use of polarized light and single crystals, moreover, provides symmetry information about the excitations observed. In this paper, we present the results of such a Raman scattering study of $CeCu_2Si_2$, in an attempt to elucidate some of the uncertainties currently surrounding this material.

II. EXPERIMENTAL DETAILS

Our investigation was conducted on oriented single-crystal samples of RCu_2Si_2 with R=Ce, La, Gd, Yb. Proper orientation was confirmed through Laue x-ray diffraction. All of the data presented were obtained on samples which had been mechanically polished with diamond paste having grain sizes down to $\frac{1}{4}$ μm. The effects on our Raman spectra, due to strain introduced by polishing, were determined by observing selected spectra from unpolished samples. No significant differences were noted between spectra from polished and unpolished samples.

All of the experiments were conducted using a polarized 4880- or 5145-Å line of an argon laser as an excitation source, and a rotating polaroid film was used to select specific polarizations of the scattered light. Measurements were made in a near-backscattering geometry, with the incident light polarized along various crystalline directions. This allowed a determination of each excitation's symmetry. However, due to the imperfect backscattering geometry used, small contributions from otherwise forbidden symmetries were observed in certain spectra. This

TABLE I. Allowed excitation symmetries for various scattering geometries in $CeCu_2Si_2$. $\hat{x}=(1,0,0)$, $\hat{y}=(0,1,0)$, $\hat{x}'=(1/\sqrt{2})(1,1,0)$, $\hat{y}'=(1/\sqrt{2})(1,-1,0)$, $\hat{z}=(0,0,1)$.

Propagation direction ($\mathbf{k}_i$)	Geometry ($\hat{e}_i,\hat{e}_s$)	Allowed symmetries
c axis	$(\hat{x},\hat{x})$	$A_{1g}+B_{1g}+E_g$ "leakage"
	$(\hat{x},\hat{y})$	$A_{2g}+B_{2g}+E_g$ "leakage"
	$(\hat{x}',\hat{x}')$	$A_{1g}+B_{2g}+2\times E_g$ "leakage"
	$(\hat{x}',\hat{y}')$	$A_{2g}+B_{1g}$
Basal plane	$(\hat{x},\hat{x})$	$A_{1g}+B_{1g}$
	$(\hat{x},\hat{z})$	E_g

"leakage" of symmetry, where expected, is noted in Table I, which delineates the allowed symmetries for the various scattering geometries used.

The spectrograph used predominantly throughout our investigation consisted of three stages, the first two acting as a nondispersive filter stage and the final stage providing dispersion. This spectrograph was used in conjunction with a multichannel detection system. A monochromator with three dispersive stages was also used in our investigation, coupled with a standard cooled photomultiplier tube detector. These instruments provided resolutions of 10 and 3 cm^{-1}, respectively.

A liquid-He cryostat, with a variable-temperature gas-flow option, was used in all our measurements for continuous adjustment of temperature down to 2 K. Temperatures were determined by obtaining the Stokes—anti-Stokes ratio from the spectra, in order to account for the temperature rise due to laser heating of the sample.

III. PHONON SPECTRUM

$CeCu_2Si_2$ crystallizes in the tetragonal $ThCr_2Si_2$ structure with space group $D_{4h}{}^{17}$-$I4/mmm$ (see Fig. 1).[12] Of the 12 optical phonons indicative of this structure, only those with the transformation properties of a second-rank tensor may couple to the incident light in a Raman scattering experiment. The Raman-active phonons associated with $CeCu_2Si_2$ are therefore $A_{1g}+B_{1g}+2E_g$ ($\Gamma_1^+ +\Gamma_3^+ +2\Gamma_5^+$). Since the wave vector of light used as an excitation source is a very small fraction of the Brillouin zone, the phonons probed are essentially at the zone center. From the site symmetries of Si and Cu in $CeCu_2Si_2$, it is known that the A_{1g} phonon involves only Si atoms, while the B_{1g} phonon is purely a Cu mode. Both Si and Cu, however, participate in the two E_g phonons. The Ce atom, sitting at a site of inversion symmetry, is consequently not involved in any Raman-active modes.

