Observation of f-Band Hybridization Gap in the Anomalous Rare-Earth Compound $YbAl_3$

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Low-temperature (< 10 K) paramagnetic spectral response $\chi''(Q,\omega)$ in $YbAl_3$ shows an abrupt step around ~ 30 meV extending to ~ 100 meV. The forward edge of the step broadens markedly and moves to lower energies with a relatively small increase in temperature (to 30 K). Disordering the Yb sublattice by dilution with Lu wipes out the inelastic step, replacing it by a broad distribution. The results give evidence of excitations across a hybridization gap in the f band.

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An interesting aspect of the anomalous rare-earth systems[1] is the question regarding the nature of the low-temperature phase, especially in pure stoichiometric compounds where the electrical resistivity tends to zero or a small residual value, as $T \rightarrow 0$ K,[2,3] and the magnetic specific heat shows strong coherence effects.[4] Although some of the low-temperature properties, magnetic susceptibility and the ratio of the specific heat to susceptibility, are amenable to the single-ion Fermi-liquid descriptions,[5,6] it is nevertheless widely believed that f states form a coherent band at low temperatures as evidenced, for example, in the de Haas–van Alphen (dHvA) measurements,[7] with a hybridization gap developing at low temperatures as a result of coupling with conduction electrons.[8–12]

Neutron-scattering measurements have been performed on several anomalous rare-earth systems to search for the existence of such a gap. Measurements[13,14] on TmSe have revealed an inelastic peak which could be interpreted in terms of excitation across a hybridization gap.[14] However, subsequent measurements by Holland-Moritz and Prager[15] on dilute $Tm_xY_{1-x}Se$ have demonstrated the single-ion character of this response. This alloy system has been well studied by lattice-constant, magnetic-susceptibility, and electrical-resistivity measurements, which also indicate the single-ion homogeneous mixed-valence character of Tm in this system.[16] In $CeSn_3$[17] the observed inelastic response could also have its origin in a gap excitation; however, as argued there, this is not a unique interpretation of the data and other single-ion descriptions[18–20] appear equally plausible.

The aim of this paper is to present results of neutron inelastic-scattering investigations of the compound $YbAl_3$ as well as the diluted compound $Yb_{0.5}Lu_{0.5}Al_3$ and the nonmagnetic isostructural compound $LuAl_3$, which give the clearest evidence so far of a hybridization gap in an anomalous rare-earth system, namely $YbAl_3$. The measurements were performed on the time-of-flight spectrometer IN4 using neutrons of incident energy 50 and 115 meV, over a wide range of scattering angles between 4.5° and 140°, simultaneously. Phonon scattering was studied in the nonmagnetic counterpart $LuAl_3$, the angular dependence of which was assumed to hold also for $YbAl_3$, and used to scale the phonon scattering observed in $YbAl_3$ at high angles, where the magnetic form factor is small, to low angles in order to separate out the magnetic spectral response. Details of this method have been given earlier.[17] We note, however, that the most interesting part of the inelastic magnetic response occurs at energies above 20 meV where the phonon contribution is relatively small.

$YbAl_3$ has the cubic Cu_3Au structure with a small anomaly in the lattice constant as compared with the neighboring $TmAl_3$ and $LuAl_3$,[21] which suggests a valence of ~ 2.95. The magnetic susceptibility[2] shows a broad maximum around 120 K and the low-temperature specific heat shows an enhanced value of the linear coefficient γ. Similar properties are common to a range of rare-earth alloys and compounds which are classified as mixed-valence systems.[1]

The scattering cross section for an isotropic paramagnet can be expressed as[22]

$$\frac{d^2\sigma}{d\Omega\, d\omega} \propto \frac{k'}{k_0} S(Q,\omega,T) \propto \frac{k'}{k_0}[n(\omega)+1]\chi''(Q,\omega,T). \quad (1)$$

