Spin gap formation in the heavy fermion skutterudite compound $CeRu_4Sb_{12}$

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$CeRu_4Sb_{12}$ is a mixed-valence Kondo-lattice system with a gap of 47 meV opening in the charge excitation spectrum, measured by the infrared spectroscopy technique. In order to study the temperature and energy and momentum dependence of the spin excitation spectrum, we have made inelastic neutron scattering measurements over a wide range of temperature between 5 and 250 K with an incident neutron energy of 100 meV. Our results measured at 5 and 60 K show that a spin gap of $\sim$30 meV opens in the magnetic spectrum and above it the inelastic magnetic response forms a continuum right up to 95 meV. Surprisingly, the spin gap shows neither wave vector Q dependence within our resolution nor temperature dependence from 5 to 100 K. On the other hand, the spin gap starts to fill up above 100 K and the magnetic response becomes purely quasielastic at higher temperatures. The dramatic change observed above 100 K can be related to the coherence temperature of the Ce $4f$ electrons while the observed Q independence of the spin gap implies that single-ion Kondo interactions are important in the gap formation mechanism. We discuss our results in terms of theoretical models.

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I. INTRODUCTION

Filled skutterudite compounds with a general formula RET_4X_{12} (RE= rare-earth elements, T=Fe and Ru, and X=Sb and P) crystallize in a unique body-centered-cubic structure (space group Im-3). These compounds have attracted considerable attention because a variety of ground states have been found within this rather simple crystal structure. Some of the ground states found in RET_4X_{12} exhibit heavy fermion behavior, magnetic ordering, metal-insulator transitions, possibly multiple superconducting phases, Kondo insulator, and hybridization gap formation.[1–6] These various ground states may result from competition between the intersite Ruderman-Kittel-Kasuya-Yosida interactions and the onsite Kondo interactions depending on rare-earth ions as in many other strongly correlated electron systems.[7–11]

In strongly correlated electron systems where localized f electrons and conduction bands are hybridized, there ought to be a gap forming in the electronic density of states near the Fermi energy E_F. This gap is called a hybridization gap. At high temperatures, hybridization gap systems are characterized by a collection of incoherent Kondo states. However, upon cooling below another characteristic temperature, the so-called coherence temperature, they develop strongly renormalized f bands, which may exhibit either insulating behavior as in $Ce_3Pt_3Bi_4$ or a coherent metallic Kondo-lattice behavior as in $YbAl_3$.[12,13] Despite intensive theoretical as well as experimental studies over two decades, a full understanding of the mechanism of the gap formation is still lacking. In particular, the roles played by the local Kondo coupling and the intersite correlations in the gap formation and its anisotropic nature are not well understood.

Among the rare-earth filled skutterudite compounds, $YbFe_4Sb_{12}$ and $CeRu_4Sb_{12}$ are of particular interest due to their strongly correlated electronic behavior in their bulk properties.[14–17] Both compounds show intermediate valence behavior in their magnetic susceptibility and electrical resistivity, which exhibits an anomalous temperature dependence below 100 K.[14,15] From the maximum around 100 K in the static magnetic susceptibility of $CeRu_4Sb_{12}$,[15] we may deduce a Kondo temperature of T_K=300 K according to the single-impurity Anderson model, $T_K=3T_{max}$, where T_{max} is the temperature at which the susceptibility exhibits a broad maximum.[18] This theoretical definition of T_K has been used for many heavy fermion systems.[19] Furthermore, the magnetic contribution to the resistivity of $CeRu_4Sb_{12}$, deduced by subtracting the resistivity of the isostructural nonmagnetic compound $LaRu_4Sb_{12}$, shows a maximum near 80 K. Above this temperature, the resistivity shows a clear $-\ln T$ dependence. The temperature dependence of its resistivity thus im-

plies that $CeRu_4Sb_{12}$ forms a coherent Kondo lattice state below about 80 K.[20] It is also of interest to note that the electronic contributions to the heat capacity of both compounds are rather large, with $\gamma = 140$ mJ/mol K^2 for $YbFe_4Sb_{12}$ and 380 mJ/mol K^2 for $CeRu_4Sb_{12}$, respectively. This large electronic heat capacity undoubtedly suggests that the low-temperature states of both compounds are of moderate heavy fermion origin.[14,15]