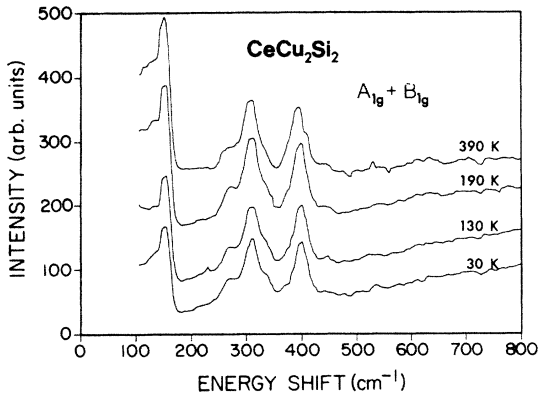

FIG. 2. $A_{1g}+B_{1g}$ spectra for $CeCu_2Si_2$ at various temperatures. Resolution: 10 cm^{-1}. The spectra have been offset for clarity.

The phonon spectrum, in a geometry which isolates the $A_{1g}+B_{1g}$ modes (see Table I), is shown at various temperatures in Fig. 2. Rather than the two phonon peaks allowed in this geometry by the $CeCu_2Si_2$ crystal structure, three features are evident, centered roughly at 150, 300, and 400 cm^{-1}. No anomalous temperature dependence is noted in any of these peaks down to 2 K. The sharp peak at 150 cm^{-1} is ascribed to the B_{1g} Cu mode, while the broader peak at 400 cm^{-1} is that of the A_{1g} Si mode. These symmetry assignments are confirmed by the spectra displayed in Fig. 3, obtained in a geometry which allows a

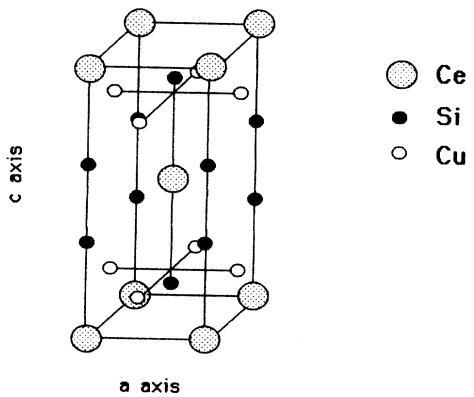

FIG. 1. $CeCu_2Si_2$ unit cell ($D_{4h}{}^{17}$-$I4/mmm$ space group).

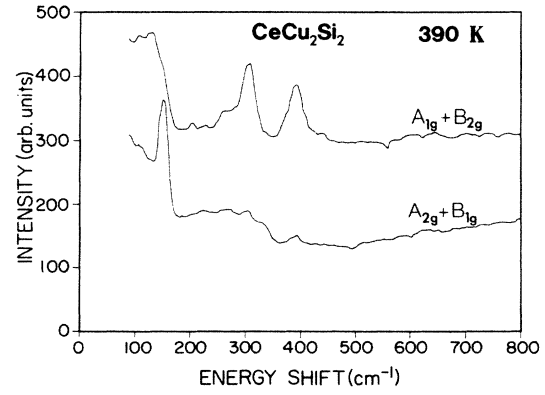

FIG. 3. $A_{1g}+B_{2g}$ (upper) vs $A_{2g}+B_{1g}$ (lower) spectra for $CeCu_2Si_2$ at 390 K. Resolution: 10 cm^{-1}. The $A_{1g}+B_{2g}$ spectrum has been shifted upwards by 70 a.u.

