# High-energy magnetic excitations of $URu_2Si_2$

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We have investigated the magnetic excitations of $URu_2Si_2$ up to 800 meV using high energy inelastic neutron scattering. There is clear evidence of magnetic scattering in the energy range up to 200 meV. This scattering can be fitted to four broad peaks which we attribute to heavily damped crystal field excitations. We also observed the $U^{4+}$ $^3H_4 \rightarrow {}^3F_2$ intermultiplet transition at 363 meV, which is a clear evidence of $U^{4+}$ of $URu_2Si_2$. We discuss our results with special attention to theoretical models proposed to explain the single ion physics of $URu_2Si_2$, in particular the antiferromagnetic transition.

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## I. INTRODUCTION

The heavy fermion superconductor $URu_2Si_2$ has recently been the subject of several experimental and theoretical studies.[1–8] From early studies, it was found that resistivity measurements showed a feature, reminiscent of a spin- or charge-density-wave-like transition, at the antiferromagnetic transition of 17.5 K before undergoing a superconducting transition at 1.5 K.[1] However, neutron diffraction measurements[2] found that an extremely small ordered moment of $0.04\mu_B$/U atom was associated with the antiferromagnetic transition, which was difficult to reconcile with a rather large entropy of $0.170R\ln 2$ released through the magnetic transition. Although the superconducting state below 1.5 K itself is an interesting subject, the main interest of research activities on $URu_2Si_2$ has centered around how we understand the small moment ordering at $T_N = 17.5$ K. Two recent NMR studies further illuminated the salient aspect of the antiferromagnetic phase.[6]

In order to explain the origin of the antiferromagnetic transition, several competing theoretical proposals[3–5] have been put forward so far. Although each scenario proposes a different mechanism for the small moment transition with the large entropy involved, they share the same view that the antiferromagnetic transition cannot be entirely due to the usual magnetic dipole ordering. Furthermore, some of these theories[3,4,7] are closely related to the exact nature of the U ion of $URu_2Si_2$ requiring either a valence admixture, a specific crystal field scheme, or specific ground and first excited states. It is therefore one of the most pressing issues concerning $URu_2Si_2$ to explore experimentally the single ion nature of the U $5f$ electrons and their crystal field states.

Neutron scattering is a very useful tool to study the single ion physics of heavy fermions. However, early inelastic neutron scattering studies[2,8] were limited in energy range and not very conclusive as to the single ion nature of the U ion, still less a full crystal field splitting. For example, the single crystal work by Broholm *et al.*[2] revealed a very dispersive low energy excitation in the energy range 2–13 meV. To our knowledge, there has been no reported inelastic neutron scattering work covering the energy range up to 100 meV, which is comparable with the overall splitting of U CEF (crystalline electric field) levels predicted from the CEF Hamiltonian in Ref. 3.

In this paper, we present inelastic neutron scattering data covering incident energies up to 800 meV that show the existence of magnetic scattering of $URu_2Si_2$ right up to 200 meV. From the analysis of our inelastic neutron scattering data using $ThRu_2Si_2$ as a phonon background material, we find that we can fit the magnetic scattering using possibly four crystal field excitations with the highest one centered at 156 meV, which is the highest CEF energy ever found in U intermetallics. Although the lowest dispersive excitation is strongly temperature dependent in agreement with the previous single crystal data,[2] the three others remain almost unchanged from 4.5 to 40 K, i.e., temperature independent within the experimental resolution. Apart from the CEF excitations, there is also an intermultiplet transition of $U^{4+}$ at 363 meV, which is temperature independent too.

## II. EXPERIMENTAL DETAILS

For our experiments, we prepared four polycrystalline samples by arc-melting high purity elements: 43 g of $URu_2Si_2$, 40 g of $(U_{0.1}Th_{0.9})Ru_2Si_2$, 30 g of $(U_{0.1}Y_{0.9})Ru_2Si_2$, and 30 g of $ThRu_2Si_2$. To ensure homogeneity of the samples, we made five or six buttons with each weighing about 8 g for one composition, and each button was flipped and melted at least ten times as described before.[9] Before the inelastic neutron scattering experiments, we checked the crystal structure of our samples by using white-beam neutrons to confirm that all the four samples were single phase with the $ThCr_2Si_2$ structure.