Recent optical studies found that both compounds exhibit a charge gap feature in their ac conductivity below 70 K with a gap energy of $\Delta_{charge} = 11.2$ meV for $YbFe_4Sb_{12}$ and 47.1 meV for $CeRu_4Sb_{12}$.[16,17] Here the charge gap means a gap in the charge degrees of freedom. The effective masses estimated from these optical studies are also large: $m^*/m_b = 25$ and 80 (where m_b is the band mass) for $YbFe_4Sb_{12}$ and $CeRu_4Sb_{12}$, respectively, in agreement with the conclusions drawn from the heat-capacity data.[15] In the same study, a universal scaling relationship was found to hold between m^* and Δ_{charge} for both compounds, in agreement with theoretical predictions.[17] An upturn in the Hall coefficient at low temperatures, together with the optical conductivity results, suggests that the carrier density of $CeRu_4Sb_{12}$ is reduced at low temperatures.[20] This conjecture was later corroborated by the low density of states (DOS) measured around E_F using ultrahigh-resolution photoemission spectroscopy.[21] A further interesting point about $CeRu_4Sb_{12}$ is that it exhibits a novel non-Fermi-liquid (NFL) behavior below 1 K in the specific heat with the unusual $T \ln T$ dependence and below 5 K in the resistivity with a $T^{1.65}$ dependence.[15] However, in this paper we focus on the nature of the hybridization gap using inelastic neutron scattering, and experimental features related to the NFL behavior will be published elsewhere.

One of the key questions regarding both $CeRu_4Sb_{12}$ and $YbFe_4Sb_{12}$ is whether there is also a gap in the spin excitation spectrum (known as a spin gap) analogous to the charge counterpart observed by the optical spectroscopy measurements. An experimental verification of the existence of a spin gap is very important to understand the nature of the charge gap seen in the optical studies of $CeRu_4Sb_{12}$. If proven either way, this key experimental result would then lead to the bare minimum Hamiltonian necessary for the description of the gap formation in $CeRu_4Sb_{12}$. If a spin gap indeed exists, then we may conjecture that the spin and charge gaps are probably, somehow, related to each other. This would then lead us to an important related question, which is whether the gap in the spin excitations, and therefore probably also in the charge excitations, might show any Q dependence. An answer to this question would be directly related to the underlying microscopic mechanism of the gap formation: intersite coupling or on-site single-ion coupling. Another interesting question is to understand how the gap formation is affected by the coherence phenomenon of the strongly correlated electrons. At this point, we note that the earlier optical study cannot tell us anything about the Q dependence because of the intrinsic limitations of the technique itself, i.e., it is a $Q = 0$ probe.

Inelastic neutron scattering is usually the best technique to answer most of the above questions if the spin excitation spectrum of a given compound shows a gap feature. We have therefore investigated the spin excitations in $CeRu_4Sb_{12}$ using this technique in order to understand the physics of its gap formation.

II. EXPERIMENTAL DETAILS

For this study, we used polycrystalline samples, which were prepared at ISSP, University of Tokyo, by the Sb-flux method with an excess of Sb (1:4:20). The mixture of constituents was sealed in an evacuated quartz tube which was initially kept at 1000 °C for 10 h before being cooled down to 650 °C at a rate of 3 °C h^{-1} inside a furnace. X-ray powder-diffraction studies revealed that all our samples crystallized in the cubic phase except for a small trace of impurity peaks of $RuSb_2$, which account for about 5% of the main cubic phase. We made our inelastic neutron scattering measurements using the time-of-flight chopper spectrometer HET at the ISIS Facility, Rutherford Appleton Laboratory, UK. We used an incident neutron energy of $E_i = 100$ meV: the energy resolution was about 4 meV at the elastic-scattering position. We measured the inelastic scattering from $CeRu_4Sb_{14}$ at 5, 60, 100, 150, and 250 K. Our scattering function $S(Q,\omega)$ measures the partial differential cross section of neutrons scattered from the sample with momentum transfer of Q and energy transfer of ω. Since we used a polycrystalline sample in this study, we in fact measured $S(Q,\omega)$ as a function of modulus of Q, $|Q|$. For more details of the measurements, see Ref. 22. In order to estimate the phonon scattering contribution, we also measured the nonmagnetic reference compound $LaRu_4Sb_{12}$ under identical conditions at 5 and 250 K. The data for $LaRu_4Sb_{12}$ at intermediate temperatures were generated using the data taken at 5 and 250 K after correction for the thermal population factor. Since Ce and La have comparable atomic masses, we can expect very similar phonon densities of states and thus similar phonon contributions to the inelastic spectra of $CeRu_4Sb_{12}$ and $LaRu_4Sb_{12}$. All our data are given in absolute units after normalizing the results to the scattering from a vanadium standard sample.

