Kondo resonance in the neutron spectra of intermediate-valent $YbAl_3$

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We have measured the dynamic susceptibility of intermediate-valent $YbAl_3$ by means of cold-neutron scattering. We find two intense magnetic excitations below 40 meV. One of these, with location around 18 meV at helium temperatures, shifts steadily toward 0 meV with increasing temperatures. While crystal field interactions are unable to account for such a behavior, this excitation is in good agreement with a transition from the f ground state to a Kondo resonance as described by the Anderson model. In particular, it definitely excludes a gaplike magnetic response with gap width $\Delta = 30$ meV as asserted earlier.

INTRODUCTION

Consider a single rare-earth ion inserted into a metallic host with d conduction electrons. This is what happens: Besides ordinary exchange, aspherical Coulomb, or higher-order types of scattering, hybridization takes place between the local f electrons and the outer conduction electrons. According to standard theory, the hybridization induces an f-level width of $\Delta = \pi N(0)V^2$, where $N(0)$ is the density of spin states at the Fermi level, and V the isotropic hybridization matrix element. Due to large intra-f-site Coulomb interactions of order eV and for a well-defined f level, $\varepsilon_f \gg \Delta$, which may be located at ε_f either above or below the Fermi level, an effective hybridization coupling constant can be derived, given by $g = \Delta/\pi|\varepsilon_f|$.[1] Owing to a considerable effort over the last years, entirely dedicated to tackle this problem, theory has shown that Kondo and intermediate-valent (IV) systems can coherently be described through this single model, called the degenerate Anderson model,[2,3] by merely adjusting the f level to values of $\varepsilon_f \simeq -1$ and 0 eV, respectively. In a trivial extension to this theory, stable systems display no hybridization ($\varepsilon_f = -\infty$) at all.

It is evident from this that primarily Ce and Yb systems are Kondo and IV systems, because they are next to an empty or filled f shell and hence have an inherent tendency to become unstable. Many (if not all) of the uncommon features, found experimentally in these systems could be explained by a single, most important finding of the Anderson model: the so-called Kondo resonance.[4] While this resonance, caused by a renormalization of the hybridized f level, now is generally accepted as the origin of various features in Kondo systems,[1] the evidence of its existence in IV systems seems less clear. In the latter, the corresponding scaling temperature of the correlation between f and conduction electrons is much higher and, typically, a couple of 100 K. Hence, in macroscopic experiments, the Kondo effect is obscured by other dominant effects at such elevated temperatures. In those cases, only high-energy spectroscopy methods, such as bremsstrahlung isochromat spectroscopy (BIS), were able to identify Kondo resonances.

Unfortunately, the observation of a Kondo resonance in the dynamic magnetic susceptibility, $\chi''(Q,\omega)$, as measured by inelastic magnetic neutron scattering, is very rare and could only be observed thus far in $CePd_3$,[5] $CeSn_3$,[6] and $CeRu_2Si_2$.[7] The effect of the resonance here is the formation of an inelastic line,[1,8,9] which stems from the transition between the (renormalized) center of the magnetic f^n ground state and the Kondo resonance of this same f^n configuration. This is contrary to BIS, which observes f^{n-1}-f^n transitions. The resonance begins to form at a characteristic temperature T_0,[1] which is related to the Kondo temperature T_K (also called the spin-fluctuation temperature, T_{sf}, in IV systems) through $T_0 = g^{1/N_f} T_K$, with N_f the degeneracy of the f level, and $g = \Delta/\pi|\varepsilon_f|$ as introduced above. The inelastic line in $\chi''(Q,\omega)$ equivalently begins to form out of a quasielastic line below T_0, and is fully developed only below $T \simeq 0.05 T_0$.[1]

In this work we will render support to the theoretical prediction that the Kondo resonance can also be observed in the dynamic susceptibility of Yb systems. For this we have employed intermediate-valent $YbAl_3$, since