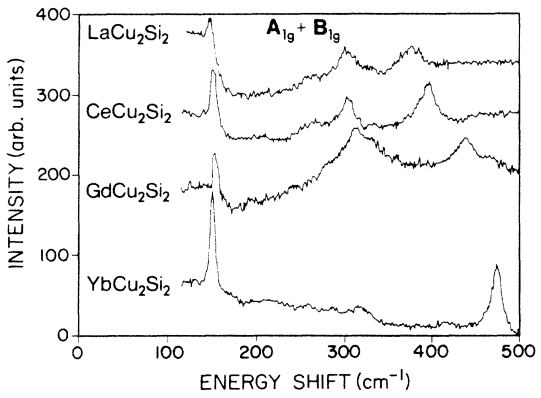

FIG. 4. $A_{1g}+B_{1g}$ spectra for RCu$_2$Si$_2$ (R=La, Ce, Gd, and Yb) at 390 K. Resolution: 3 cm^{-1}. The La, Ce, and GdCu$_2$Si$_2$ spectra have been scaled by 1.5× compared to YbCu$_2$Si$_2$. The spectra have been offset.

separation of the A_{1g} and B_{1g} symmetries. Figures 2 and 3 also indicate a very broad feature below 150 cm^{-1}, displaying mixed $A_{1g}+B_{1g}$ symmetry. This structure is presumed due to disorder, although its origin is otherwise uncertain.

Like the Si peak, the errant peak at 300 cm^{-1} displays A_{1g} symmetry and a large linewidth. Moreover, its presence in other RCu$_2$Si$_2$ compounds implies that it is of structural rather than electronic origin (see Fig. 4). Several features of this unexpected peak suggest that it is a Cu A_{1g} mode resulting from disordered substitution of Cu onto Si sites. First, the observed energies of the two A_{1g} peaks are consistent with a simple scaling of the Cu and Si masses. Secondly, the large widths associated with both of these peaks indicates some degree of disorder in the material. Finally, the required orthogonality of phonon modes demands that the two A_{1g} peaks result either from different crystal phases in the sample, or from two-mode behavior due to different elements sitting at equivalent sites. The absence of x-ray evidence for additional phases in our sample further suggests the latter possibility. Evidence for substitutional disorder is particularly interesting in light of the peculiar volume dependence of T_c noted in CeCu$_2$Si$_2$.[6] Specifically, compared with stoichiometric CeCu$_2$Si$_2$, Cu-rich CeCu$_{2.2}$Si$_2$ has been shown to display a compressed lattice and a high value of T_c (T_c=0.68 K), while Cu-deficient CeCu$_{1.9}$Si$_2$ manifests an expanded lattice and an absence of superconductivity. Our data suggest that excess Cu may be accommodated by substituting onto Si sites. What influence this might have on superconductivity is not clear, and a more thorough investigation of the phonon spectrum vs T_c (i.e., Cu concentration) is therefore merited.

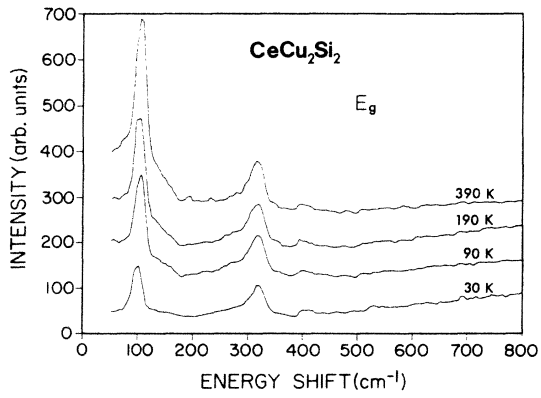

FIG. 5. E_g spectra for CeCu$_2$Si$_2$ at various temperatures. Resolution: 10 cm^{-1}. The spectra have been offset.

TABLE II. Observed phonon frequencies in RCu$_2$Si$_2$ at 390 K.