III. RESULTS AND DISCUSSION

Since it is very important to estimate the correct nonmagnetic contribution to the measured spectra for the analysis of the magnetic response of Ce compounds, we used two different methods of obtaining the nonmagnetic contribution for $CeRu_4Sb_{12}$. In the first method, we used the so-called scaling method in which we estimated the nonmagnetic contribution at low scattering angles ($\phi_{av} \sim 19°$) from the measured scattering of $CeRu_4Sb_{12}$ at high scattering angles ($\phi_{av} \sim 135°$) by using an energy dependent scaling factor as determined from the direct measurements on $LaRu_4Sb_{12}$. This procedure is based on two assumptions: first, the magnetic scattering intensity, which is proportional to the square of the Ce^{3+} magnetic form factor $F(Q)^2$, is negligible in our high scattering angle data and second, the scaling factor should be the same for both $CeRu_4Sb_{12}$ and nonmagnetic $LaRu_4Sb_{12}$. In the second method, we employed a direct

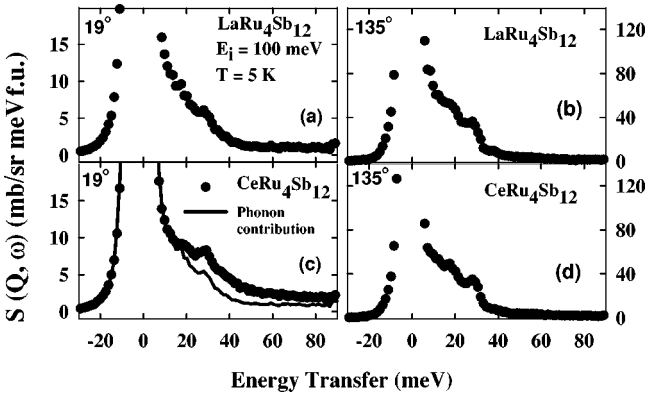

FIG. 1. (a,b) $LaRu_4Sb_{12}$ and (c,d) $CeRu_4Sb_{12}$ spectra taken at 5 K for low scattering angles (19°, $Q_{elastic}=2.29$ Å^{-1}) and high scattering angles (135°, $Q_{elastic}=12.84$ Å^{-1}). The solid line in (c) shows our estimated nonmagnetic phonon contribution using the low angle data of $LaRu_4Sb_{12}$ (see the text).

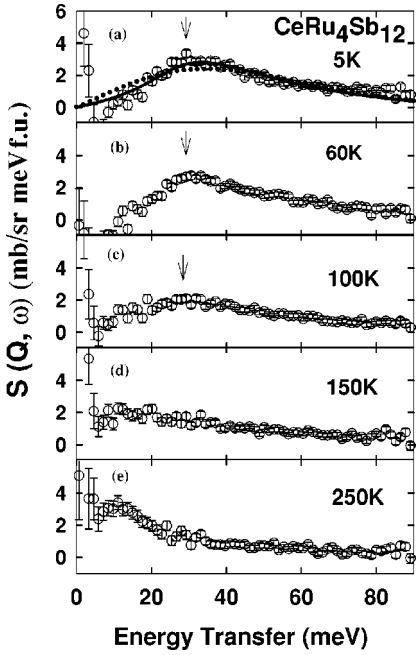

FIG. 2. (a)–(e) The magnetic response from $CeRu_4Sb_{12}$ at low scattering angles (19°) after subtracting off the nonmagnetic scattering using the second method (see the text) at several temperatures. The solid and dotted lines in (a) show the curve fitting results for the Kuramoto-Muller-Hartmann (KMH) spectral function and the Lorentzian spectral function, respectively (see the text). The arrow shows the position of the spin gap.