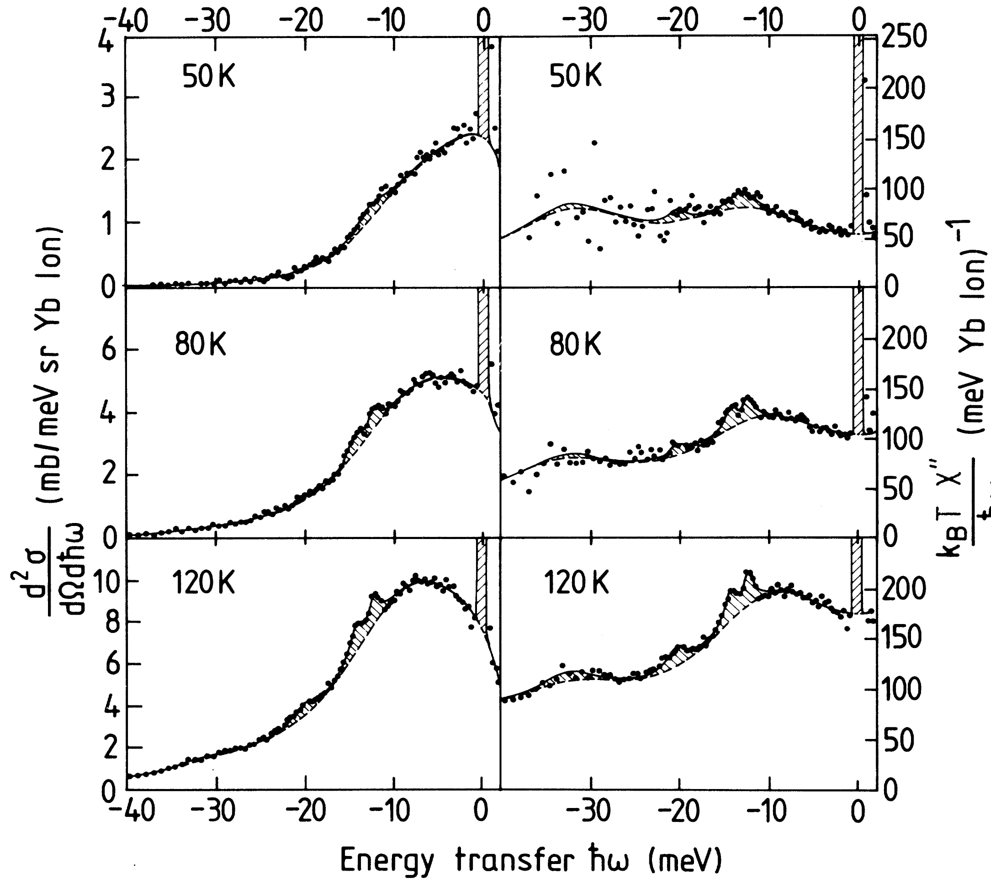

FIG. 1. The scattering spectrum of $YbAl_3$ at $T=50$, 80, and 120 K. On the left side, the as-measured, background-corrected spectrum is depicted, whereas, on the right-side, the symmetrical representation $k_B T\chi''(\hbar\omega)/\hbar\omega$ has been chosen. The solid line is a fit to the spectrum, with two inelastic magnetic lines below $\hbar\omega=40$ meV in addition to the nonmagnetic phonon and incoherent elastic contributions (hatched area). The scattering angle is $\theta=18°-71°$, and $Q=2.2\pm0.4$ Å^{-1} at $\hbar\omega=-12$ meV.

it is a cubic system. An average valence $v=2+n_f$ of 2.85 ± 0.1 ($n_f=0.85\pm0.1$) independent of temperature,[10–12] can be derived from a variety of results published in literature (see, also, Ref. 13). Hereby, the results from a systematics of the susceptibility of Yb compounds[14,15] and from RAl_3 lattice parameters[14] (where R is a heavy rare earth) define the upper valence bound, and Mössbauer,[10,16] x-ray photoemission spectroscopy (XPS),[17–19] and x-ray absorption data[20,21] are at the lower bound. Moreover, this valence is based essentially on electronic interactions[22] and not on lattice pressure, which explains the otherwise contradictory results of $Yb_xSc_{1-x}Al_3$.[15]

We will also show that, contrary to a previous work[23] done on inelastic neutron scattering, and in agreement with various macroscopic data, there exists no hybridization gap in $YbAl_3$.