Inelastic neutron scattering measurements were made with the HET (high energy transfer) chopper spectrometer at the UK ISIS spallation neutron source. Neutrons are scattered from the sample into two forward detector banks, one at low scattering angles $\phi = 2.6° \rightarrow 7.2°$ at a distance of 4 m from the sample position, and a second bank covering the higher scattering angles $\phi = 9.3° \rightarrow 28.7°$ at a distance of 2.5 m from the sample. Two high-angle detector banks are located at $\phi = 110.4° \rightarrow 138.7°$. Because of the geometrical ar-

 

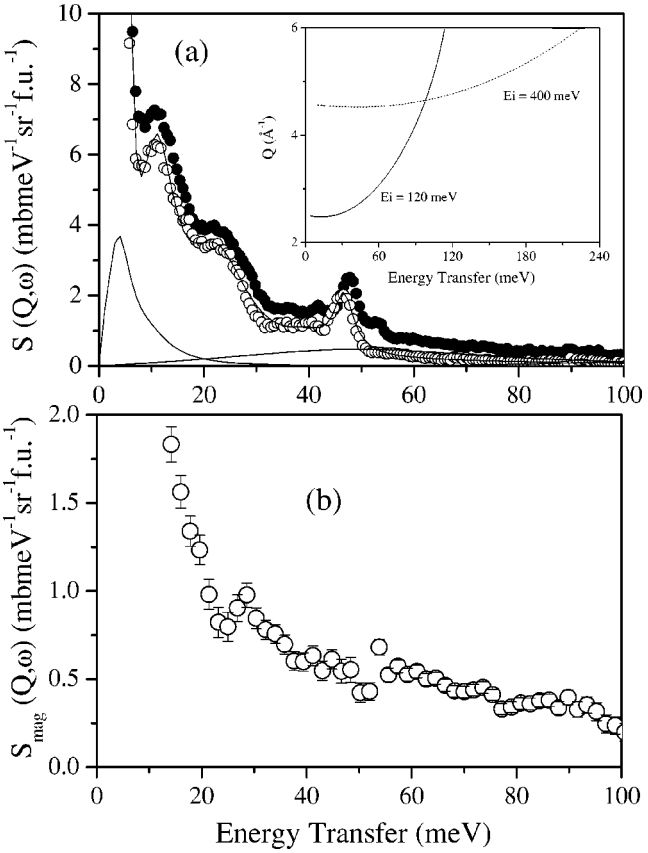


FIG. 1. (a) Inelastic spectra of $URu_2Si_2$ (closed symbols) and $ThRu_2Si_2$ (open symbols) measured with the 2.5-m low angle detector bank on HET at 22 K with an incident neutron energy of $E_i = 120$ meV. The line underneath the open symbols is the fitting result (see the text). The full line underneath the closed symbols is the sum of phonon spectra from the above fitted function and magnetic excitations for $URu_2Si_2$ (shown at the bottom of the figure) centered at 8, 48.6, and 99.2 meV, respectively. In the inset is shown the $E-Q$ relationship calculated for the sum of 2.5 m low angle bank with $E_i = 120$ and 400 meV. (b) Magnetic scattering obtained using the high angle bank data of the $URu_2Si_2$ with a scale factor from the $ThRu_2Si_2$ data (see the text).

rangement of the detectors with respect to the sample, the energy ($E$)–momentum ($Q$) relationship is non-trivial for each energy transfer with a given initial energy $E_i$. This is illustrated in the inset of Fig. 1 for the sum of the 2.5-m low angle bank with incident energies of 120 and 400 meV.

The scattering function $S(Q,\omega)$ in absolute units of $\mathrm{mb\,meV^{-1}\,sr^{-1}\,f.u.^{-1}}$ as a function of wave-vector transfer $Q$ and energy transfer $\hbar\omega$, is obtained from the raw time-of-flight data by normalizing to the incoherent scattering from a flat vanadium slab standard sample for each chosen incident energy, and then to the incident flux using the integral of the incident beam monitor.