The observed paramagnetic spectral response in $YbAl_3$ is shown in Fig. 1 for several temperatures. In Fig. 1 we show data extending to ~ 40 meV which were obtained with neutrons of incident energy $E_i = 50$ meV. A higher energy range, $\lesssim 100$ meV, was covered with neutrons of incident energy $E_i = 115$ meV, Fig. 2, but with correspondingly poorer energy resolution ($\Delta E/E_i \sim 6\%$ for both energies). In both sets of data the magnetic response shows a steplike increase of intensity around ~ 30 meV, the step appearing somewhat broader in Fig. 2 because of the poorer energy resolution. There is also a small level of magnetic intensity at energies below 30 meV which forms part of the broad quasielastic response, which, however, is much weaker than in TmSe[13–15] and $CeSn_3$.[17]

Many of the current theoretical treatments of mixed-valence phenomena are based on the $U \rightarrow \infty$ limit of the Anderson impurity model[23] or the Ander-

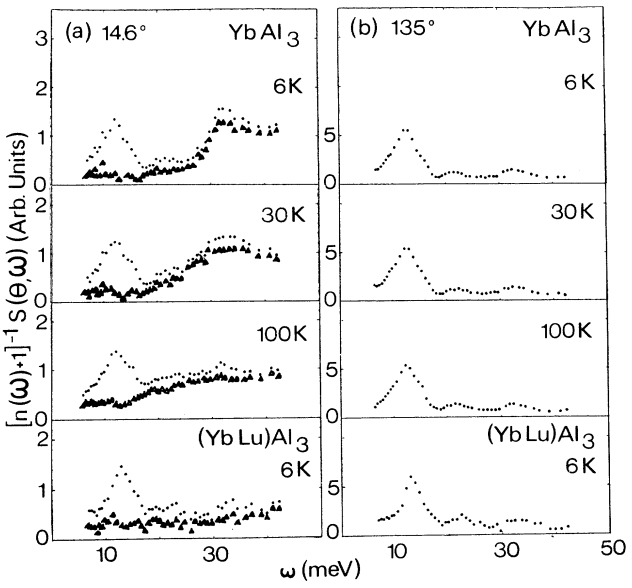

FIG. 1. The spectral response $[n(\omega)+1]^{-1}S(\theta,\omega)$ measured at (a) $2\theta=14.6°$ and (b) $2\theta=135°$, for $YbAl_3$ and $Yb_{0.5}Lu_{0.5}Al_3$ samples at various temperatures. The high-angle (135°) spectra give phonon scattering only which is subtracted out from the total intensity measured at low angles to obtain the magnetic contribution shown by triangles.

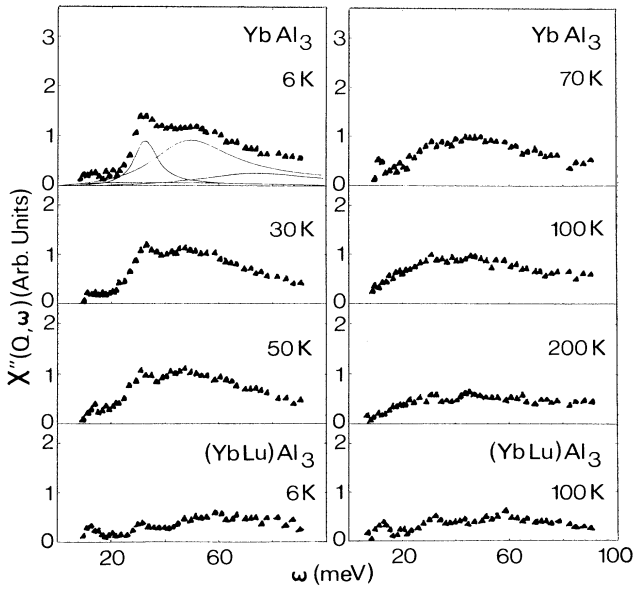

FIG. 2. The magnetic spectral response $\chi''(Q,\omega)$ at various temperatures for $Q_0=1.3$ Å^{-1}, corrected for the Yb^{3+} form factor. The energy range of the data is twice that in Fig. 1. The continuous curves represent the Lorentzian decomposition of the 6-K spectrum.

son lattice model, where U is the interatomic exchange. Both models predict a low-temperature inelastic spectral response roughly similar to the one observed here. There are, however, important differences in the temperature evolution of the inelastic spectrum in the two cases, as illustrated in Fig. 3 and in the effect of disorder produced by dilution with nonmagnetic rare earths.