EXPERIMENT AND RESULTS

Polycrystalline $YbAl_3$ at the amount of 8.5 g was prepared by growing it from an excess aluminum composition. As anticipated from x-ray-diffraction patterns, it did not include any second phase, such as $YbAl_2$. By arc melting also, a nonmagnetic reference sample $LuAl_3$ (7.7 g) was prepared and annealed for 4.5 days, as described in Ref. 12. $LuAl_3$ turned out to be polluted by the neighboring phase $LuAl_2$ by roughly 5%. This apparently proves the flux-grown method to be the superior technique for the preparation of these Al-rich phases. The

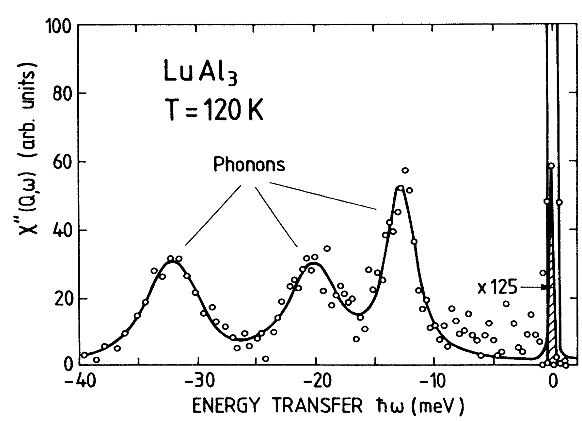

FIG. 2. The phonon spectrum of the nonmagnetic reference $LuAl_3$ at $T=120$ K. The solid line is a fit to the spectrum.

lattice constants turned out to be $a_0=4.203\pm0.003$ Å (4.190 ± 0.003 Å) for $YbAl_3$ ($LuAl_3$) and hence concurs with those given in literature.[12]

Inelastic neutron scattering was performed on these samples with the time-of-flight spectrometer IN6 (Institut Laue-Langevin, Grenoble) with cold neutrons ($E_0=3.07$ meV) at $T=1.3$, 7, 20, 50, 80, and 120 K. The data were corrected by means of additional background measurements, and a vanadium-calibration run allowed for placing the data on an absolute scattering scale. A numerical estimation of the multiple-scattering contribution revealed that it does not exceed 3% of the total inelastic spectra over the entire energy-transfer region. This low value, which is due to the almost absent Bragg scattering of the sample and to the high absorption of ytterbium, can be neglected compared to the statistical error of our spectra.

In Fig. 1 the spectra at 50, 80, and 120 K are shown for the forward-scattering angles (low momentum transfer, Q). The small nonmagnetic contributions could easily be identified in two independent ways, namely, by comparison with the phonon scattering of $LuAl_3$ (Fig. 2), which should exhibit a practically identical phonon density of states, and by comparison with the spectra at backward-scattering angles (high Q) of $YbAl_3$. The latter is also a quite common technique, since, for increasing Q, the phonon-scattering intensity strongly increases with Q, while the magnetic scattering decreases due to its magnetic form factor $F^2(Q)$. The predominant optical and/or zone-boundary, acoustical phonon modes, as derived from these procedures, are located at 12.8, 20.2, and 32.1 meV.