subtraction method to estimate phonon contributions using $LaRu_4Sb_{12}$ as our phonon blank material, after allowing for a difference in the total scattering cross section $\sigma(CeRu_4Sb_{12})\sim 0.9\sigma(LaRu_4Sb_{12})$. In our analysis, both methods produced a very similar magnetic response that gave us confidence in the data analysis. However, since the second method gave slightly better behaved results in subtracting the nuclear elastic peak at zero energy transfer, in this paper we present all our data analyzed using the second method.

Figures 1(a)–1(d) show the total spectra from $CeRu_4Sb_{12}$ and $LaRu_4Sb_{12}$ measured at 5 K with an incident neutron energy of 100 meV for the low ($\sim$19°) and high ($\sim$135°) scattering angles. At the low scattering angle corresponding to $Q_{elastic}=2.29$ Å^{-1} the total spectra from $CeRu_4Sb_{12}$ contains both magnetic and phonon scattering contributions. On the other hand, the magnetic contribution is negligibly small at the high scattering angle corresponding to $Q_{elastic}=12.84$ Å^{-1} because of the very small form factor of Ce $4f$ electrons for such a large Q value. As shown in Figs. 1(a) and 1(b), the inelastic response of $LaRu_4Sb_{12}$ shows two clear peaks due to one-phonon scattering at $\sim$19 and $\sim$30 meV and weak multiple scattering above 40 meV. As expected, the high scattering angle data of $CeRu_4Sb_{12}$ appear to be very similar to those of $LaRu_4Sb_{12}$, which indicates that the phonon scattering is in fact almost identical for the two compounds. This then justifies our use of the direct subtraction method to estimate the phonon contribution to the total spectra of $CeRu_4Sb_{12}$. To make this point clearer, we overlay the estimated phonon contribution as a solid line along with the total spectra (filled symbols) in Fig. 1(c). This shows a clear sign of a broad magnetic response in $CeRu_4Sb_{12}$ above 15 meV which extends right up to 95 meV.

The magnetic response of $CeRu_4Sb_{12}$, after subtracting the phonon and elastic nuclear scattering, is shown for several temperatures in Fig. 2. As can be seen in Fig. 2(a) for 5 K, the magnetic scattering is almost absent for energy transfers below 10–15 meV: it starts to develop with increasing energies and exhibits a broad peak at 30 meV. According to theoretical studies,[8] the peak position can be regarded as an estimate of the magnitude of the spin gap. For energy transfers higher than 30 meV, the magnetic scattering falls off gradually, and there is still a visible sign of magnetic scattering even at the energy transfer of 95 meV. On increasing the temperature to 60 K, there is very little change in the data regarding the intensity, position, and width of the magnetic scattering [see Fig. 2(b)]. The first visible temperature dependence was observed when the sample was heated through the coherence temperature of $T_{coh}=80$ K. As shown in Fig. 2(c), the spin gap feature starts to fill up at 100 K while the peak position hardly moves compared with the data taken at lower temperatures. We recall that the static magnetic susceptibility also exhibits a maximum at 100 K, which implies $T_K=300$ K according to the single-impurity Anderson model.[15,18] It is to be noted that for valence-fluctuating systems the position of an inelastic peak can be taken as an estimate of the Kondo temperature.[13] A further rise in temperature to 150 K completely destroys the gap in the magnetic response, which can now be described by a broad quasielastic peak. At 250 K, some intensity of the magnetic scattering at high energy transfers shifts towards lower energies and its shape becomes purely quasielastic. We note that the peaklike structure seen near $\sim$10 meV at 250 K is an artifact arising from the difficulties of making a precise subtraction of the elastic line. The overall drastic change in the magnetic response between 60 and 250 K again suggests that the temperature dependence of the spin gap is quite different from that of a conventional band-structure gap. The collapse of the inelastic gaplike response and the appearance of the