In the former, i.e., the single-impurity models, the inelastic excitation corresponds to the energy difference Δ between the localized f state and the conduction band which, therefore, should not be strongly affected by changes in temperature which are small relative to the energy difference Δ, as illustrated in Fig. 3. In this model,[20] as the temperature increases the inelastic spectral response melts away into the broad quasielastic spectrum. However, this transfer of spectral intensity is not unlike that for a crystal-field excitation in the presence of strong conduction-electron local-moment coupling.[24] In the crystal-field case, however, the ground state can be magnetic (e.g., for Kramers ions, Ce^{3+}, Yb^{3+}, etc.) with the energy width of the quasielastic response varying linearly with T (Korringa law), whereas measurements on several mixed-valence systems such as $CeSn_3$ show that the quasielastic response remains broad as $T\rightarrow 0$ K, yielding a finite low-temperature static susceptibility (rather than a Curie-Weiss susceptibility).[17] Except for this difference the earlier results in $CeSn_3$ appear consistent with the crystal-field picture. In these single-ion models disorder produced by dilution with nonmagnetic rare earths should have no qualitative effect on the inelastic magnetic response as found, for example, in TmSe.[15]

The situation in the Anderson lattice model is, however, quite different. In this model the f states form a coherent band and the f-state conduction-electron mixing yields a hybridization gap at low temperatures with the Fermi level lying somewhere close by, its exact position depending on the position ϵ_f of the unper-

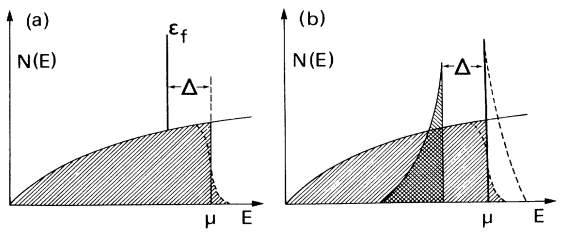

FIG. 3. A schematic representation of the f and conduction-electron states. (a) corresponds to the localized f-state model (Ref. 20) with Δ the energy difference between the position ϵ_f of the f state and the Fermi level (chemical potential) μ. (b) represents the band model (Ref. 9) with hybridization gap Δ. The Fermi level is assumed to be at the band edge, which yields strong thermal smearing and softening effects (Ref. 9).

turbed f level relative to the conduction band[9] [Fig. 3(b)]. It appears that in the case of $YbAl_3$ the Fermi level μ is pinned close to one of the two sharp band edges. Hence at low temperatures we observe a relatively sharp steplike increase of intensity but with increasing temperature the step broadens very rapidly because of thermal smearing and μ falls rapidly into the band gap.[9] Thus the broadening is accompanied by an apparent softening, i.e. reduction, of the gap separation Δ.

Further support for the observed gap excitation is provided by measurements on the diluted compound $Yb_{0.5}Lu_{0.5}Al_3$ which show no evidence of any inelastic step or hump, but only a broad quasielastic distribution extending to high energies ($\gtrsim 100$ meV), Figs. 1 and 2. Since the lattice constant of $LuAl_3$ is very close to that of $YbAl_3$ (only 0.25% smaller)[2,21] and since the thermal expansions of the two materials are also closely similar,[21] dilution with Lu should not have any significant influence on the valence of Yb in $YbAl_3$. However, since the periodic Yb lattice is now broken up, the f band and the band gap become smeared out, and the structure in the inelastic response is lost.

In the absence of theoretical models for the observed magnetic spectral response, we have, for a qualitative interpretation of the data, attempted to decompose the low-temperature spectral response into a weak, broad, Lorentzian quasielastic component plus three Lorentzians centered on finite energies at ~ 32, 46, and 70 meV. The first at 32 meV has a negligibly small intrinsic width (< 0.5 meV), consistent with the abrupt steplike increase in intensity occurring there, whereas the other two have half-widths of ~ 12 and ~ 15 meV, respectively. These Lorentzian components of the 6-K spectrum are sketched in Fig. 2.