All spectra of $YbAl_3$ at low Q (Fig. 1) were then fitted by our assuming the existence of a quasielastic (QE) and several inelastic magnetic Lorentzian lines, in addition to the aforementioned phonon scattering (indicated by the hatched area in Fig. 1). The fitting procedure revealed that, at all temperatures measured, the spectra below 40 meV energy transfer can best be described by *no* QE and two inelastic lines and by a broad magnetic contribution at around 60 meV. Of course, we cannot strictly rule out any QE line, but a reasonably intense QE line would have shown up in our spectrum at $T=120$ K, if its linewidth [half-width at half maximum (HWHM)] would have been in the range of $0.1<\Gamma_{QE}<50$ meV. Our result on the QE line is in agreement with the finding of Murani,[23] who claimed that if there exists a QE line at all, it must exceed $\Gamma_{QE}>100$ meV.

In the 1.3- and 7-K spectra, magnetic scattering is insignificant compared with statistics—which is why we neglect them for further discussion—though they are still in accordance with the results described above.

The two magnetic lines observed in our spectra at 50 K are centered at 12.2 and 32.2 meV. Their linewidths (HWHM) turned out to be roughly equal, with $\Gamma_{IN}=10.7\pm0.5$ meV for $T\geq80$ K. The position of the lowest-lying excitation slowly increases with decreasing temperature ($\Delta_1=9.5$, 10.3, and 12.2 meV at $T=120$, 80, and 50 K), while its linewidth seems to slightly decrease ($\Gamma_{IN}=9.6\pm2$ meV at $T=50$ K), however, being always located above the $\Gamma=kT$ line. We point out that this excitation is true inelastic at low temperatures, although the value of its linewidth is comparable to that of its location. Its inelasticity is based on the fact that the quality of the fit, the sum of squares, χ^2, decreases dramatically if one assumes the line to be of QE shape. A direct confirmation of its inelasticity can best be obtained by a visual inspection of the symmetrized spectrum displayed on the right side of Fig. 1. Here a QE line would be a Lorentzian, symmetrical around the elastic line, which obviously is not the case. As a result of its steady shift toward a 0-meV location with increasing temperature, it will, however, finally turn into a QE Lorentzian line somewhere above $T=120$ K.

DISCUSSION

In order to get a more comprehensive description of the magnetic response of $YbAl_3$, we now also adapt the neutron-scattering results of Murani.[23] Because of the use of thermal neutrons, he achieved better energy resolution at high-energy transfers on the energy-loss side of the neutrons. This enabled him to distinguish three inelastic, magnetic excitations above 30 meV, namely, at 32, 46, and 70 meV, where the last two lines are in agreement with our broad magnetic scattering around 60 meV. By a comparison with our results, we recognize that not three but totally four inelastic magnetic lines are present in $YbAl_3$ at helium temperatures, namely, at

$$\Delta_1=18\pm3 \text{ meV} \quad (\text{extrapolated for } T\to0)\ ,$$

$$\Delta_2=32.2 \text{ meV}\ ,$$

$$\Delta_3=46 \text{ meV}\ ,$$

$$\Delta_4=70 \text{ meV}\ .$$

There is one conclusion we can draw immediately from these locations: There is *no gaplike magnetic response* in $YbAl_3$ with gap width $\Delta=30$ meV, as asserted by Murani,[23] because the temperature-dependent line around 18 meV would lie straight within this gap. This is in agreement with other macroscopic measurements, such as static susceptibility,[14,15] which merely displays a Curie-Weiss behavior down to $T=150$ K, or with resistivity data,[11,24] showing no anomaly at all.