### III. EXPERIMENTAL RESULTS AND ANALYSIS

In order to investigate the magnetic excitations of $URu_2Si_2$ up to 100 meV, we measured inelastic spectra with an incident neutron energy of 120 meV, giving a resolution of a FWHM (full width at half maximum) of 3.4 meV at the elastic peak position and a FWHM of 1.6 meV at 100 meV energy transfer. We show the inelastic spectra of both $URu_2Si_2$ (closed symbols) and $ThRu_2Si_2$ (open symbols) taken at 22 K in Fig. 1(a). Since $ThRu_2Si_2$ has a very similar molar weight to $URu_2Si_2$ (the weight difference between the two compositions is about 1.2 % of the total weight), we have used $ThRu_2Si_2$ as a phonon background material. We note that both spectra show indeed very similar features over the entire energy range. One noteworthy point is the strong phonon peak seen at 46.6 meV in $ThRu_2Si_2$. As one can see, in $URu_2Si_2$ this peak has clearly moved to the slightly higher energy position of 47.7 meV. Such a shift of the phonon peak to a higher energy is totally unexpected since $URu_2Si_2$ has a higher atomic weight than $ThRu_2Si_2$, so we expect any phonon mode to move, if at all, toward lower energies. That the 46.6-meV peak moves instead toward a higher energy indicates that some interatomic interaction becomes stiffer by 6% in $URu_2Si_2$ than in $ThRu_2Si_2$, or it may be the effect of a magnon-phonon interaction. However apart from the phonon-related features, one can note that there is an overall difference between the two spectra right up to 100 meV which we attribute to magnetic excitations of U $5f$ electrons. We can obtain magnetic contributions from Fig. 1(a) using either the $ThRu_2Si_2$ data after allowing for the 46-meV phonon peak shift or high angle bank data of the $URu_2Si_2$ with a scale factor obtained from the $ThRu_2Si_2$ data as shown in Fig. 1(b). In both cases, we find that there is a very broad and strong magnetic scattering above 30 meV, which extends up to at least 100 meV. Our data[10] also show strongly asymmetric magnetic scattering below 20 meV, as seen in Refs. 2 and 8.

Although it is not clear from the data shown in Fig. 1 alone that there is further magnetic scattering above 100 meV, extra evidence can be found in data taken with the higher incident energy of 400 meV, giving a resolution of a FWHM of 12 meV at the elastic peak position and a FWHM of 5.5 meV at 350-meV energy transfer. We show the data of $URu_2Si_2$ (closed symbols) and $(Th_{0.9}U_{0.1})Ru_2Si_2$ (open symbols) taken at 22 K from 50 to 250 meV in Fig. 2. Since the latter composition has a very small U concentration, we can use it as a phonon background material without any problem. Most scattering below 60 meV occurs through phonon-related features. However, there is a clear difference between the two spectra from 70 to 200 meV. In order to obtain the magnetic contribution to the spectrum of $URu_2Si_2$, we first fitted the spectrum of $(Th_{0.9}U_{0.1})Ru_2Si_2$ as shown by the full line in the figure. Then we subtracted the fitting line from the $URu_2Si_2$ data [see the inset of Fig. 2(a)]. This difference can be fitted to two magnetic peaks centered at about 100 and 160 meV, respectively. Even though there is evidence of two-phonon peaks at 93 and 95 in the two compounds, there is additional magnetic scattering in $URu_2Si_2$ in this energy range. We have also estimated the magnetic scattering using the high angle data of $URu_2Si_2$ with a scale factor obtained from the $(Th_{0.9}U_{0.1})Ru_2Si_2$ data [see Fig. 2(b)], which also show the presence of the magnetic scattering right up to 200 meV.