	Frequency (cm^{-1})		(Resolution 3 cm^{-1})	
Phonon	Ce	La	Gd	Yb
B_{1g}	151	146	152	150
A_{1g} (Cu)	304	299	313	319
A_{1g} (Si)	398	376	438	474
E_g	105			
E_g	317			

Figure 4 compares the $A_{1g}+B_{1g}$ spectra of the four isostructural compounds considered in our study. One first notes that while the B_{1g} Cu phonon frequency is insensitive to the rare-earth constituent of the crystal, the A_{1g} Si frequency is strongly influenced, hardening from 376 cm^{-1} in LaCu$_2$Si$_2$ to 474 cm^{-1} in YbCu$_2$Si$_2$. The A_{1g} Cu mode also displays a hardening between these compounds, although the shift is much less dramatic due to the heavier mass of Cu. This behavior confirms the expectation that the A_{1g} breathing mode around the rare-earth ion should be particularly sensitive to the atomic volume of the rare-earth ion (see Fig. 1). Also indicated in Fig. 4 is the weakness of the YbCu$_2$Si$_2$ A_{1g} Cu peak relative to the same mode in La, Gd, and CeCu$_2$Si$_2$. This implies a lesser degree of disorder in this YbCu$_2$Si$_2$ sample. Indeed, the corresponding sharpness of the A_{1g} Si phonon in YbCu$_2$Si$_2$ lends further credence to the interpretation that substitutional disorder is responsible for the unexpected peak in CeCu$_2$Si$_2$.

The two additional Raman-active modes of E_g symmetry can only be observed in a scattering geometry with the propagation vector along the low symmetry direction, i.e., the basal plane (see Table I). The resulting spectra are shown in Fig. 5 at various temperatures, with the two E_g modes clearly evident at roughly 100 and 320 cm^{-1}. Again, no anomalous temperature dependence is observed down to 2 K. Table II summarizes the results of the phonon spectrum at room temperature.

IV. CRYSTAL-FIELD EFFECTS

In the presence of a cubic crystal field, the Ce^{3+} $J=\frac{5}{2}$ multiplet is expected to split into a $\Gamma_7+\Gamma_8$ pair, with two- and fourfold degeneracies, respectively. Further reduction of symmetry with a tetragonal distortion, splits the Γ_8 level into a $\Gamma_7+\Gamma_6$ doublet (see Fig. 6). Electronic transitions between these levels should manifest the symmetries allowed by the direct products of these states:

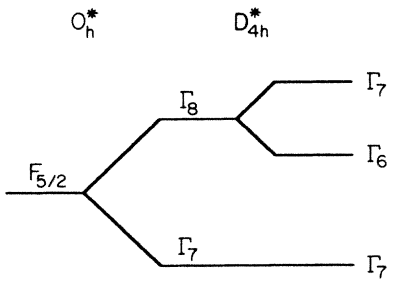

FIG. 6. Splitting of the $J=\frac{5}{2}$ Ce^{3+} level in subsequent cubic (O_h^*) and tetragonal (D_{4h}^*) crystal fields.

$$\Gamma_7\otimes\Gamma_7=\Gamma_1^+\oplus\Gamma_2^+\oplus\Gamma_5^+\ (A_{1g}\oplus A_{2g}\oplus E_g)\ ,$$

$$\Gamma_7\otimes\Gamma_6=\Gamma_3^+\oplus\Gamma_4^+\oplus\Gamma_5^+\ (B_{1g}\oplus B_{2g}\oplus E_g)\ .$$

In $CeCu_2Si_2$, crystal-field excitations were first observed using neutron scattering, with levels reported at 140 and 364 K (100 and 260 cm^{-1}).[7] Subsequent neutron scattering studies, while clearly observing the peak at higher energy, have been unable to confirm the lower energy transition.[8,10] Furthermore, specific-heat measurements have shown a specific-heat anomaly in $CeCu_2Si_2$ which has been accurately modeled as a Schottky anomaly involving two closely spaced crystal-field levels near 260 cm^{-1} (360 K).[13] Theoretical work on crystal-field effects in $CeCu_2Si_2$ also supports the notion of two closely spaced levels,[14] finding that such a scheme best models the measured anisotropy in the magnetic susceptibility.[15]

We observe crystal-field excitations as a broad hump in the $A_{2g}+B_{1g}$ spectra of Fig. 3 centered roughly at 290 cm^{-1}. This identification is supported by the temperature dependence of the $A_{2g}+B_{1g}$ spectrum illustrated in Fig. 7. As expected of electronic transitions, the crystal-field peak at 290 cm^{-1} narrows and intensifies as the temperature is lowered, mimicking the sharpening Fermi factor. The $A_{2g}+B_{2g}$ spectra shown in Fig. 8, further exemplify the temperature dependence of the crystal-field transition. The appearance of the crystal-field peak in both of these spectra confirms that it has the symmetry of the purely antisymmetric representation of the $CeCu_2Si_2$ space group, A_{2g}, characteristic of a Γ_7-Γ_7 transition. No evidence of a Γ_7-Γ_6 transition is seen.