We can only speculate why Murani was not able to observe that line in his spectra and hence arrived at his misleading conclusion. First, we have employed cold neutrons, whereas he used thermal neutrons. For thermal neutrons, a heavily increased double scattering, hand in hand with a higher momentum transfer, drastically enhances the phonon contribution which, in turn, heavily interferes with Δ_1 in his spectra. Second, a problem arises from the kind of representation, the dynamic susceptibility, $\chi''(\omega)$, that he chose in his figures. Since $\chi''(\omega)\propto\omega F(\omega)$, with $F(\omega)$ the normalized shape function of all QE and inelastic excitations, the displayed scattering intensity at low-energy transfers is linearly reduced compared with that at higher energies. This (quite common) choice of scale might have also contributed to the failure to observe the magnetic excitation Δ_1 in the thermal neutron spectra.

In order to understand, at least, the low-energy excitation spectrum of $YbAl_3$, let us summarize the results of theory relevant to what we measure. Interestingly enough, essentially all theories based on the degenerate Anderson model, and those that deal with the dynamic susceptibility,[1,7,8] predict an inelastic excitation in $\chi''(\omega)$ for $T < T_0$ if the degeneracy of the f ground state, N_f, is larger than 2. Its common feature is that it evolves from the QE response function at T_0 and that its position then constantly increases with decreasing temperature, until it is fully developed only below $T \simeq 0.05 T_0$ (Ref. 1) with a linewidth comparable to its excitation energy. A detailed analysis of its origin[8] shows that it stems from a transition between the (renormalized) center of the magnetic f^n ground state and the Kondo resonance of this same f^n configuration. We find it noteworthy to mention that to date there exist no other models or theories that are able to account for temperature-dependent locations of inelastic magnetic excitations in the paramagnetic state.

Comparing these predictions with our results, we recognize that the excitation Δ_1 displays a striking similarity to the theoretically predicted line, if one assumes T_0 to be about 300–400 K. We hence assert that in $YbAl_3$, a Kondo resonance exists, located about 18 meV below the center of gravity of the $4f^{13}$ state.[1] The corresponding excitation to this resonance has a residual width of about $\Gamma_0 = 7.0 \pm 1$ meV (HWHM). We, henceforth, call this excitation in our spectra the Kondo excitation Δ_K. We also mention that the common relation $\Gamma_0 = \pi\Delta_K / N_f$,[1,25] which correlates the position and width of the Kondo resonance with degeneracy N_f for $T \rightarrow 0$, surprisingly also seems to hold for the position and width of our inelastic Kondo excitation. Using the measured value for Δ_K, and $N_f = 8$ for the full Hund's-rule ground state (see below), we find that $\Gamma_0 = 7.1$ meV, in excellent agreement with the measured value. This accordance seems to indicate that the measured dynamic susceptibility, $\chi''(\omega)$, is a close mapping of the Kondo resonance for $T \rightarrow 0$.

The interpretation of our $YbAl_3$ data at low temperatures by means of a Kondo resonance is in accordance with many other experimental results. First, we recall that BIS spectra[17] also reveal a Kondo resonance located just above (BIS is unable to provide a detailed numerical value) the Fermi level. Second, a commonly observed residual static susceptibility, $\chi_{\rm stat}(0)$, followed by a maximum at elevated temperatures, is also thought to be a manifestation of a Kondo resonance. Quantitatively speaking, an analysis of $\chi_{\rm stat}(0) = 4.6 \times 10^{-3}$ emu/mol,[14,15] in terms of T_K via $\chi_{\rm stat}(0) = \mu_{\rm eff}^2 n_f / 3k_B T_K$ ($N_f = 8$, $n_f = 0.85$), yields $T_K = 475$ K. Since the quite unstable Yb ion in $YbAl_3$ implies a coupling constant not much smaller than unity, g^{1/N_f} is close to unity, and hence $T_0 \simeq T_K$, in agreement with our findings. Third, from our cold-neutron spectra, the intensity of the Kondo excitation was found to be nonvanishing for $T \rightarrow 0$. This can be taken to calculate the static susceptibility through the well-known sum rule:[26]

$$\chi_{\rm stat}(T) = \mu_B^2 \int_{-\infty}^{+\infty} \frac{1 - e^{-\beta\hbar\omega}}{\hbar\omega} S_{\rm inc}(\hbar\omega) d(\hbar\omega) ,$$