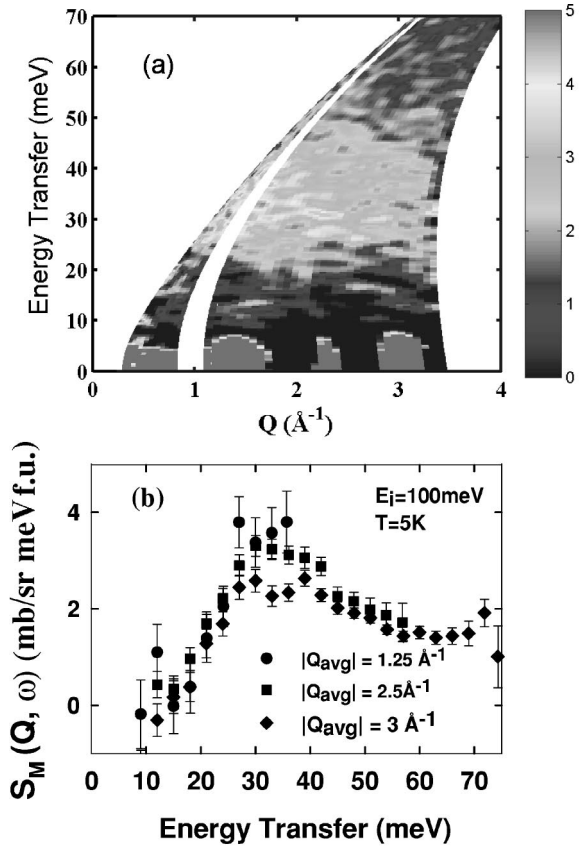

FIG. 3. (a) The contour map of the magnetic scattering taken at 5 K as function of energy and $|Q|$. (b) Energy dependence of the magnetic scattering at a few selected $|Q|$ positions.

quasielastic scattering at higher temperatures observed in $CeRu_4Sb_{12}$ are similar to that observed in $Ce_3Bi_4Pt_3$ and $YbAl_3$ and also in agreement with the predictions of theoretical models.[8,9,11]

In order to analyze further the magnetic scattering measured at 5 K, we fitted the data using two model functions; one is a Lorentzian function and the other the Kuramoto-Muller-Hartmann (KMH) function.[23] It is to be noted that a Lorentzian function has a symmetric line shape, while that of the KMH function has an asymmetric line shape. The asymmetry depends on the values of the parameters and has been experimentally observed for $YbAl_3$.[13] A further advantage of the KMH function is that it allows us to estimate the $4f$ occupancy. The physics behind the KMH function is that it is derived from the single-impurity Anderson model. Our curve fitting results are given in Fig. 2(a) as a dotted line for the Lorentzian function and a solid line for the KMH function. Although neither function yields an exact fit to our experimental data, the KMH function describes the data slightly better than does the Lorentzian function. Furthermore, we were able to estimate the $4f$ occupancy ($\langle n_f \rangle$) from the curve fitting parameter using the KMH function $\alpha = \sin(\pi \langle n_f \rangle / N)$, where N is the degeneracy of the $4f$ state. Our estimated value is $\langle n_f \rangle \sim 0.798(3)$, which is consistent with the mixed-valence behavior observed in the static susceptibility. To check further the value of $\langle n_f \rangle$, we have also calculated the value of the effective paramagnetic moment

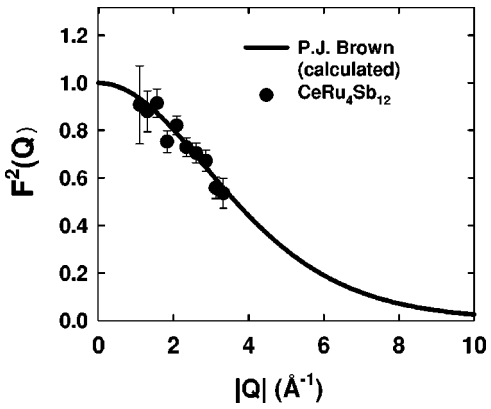

FIG. 4. The Q dependence of the inelastic peak intensity integrated over energies from 25 to 40 meV (symbols). The solid line represents the square of the Ce^{3+} magnetic form factor calculated using Brown's method (Ref. 25).