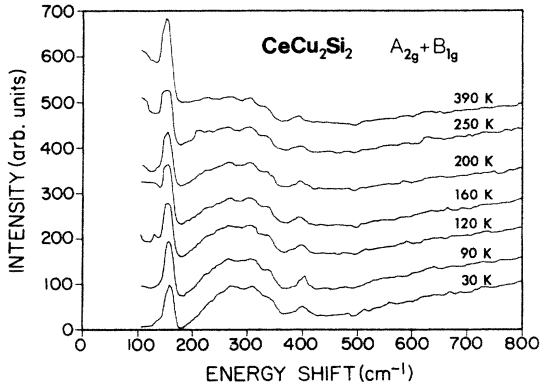

FIG. 7. Temperature dependence of the $A_{2g}+B_{1g}$ spectra of $CeCu_2Si_2$. Resolution: 10 cm^{-1}. The spectra have been offset.

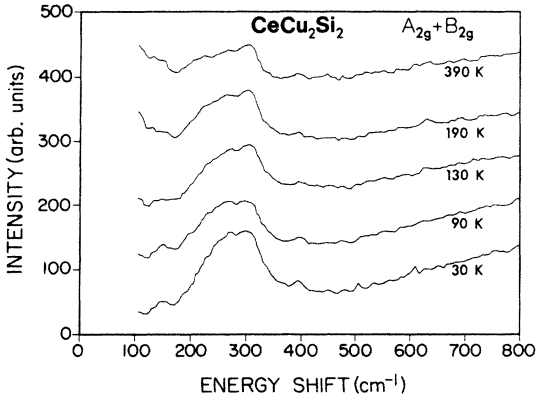

FIG. 8. Temperature dependence of the $A_{2g}+B_{2g}$ spectra of $CeCu_2Si_2$. Resolution: 10 cm^{-1}. The "hump" in the crystal-field peak near 300 cm^{-1} is due to leakage of the E_g phonon. The spectra have been offset.

A more dramatic confirmation of f-electron involvement in the A_{2g} excitation is shown in the comparison of the $A_{2g}+B_{2g}$ spectrum of $CeCu_2Si_2$ with that of the isostructural d-band metal $LaCu_2Si_2$ (Fig. 9). There is clearly no evidence of an analogous A_{2g} structure in the latter material.

The temperature dependence of the crystal-field linewidth [full width at half maximum (FWHM)] observed in our investigation is summarized in Fig. 10. This temperature dependence has been calculated only for cubic Kondo systems,[16,17] but the results adequately describe the general features of our observed linewidth in anisotropic $CeCu_2Si_2$. In these models, the dominant damping mechanism at high temperatures ($\delta \ll T$) results from elastic scattering (i.e., creation of electron-hole pairs) within each of the crystal-field levels, giving a linear dependence of linewidth on temperature:[17]

$$\Gamma=4\pi[n(E_F)]^2(|J_{77}|^2+2|J_{88}|^2)T\quad(\delta\ll T)\ .$$

Here, J_{77} and J_{88} are exchange integrals between electrons

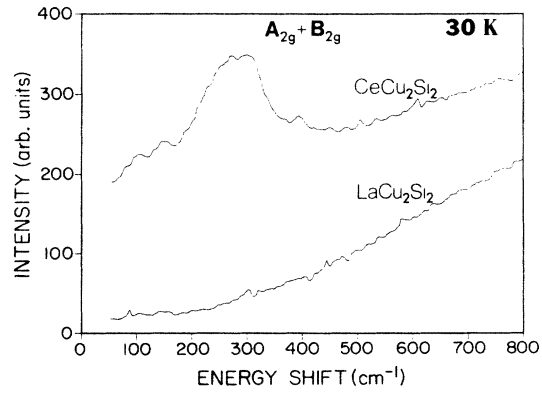

FIG. 9. Comparison of $A_{2g}+B_{2g}$ spectrum of $CeCu_2Si_2$ (upper) with that of $LaCu_2Si_2$ (lower) at 30 K. Resolution: 10 cm^{-1}.