where $S_{\rm inc}(\hbar\omega)$ is the incoherent scattering function of the Kondo excitation, and $\beta \equiv (k_B T)^{-1}$ is the inverse temperature. From this we derive (at 50 K) $\chi_{\rm stat} = 8.5 \times 10^{-3}$ emu/mol, which has to be compared with the above-mentioned measured residual bulk value of about $\chi_{\rm stat}(0) = \chi'(Q=0, \omega=0) = 4.6 \times 10^{-3}$ emu/mol.[14] Since $\chi_{\rm stat}$ remains constant below 50 K,[14] we believe that the remaining discrepancy is due to a Q dependence, $\chi''(Q, T)$, other than the magnetic form factor of a free Yb^{3+} ion, which is already accounted for in the above equation.

Finally, Shimizu *et al.*[27] observed a $4f$ relaxation rate by NMR with a linewidth of $\Gamma_{\rm NMR} = 83$ meV for $T < 100$ K, which is related to the dynamic susceptibility through[8,27]

$$\frac{1}{\Gamma_{\rm NMR}} = \frac{1}{\chi_{\rm stat}(0)} \lim_{\omega \rightarrow 0} \frac{\chi''(\hbar\omega)}{\hbar\omega} .$$

$\Gamma_{\rm NMR}$ coincides with a QE linewidth, $\Gamma_{\rm QE}$, as measured by neutrons only if $\chi''(\omega)$ is a truly QE Lorentzian line. However, in our case, within fair approximation, the resonance is an inelastic line of Lorentzian shape (see Fig. 1), with characteristic width Γ_0 (HWHM) and excitation energy Δ_K. For this case, we derive from the above equation that

$$\frac{1}{\Gamma_{\rm NMR}} = \frac{\Gamma_0}{\Gamma_0^2 + \Delta_K^2} .$$

Substituting the extrapolated values of $\Gamma_0 = 7.0$ meV, and $\Delta_K = 18$ meV, for $YbAl_3$ as mentioned above, we derive $\Gamma_{\rm NMR} = 53 \pm 20$ meV. Considering our approximations made, this is not far off the observed NMR value.

Concerning the inelastic lines at 32.2, 46, and 70 meV, we share the opinion of Murani, that it is unlikely that they all are caused by crystal-field (CF) transitions. In $YbAl_3$ the Yb ions with $J = \frac{7}{2}$ occupy sites with cubic point symmetry, giving rise to only two inelastic CF transitions.[28] Therefore, at least one of the observed inelastic transitions must be a non-CF one. Moreover, the total CF splitting can be estimated to be of only 10 meV or even less.

One way of doing this is to start out from the systematics of the rare-earth (R) CF parameters of the near, cubic RAl_2 series, which have been studied extensively in the past.[29] For a fictitious trivalent $YbAl_2$, one derives $x = 0.74$ and $W = -0.31$ meV from this systematics, which corresponds to a total splitting of 6.9 meV. This agrees with the more crude estimate, that the total splittings of all heavy RAl_2 do not exceed 10 meV, and so should $YbAl_2$. To apply these findings to $YbAl_3$, empirical results[29] now indicate that neighboring crystal phases, especially those with only minor shifts in composition, usually share the same magnitude of CF strength, so that we expect $YbAl_3$ to display a total CF splitting below 10 meV, as well.

Another independent estimate comes from $ErAl_3$, the only RAl_3 compound studied thus far for CF excitations.[30] Its highest CF excitation is found to be at 8.9 meV and therefore also renders support to 10 meV as an upper limit for $YbAl_3$.