Since we have determined the magnetic scattering in ab-

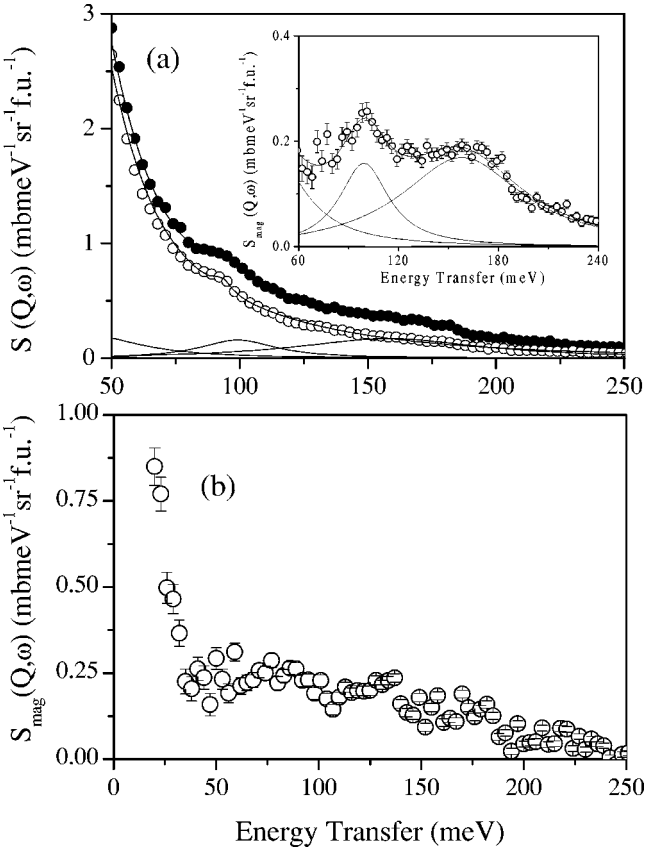


FIG. 2. (a) The inelastic spectra of $URu_2Si_2$ (closed symbols) and $(Th_{0.9}U_{0.1})Ru_2Si_2$ (open symbols) taken at 22 K with an incident energy of $E_i = 400$ meV. The full line is the curve fitting results for the spectra of $(Th_{0.9}U_{0.1})Ru_2Si_2$. The inset shows the blown-up picture of the magnetic scattering obtained using the $(Th_{0.9}U_{0.1})Ru_2Si_2$ data as a phonon blank material. The full line through $URu_2Si_2$ data is the curve fitting results using the phonon spectra and three DHSO functions (also shown) centered at 48.6, 99.2, and 158.0 meV. (b) Magnetic scattering obtained using the high angle bank data of the $URu_2Si_2$ with a scale factor from the $(Th_{0.9}U_{0.1})Ru_2Si_2$ data (see the text).

solute units, we can compare our data directly with other bulk properties. Inelastic neutron scattering data can be used to estimate the effective magnetic moment involved in the magnetic scattering process using the formula[11]

$$\mu_{eff}^2 = \frac{1}{48.6}\int \frac{S(Q,\omega)}{f^2(Q)} d\omega, \tag{1}$$

where $f(Q)$ is the form factor of $U^{4+}$. The appropriate form factor for each data set has been used in accordance with the $Q$ dependence of the energy transfer [see the inset of Fig. 1(a)]. Using this equation, we found that the magnetic scattering integrated up to 200 meV accounts for $2.50\mu_B$/U atom; for comparison, the ionic value of $U^{4+}$ is $3.51\mu_B$. When we integrated the data up to 20 meV only, we obtained an effective moment of about $1.39\mu_B$ in comparison with the effective moment of $1.20\mu_B$ from the single crystal data.[2] Therefore, one can see that the high energy magnetic scattering has considerable strength, almost comparable to the low energy excitation seen previously. In order to check if the magnetic scattering we observed in our data can also account for the bulk susceptibility, we have calculated the real part of static isothermal susceptibility, $\chi(Q=0,\omega=0)$, using our inelastic neutron scattering data and the following formula:[11]

$$\chi = \int \{1+n(\omega)\} \times \frac{S(Q,\omega)}{\omega f^2(Q)} d\omega. \tag{2}$$

According to our calculation, the estimated bulk susceptibility is about $6\times10^{-3}$ emu/mole, in comparison with powder averaged bulk susceptibility value of about $3\times10^{-3}$ emu/mole at 22 K.[1] The calculation of $\chi$ is strongly influenced by the details of the low-energy part of the magnetic scattering, due to the $1/\omega$ factor in Eq. (2). Since our experiments were primarily aimed at studying the magnetic scattering at higher energies, this estimate of $\chi$ is reasonably satisfactory.