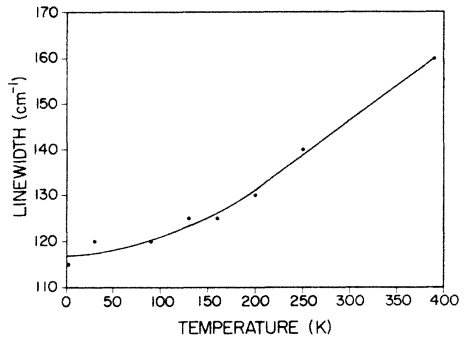

FIG. 10. Observed crystal-field linewidth (FWHM) vs temperature for A_{2g} crystal-field peak in $CeCu_2Si_2$. Resolution: 10 cm^{-1}. Line drawn is a guide to the eye.

within the Γ_7 and Γ_8 crystal-field levels, respectively, while $n(E_F)$ is the conduction-band density of states at the Fermi energy.

At low temperatures ($T \ll \delta$), damping chiefly results from transitions between the crystal-field levels, promoted by the exchange interaction between the conduction electrons and the Ce^{3+} $4f$ electron. This leads to a saturation of the linewidth at sufficiently low temperatures, as described by[17]

$$\Gamma = 4\pi[n(E_F)]^2 \left[|J_{78}|^2 \delta \frac{1+2e^{-\delta/T}}{1-e^{-\delta/T}} \right] \quad (T \ll \delta) .$$

The crystal-field splitting is described by δ in this relation, while J_{78} is the exchange term between the Γ_7 and Γ_8 levels.

An informal application of these results to $CeCu_2Si_2$ ($\delta = 406$ K), presuming equal exchange terms and a weak splitting of the Γ_8 level, indicates that these two mechanisms should be of roughly equal importance down to about 160 K. Below this temperature, the inelastic damping term begins to predominate quickly. This behavior is reflected in our observed linewidth, wherein one notes a linear dependence above 200 K, with saturation occurring at lower temperatures (see Fig. 10).

V. SUMMARY

Several interesting features evolved from our Raman scattering investigation of $CeCu_2Si_2$. In the phonon spectrum, the appearance of an additional A_{1g} mode has provided evidence for substantial Cu occupancy of Si sites. The importance of this disorder to any of the novel properties of $CeCu_2Si_2$ has yet to be determined. The electronic excitation spectrum consists of a Γ_7-Γ_7 crystal-field transition, displaying purely A_{2g} symmetry. Transitions between other levels were notably absent, presumably due to the weak matrix elements involved. Finally, the linewidth of the observed crystal-field peak has been shown to demonstrate a temperature dependence which is consistent with calculated relaxation mechanisms in Kondo systems.

ACKNOWLEDGMENTS

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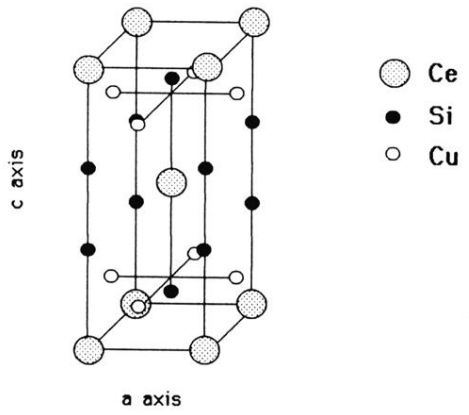

FIG. 1. $CeCu_2Si_2$ unit cell (D_{4h}^{17}-$I4/mmm$ space group).