Based on this estimate of the CF splitting, we will now determine the degeneracy of the $4f$ ground state, and the Wilson ratio following from that. A total CF splitting of less than 10 meV implies that it is always smaller or comparable with the linewidth of the Kondo excitation. This ensures that the entire $J=\frac{7}{2}$ state is involved in the spin dynamics of $YbAl_3$, implying that all CF states contribute equally to it. Hence, within our interpretation, the Kondo excitation Δ_K is based on the fully degenerate $J=\frac{7}{2}$ Hund's-rule state, with degeneracy $N_f=8$ throughout any temperature and, in particular, in the presence of the coherent interactions below the Kondo temperature.

Support of this comes from the application of the analytic function of the Kondo excitation[31] to our measured spectra points of Δ_K. Such a fit, which turned out to have a quality similar to that with just an inelastic Lorentzian, yields a degeneracy of $N_f=6.7$. This value, which is rooted only in the line shape and not in the line intensity, is closer to $N_f=8$ than to any other plausible degeneracy for a Kramers ion. Also, the Wilson ratio favors $N_f=8$, which under this premise turns out to be

$$R=\pi^2 k_B^2 \frac{\chi_{\text{stat}}(0)}{\mu_{\text{eff}}^2 \gamma}=1.1 \ .$$

Here, we have used the values $\chi_{\text{stat}}(0)=4.6\times 10^{-3}$ emu/mol,[14] and $\gamma=45$ mJ/(mol K^2),[11] as given in literature.

To us the facts are overwhelming that the f ground state is fully degenerate. However, we do not want to dismiss the existence of some data, which are not fully consistent with an eightfold-degenerate ground state. At $T=300$ K, close to T_K, the measured static susceptibility of $YbAl_3$ (Ref. 14) is by a factor of 5 lower than that of the entire $J=\frac{7}{2}$ multiplet. Also, from our data it follows that, for $T<T_K$, the magnetic moment corresponding to the intensity of our Kondo excitation is less than the full $J=\frac{7}{2}$ value. When also accounting for the Q dependence, mentioned above, our intensity is in better agreement with a doublet ground state. These two findings might be explained by assuming that some of the measured excitations above 30 meV might be attributed to CF excitations. On one hand, this explanation is partly supported by theoretical calculations,[32] according to which hybridization between f and conduction electrons also contributes to the CF splitting directly. It could be argued then that, owing to a strongly anisotropic hybridization, the CF splitting is indeed strongly enhanced. On the other hand, the same theory predicts a T dependence for such CF line positions Δ ($\Delta \propto 1/T$ for $T \gg T_K$), which could not be observed. The origin of the three inelastic lines above 30 meV, therefore, is still an issue, and, needless to say, their interpretation as transitions to higher J multiplets is unlikely, since the first excited multiplet is expected to be located at about 1.2 eV above the ground state.

CONCLUSION

We summarize the above results in the following statements. The existence of a magnetic excitation below 30 meV evidently invalidates the existence of a gaplike magnetic response, with gap width $\Delta=30$ meV, as asserted earlier.[23] At helium temperatures, no quasielastic and four inelastic magnetic excitations are existent below 100 meV. While, for those three lines above 30 meV, a coherent interpretation of their origin and nature remains uncertain, an excitation found around 18 meV is most likely to stem from a Kondo resonance. Our results indicate that its underlying degeneracy is identical with that of a full $J=\frac{7}{2}$ ground state, except that its intensity is below a corresponding value. All these findings fit nicely with current theories on this subject. $YbAl_3$ is the first Yb compound where the Kondo resonance could be observed directly, but there are indications that the Kondo excitation is also present in $YbPd_2Si_2$ (Ref. 33) and YbCuAl.[34] Even for $YbCu_2Si_2$ (Ref. 35) (results of our group), a fit to the low-temperature spectrum with only a QE line is not perfect, but these data are more compatible with an inelastic excitation. This class of Yb compounds therefore presents itself as the natural counterpart to those Ce IV systems, such as $CePd_3$, $CeSn_3$, or $CeRu_2Si_2$, where a Kondo resonance was also observed.

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