In order to further analyze the data and make a comparison with relevant theories, we first fitted the inelastic spectrum of $ThRu_2Si_2$ seen in Fig. 1(a) using one elastic component with the peak function of the HET instrument and five peaks describing the phonon spectra. Throughout our analysis, we always used the response function of a damped simple harmonic oscillator (DSHO) to describe an inelastic peak; this has a better behaved tail than the usual Lorentzian function. To illustrate the accuracy of our fitting to the phonon spectra of $ThRu_2Si_2$, our fitting results are shown as a line underneath the data points (open circles). In order to subtract off the phonon spectrum from the data of $URu_2Si_2$, we used the fitted functions with every parameter fixed except for the position of the strong phonon peak at 46.6 meV. Using the modified phonon spectrum function, we find that at least two additional DSHO functions are needed in order to describe the magnetic excitations of $URu_2Si_2$ below 100 meV. Through a simultaneous fitting of the magnetic scattering shown in Fig. 1(a) and the inset of Fig. 2(a), we found the position and width of the four peaks (see Table I). However, we varied the intensity of each peak in accordance with the proper $E$-$Q$ relationship of each configuration and the form factor of the $U^{4+}$ ion. For example, the intensity of the peak at 48.6 meV is about three times smaller for $E_i = 400$ meV than for $E_i = 120$ meV, which is in good agreement with the form factor for respective $Q$ values estimated for each configuration. Similarly, the intensity of magnetic scatterig below 20 meV is also adjusted for form factor corrections by comparing two data sets taken with

TABLE I. Energy transfer $\epsilon$ and FWHM (full width at half maximum) $\Gamma$ of CEF excitations for $URu_2Si_2$, obtained from the data taken at 22 K.

| $\epsilon$ (meV) | FWHM $\Gamma$ (meV) |
|---|---|
| 5 | 7 |
| $49\pm1$ | $64\pm2$ |
| $99\pm1$ | $36\pm2$ |
| $158\pm2$ | $89\pm3$ |

$E_i = 25$ and 120 meV. Since the widths of the peaks are much larger than the instrument resolution, our simulation finds that convolution with the instrument resolution function has negligible effects on the DSHO fitting functions apart from the lowest excitation centered around 5 meV.

The full lines through the data points of $URu_2Si_2$ in Figs. 1 and 2 are the fitting result of magnetic spectra plus phonon scattering. The four DSHO functions used for the fitting of magnetic contributions are shown at the bottom of the figures. The lowest excitation below 20 meV is the dispersive mode found in the previous single crystal work.[2] However, the three excitations above 30 meV have not been reported before. From the data taken with the incident energy of 120 meV at 4.5 and 40 K, we find that most of the magnetic excitations are temperature independent within the experimental resolution. The only exception is the lowest energy excitation showing a very drastic reduction in intensity around the energy range of 5–10 meV, in agreement with the previous single crystal data.[2] We acknowledge that the actual position and intensity of the peaks may vary depending on how we model the magnetic scattering, in particular the peak around 100 meV. As we stressed earlier, however it is clear that the magnetic scattering is present even at very high energy. Nevertheless, we caution that the set of parameters given in Table I may not be unique. We note that these values were obtained from least square fitting procedures with the peak positions and widths as free parameters. In our analysis of the magnetic scattering, one may question particularly the position of the peaks found at 49 and 99 meV, since there are strong phonon and two-phonon peaks near these energies. Although one may vary the peak positions individually, however we believe that one needs magnetic scattering centered around those particular energies in order to explain the experimental data.

Given the large width of the observed CEF excitations, it is unlikely that we will be able to obtain quantitative reproduction of the spectra using the CEF Hamiltonian. Furthermore, since the excitations overlap in the data, the CEF levels might well be to some extent mixed together through intervening conduction electron states. However, even a qualitative comparison[12] with Ref. 3 shows that the strong feature at 40–60 meV, never reported previously, to our knowledge, is consistent with Santini and Amoretti's model:[3] a transition of $\Gamma_3 \rightarrow \Gamma_5^1$. For us to identify the origin of two peaks at 99 and 158 meV needs more theoretical studies; but they might be due to $\Gamma_3 \rightarrow \Gamma_4$ and $\Gamma_3 \rightarrow \Gamma_5^2$ transitions, respectively.