μ_{eff} of the Ce ion using a moment sum rule: $\int S(Q,\omega) d\omega = A \mu_{eff}^2 F^2(Q)$, where $A = 48.6$ mb sr$^{-1} \mu_B^{-2}$ and $F(Q)$ is the magnetic form factor. By performing the numerical integration over the whole experimental energy transfer range up to ± 97 meV, we have deduced the value of the effective magnetic moment to be $\mu_{eff} = 2.14 \pm 0.3 \mu_B$ at 5 K. This gives $\langle n_f \rangle \sim 0.710(9)$, which is in good agreement with the value obtained from the curve fitting results using the KMH function. We note that $\langle n_f \rangle$ obtained from the numerical integration should be considered as a lower limit of $\langle n_f \rangle$ because our integration is arbitrarily truncated at the energy transfer of 97 meV.

We now discuss the wave-vector (Q) dependence of the magnetic response. In Fig. 3(a), we show a contour plot of the magnetic scattering at 5 K as function of energy transfer and $|Q|$. We can see from this plot that the scattering exhibits a broad peak at 30 meV that is independent of $|Q|$. To make this point clearer, we have made constant $|Q|$ cuts at three different values of $|Q|$ as shown in Fig. 3(b). This picture further confirms the nearly Q independence of the magnetic response. One should bear in mind that the effects of the renormalized bands on the spectral response are expected at lower values of Q than are possible to access with a finite energy transfer $\geqslant 30$ meV and an incident neutron energy of 100 meV.[13,24] In Fig. 4 we have plotted the intensity of the magnetic scattering, integrated between 25 and 40 meV energy transfer, as a function of $|Q|$. The Q dependence of the peak intensity agrees well with the Q dependence of the square of the Ce^{3+} magnetic form factor (solid line) calculated using Brown's method.[25]

The strong temperature evolution and nearly Q independence of the spin gap immediately raises an important question. What is the origin of the spin gap? The fact that the observed magnetic response is very broad indicates that $CeRu_4Sb_{12}$ is in a strong-coupling limit, and hence one can naively discard the role of magnetic correlations and spin-density waves in the gap formation. This then leaves us with only the viable scenarios based on the hybridization (V_{cf}) scheme between $4f$ and conduction electrons such as the Anderson model. The presence of the hybridization in heavy fermion compounds naturally gives rise to Kondo effects.

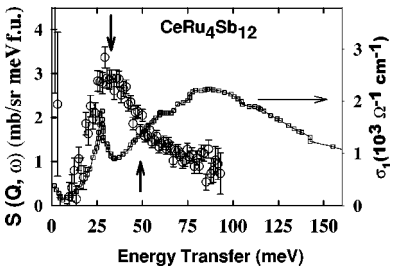

FIG. 5. The inelastic magnetic response at 5 K, $S(Q,\omega)$, superimposed on the results for the real part of the optical conductivity, $\sigma(\omega)$ at 10 K from Ref. 17. The upper and lower arrows show the positions of the spin gap and the charge gap, respectively.

Theoretical calculations based on such a single-impurity Anderson model indeed show a gap-type response in the dynamical susceptibility at low temperatures.[7] Further calculations based on the Anderson lattice model (ALM) also show that a gap is opened in the electron density of states near E_F depending on the hybridization amplitude, V_{cf}.[8–11] Indeed, the spin gap seen in the ALM shows a weak Q dependence and, simultaneously, a strong temperature dependence.[8,9] In this case, the magnitude of the indirect gap is $\sim V_{cf}^2/W$ (where W is the width of conduction band), while the direct gap is $\sim V_{cf}$.[11] Therefore, a system would be semiconducting if E_F lies in the gap or metallic if it is outside the gap. The observed Q independent response in $CeRu_4Sb_{12}$ indicates clearly that the gap arises from the single-ion Kondo interactions. On the other hand, the temperature evolution of the response suggests that the coherence of the Kondo lattice also plays an important role in the gap formation. The importance of two characteristic temperatures, the single-ion Kondo temperature and the coherence temperature $T_{coh}=(0.4–0.6)T_K$, in the gap formation of Kondo insulators has been realized in the 1D (one-dimensional) ALM with the quantum Monte Carlo method and in the infinite-dimensional ALM within dynamical mean-field theories.[11,26] According to these models, the gap in the strongly correlated electron band starts to open at T_{coh}, in agreement with the present experimental observation in $CeRu_4Sb_{12}$. The ratio of $\Delta_{charge}/k_BT_K\sim 1.82$ for $CeRu_4Sb_{12}$, which is in good agreement with that of ~ 1.7 for $Ce_3Bi_4Pt_3$ $\sim 1.9–2.3$ for CeRhSb and $\sim 1.7–2.0$ for CeRhAs.[27,28] This agreement strongly supports the view that the Kondo energy is an essential physical parameter to describe the gap in these compounds. Since the Kondo energy is *a priori* independent of temperature, it would be in good agreement with the observed temperature independence of the gap size from 5 to 100 K in $CeRu_4Sb_{12}$. It is also interesting to note that the measured dynamical response of both $Ce_3Bi_4Pt_3$ and $YbAl_3$, which exhibit strong temperature dependence, has been explained on the basis of the ALM.[9,12,13]

A further important point is that for $CeRu_4Sb_{12}$ the magnitude of the spin gap ($\Delta_{spin}\sim 30$ meV) derived from our neutron scattering experiments is smaller than that of the charge gap ($\Delta_{charge}\sim 47$ meV) deduced from the optical study (see Fig. 5). A similar difference between the spin gap and the charge gap has been previously observed for the metallic heavy fermion $YbAl_3$ ($\Delta_{spin}=30$ meV and $\Delta_{charge}=100$ meV),[13,29] as well as in Kondo insulator compounds such as $Ce_3Bi_4Pt_3$ ($\Delta_{spin}=12$ meV and $\Delta_{charge}=36$ meV),[12,27] CeNiSn ($\Delta_{spin}=2-4.5$ meV and $\Delta_{charge}=10$ meV),[30,31] and YbB_{12} ($\Delta_{spin}=14$ meV and $\Delta_{charge}=25$ meV).[32,33] For all these materials, the spin gap is smaller than the charge gap. This then leads to an immediate question: whether the spin gap and the charge gap are due to the same phenomenon and the two gaps open in different electronic states/bands, respectively. Presently, there exist a few theoretical models which predict that the spin gap is smaller than the charge gap.[11,34] For example, exact calculations for the ground state of a 1D Kondo-lattice model indicate a smaller spin gap than the charge gap.[34] The difference between the two gap energies could be understood as an additional energy needed to delocalize the charges and hence $\Delta_{charge}\geqslant\Delta_{spin}$. The results of the periodic Anderson model within the dynamical mean-field theory also show a smaller spin gap than the charge gap.[11] According to this model, the difference between the two gap energies can be interpreted in terms of an extra energy that the conduction electrons contribute to the optical response, which measures a charge gap (i.e., a direct gap).[11] In this same model, the localized f electrons contribute to the inelastic neutron response that measures a spin gap (i.e., an indirect gap).[9] The observed ratio of the change and spin gap is $\Delta_{charge}/\Delta_{spin}\sim 0.65$ for $CeRu_4Sb_{12}$. According to the theoretical calculations based on the 1D ALM and infinite-dimensional ALM, the ratios of the two gap energies are 0.3–0.4 and 0.7–0.9, respectively.[11,26,28]

IV. CONCLUSIONS

In summary, the present work reveals experimental information about the dynamical magnetic response of $CeRu_4Sb_{12}$. Direct evidence for the existence of a spin gap ($\Delta_{spin}\sim 30$ meV) in the strongly hybridized bands near the Fermi level is provided by our inelastic neutron scattering study. The nearly Q-independent response indicates that the spin gap arises via the single-ion Kondo interaction. On the other hand, the anomalous temperature dependence of the magnetic response below and above the coherence temperature (80 K) suggests that the coherence of the Ce $4f$ electrons also plays an important role in the gap forming mechanism. The large difference observed between the charge gap (~ 47 meV) determined from the optical study and the spin gap (~ 30 meV) determined from this inelastic neutron study can be understood in terms of theoretical model calculations.[9,11,26,34]

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