Studies using even higher incident energies such as 700 and 850 meV further reveal an interesting feature around 363 meV, as shown in Fig. 3. By comparing the spectra of both $URu_2Si_2$ and $ThRu_2Si_2$, we can confirm that it is from the U $5f$ electrons. Studies of other U dilute compounds, $(U_{0.1}Th_{0.9})Ru_2Si_2$ and $(U_{0.1}Y_{0.9})Ru_2Si_2$, do not produce such a feature. Curve fitting gives the center of the peak at $364 \pm 1$ meV with a FWHM of $24 \pm 1.0$ meV, larger than the instrument resolution of a FWHM of 15 meV at this energy transfer. The difference between the two spectra below 300 meV is due to the magnetic scattering seen in Fig. 2. The origin of the peak can be understood from comparison

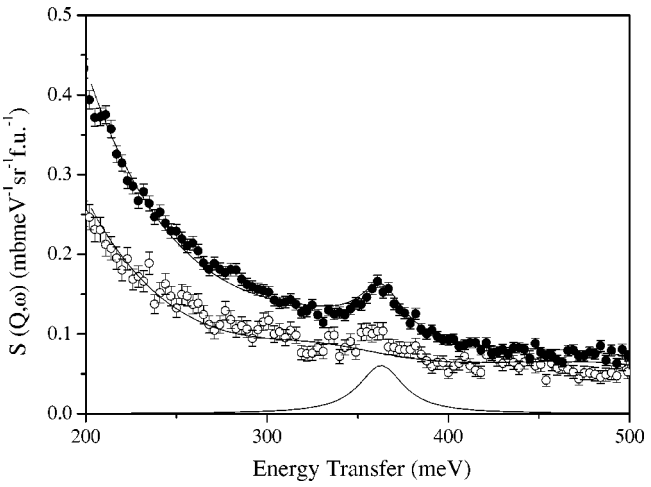


FIG. 3. The inelastic spectra of $URu_2Si_2$ (closed symbols) and $ThRu_2Si_2$ (open symbols) taken at 22 K with an incident energy of 700 meV. The full line underneath the open symbols is the curve fitting result for the spectra of $ThRu_2Si_2$. The full line underneath the closed symbols is the sum of phonon and magnetic contributions plus an intermultiplet transition at 363 meV, shown at the bottom of the figure (see the text).

with high energy excitations in other U compounds. Using the free-ion parameters of $UO_2$, the energy of the lowest intermultiplet transition for $U^{4+}$ ions is estimated at 448 meV for $^3H_4 \rightarrow {}^3F_2$.[13] On the other hand, a typical localized U metal, $UPd_3$, shows it at 395 meV.[14] Probably strong hybridization between $f$ electron and conduction electrons of $URu_2Si_2$ further lowers the transition energy to 363 meV, as is often the case with strongly correlated electron systems.[15] It is rather surprising in the first place that we even observe an intermultiplet transition in a heavy fermion superconductor $URu_2Si_2$ similar to that of $UPd_3$, which shows very well-defined CEF excitations.[16] Therefore the observation of the 363-meV excitation constitutes compelling evidence of the $U^{4+}$ state of $URu_2Si_2$.[17] There is very little temperature dependence of the intermultiplet peak. It was suggested[4] that the mixed valence behavior of the U ion might be responsible for the unusual antiferromagnetic transition of $URu_2Si_2$. That the intermultiplet peak is temperature independent, and is as narrow and strong as that in $UPd_3$, however, make this scenario very unlikely.

Finally, the importance of our work regarding the physics of $URu_2Si_2$ can be threefold: (i) the most extensive experimental studies of the crystal field level splitting of the U ion of $URu_2Si_2$, (ii) the finding of magnetic scattering right up to 200 meV, and (iii) the observation of an intermultiplet transition, the definite evidence of $U^{4+}$. Thus our experiment puts a strict test on any conceivable theory for the single ion physics of $URu_2Si_2$.

In summary, we have investigated the high energy excitations of $URu_2Si_2$. From our results, we find that $URu_2Si_2$ has strong magnetic scattering up to 200 meV, which can be modeled with four broad CEF magnetic excitations. The observation of the intermultiplet transition also suggests that $U^{4+}$ cannot possible be mixed valence.

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