If the above decomposition is forced through at higher temperatures we find that the first inelastic peak must be allowed to broaden very rapidly and also to soften, i.e., move to lower energies with increasing temperature. The broadening and the accompanying softening are so rapid that by ~ 50 K the whole spectrum is indistinguishable from a broad quasielastic spectrum centered on zero energy of half-width 40 ± 10 meV.

It has been suggested that hybridization of the f states with conduction electrons leads to a nondegenerate ground state with low-temperature Fermi-liquid behavior.[5,6] We could thus identify the lower half of the split f band with the nondegenerate state and assume that the degeneracy of the f^{13} configuration of the upper half is partially lifted by the cubic crystal field into two doubletlike (Γ_6 and Γ_7) and a quartetlike (Γ_8) states. Hence within such a picture the three inelastic peaks plus a quasielastic response appear as a qualitatively reasonable decomposition of the observed spectral distribution. We emphasize, however, that interpretation of the observed inelastic response as simple crystal-field excitations can be excluded since for the Yb^{3+} ion the ground state must be the Kramers doublet (i.e., magnetic). Hence a significant amount of quasielastic scattering is expected, much larger than actually observed, whatever the crystal-field parameters. We note in this connection that inclusion of coupling to conduction electrons only enhances the quasielastic contribution at the expense of spectral weight in the inelastic peaks,[24] so that the near absence of quasielastic scattering in $YbAl_3$ at low temperatures rules out any crystal-field descriptions.

It is useful to compare and contrast the present observations in $YbAl_3$ with those in TmSe[13-15] and $CeSn_3$.[17] In the latter two systems the spectral response at low temperatures consists of one well-defined inelastic peak as well as a central quasielastic component. In $YbAl_3$, on the contrary, the observed spectrum has a negligibly small weight in the quasielastic component and the inelastic spectrum shows a steplike increase around 30 meV with the total response extending to well above 100 meV. Such a peculiar extended spectral response which clearly cannot be represented by a single broad inelastic peak, has previously not been observed in any anomalous rare-earth system.

Another significant difference between TmSe and $YbAl_3$ is in the temperature evolution of the magnetic response. In polycrystalline TmSe the inelastic peak at 10 meV is relatively broad (~ 4 meV, full width at half maximum).[13] With increasing temperature the peak broadens further and also softens.[13] In single-crystal samples, however, the width of the peak is resolution limited ($\lesssim 0.5$ meV) and any softening with increasing temperature is relatively small.[14] The presence in TmSe of the quasielastic scattering at low temperatures and the gradual disappearance of the inelastic peak into the quasielastic spectrum with increasing temperature (at 50 K the spectral weight is still $\sim 50\%$) is not very different from that expected for a crystal-field excitation in the presence of strong conduction-electron coupling.[24] In $YbAl_3$ the width of the forward edge of the inelastic spectrum is resolution limited but nevertheless shows extremely strong broadening and softening effects such that by ~ 50 K the whole spectrum is indistinguishable from a quasielastic continuum. We recall that in contrast to TmSe there is negligible quasielastic scattering in $YbAl_3$ at low temperatures.

The observed inelastic response in $YbAl_3$ follows the normal Q dependence at these moderate Q values investigated. In fact the effects in the spectral response due to band character are expected at very much lower Q's (see for example Ref. 12) which are almost impossible to reach at finite energy transfers of interest ($\gtrsim 30$ meV) with thermal-energy neutrons.

We recall that measurements in TmSe at 4.6 K, close to its antiferromagnetic transition temperature T_N (3.2 K), show some dispersion as well as an anomalous Q dependence of the intensity of the inelastic peak. These effects, however, could have their origin in antiferromagnetic correlations. The fact that the inelastic peak in TmSe remains unmodified below T_N apparently contradicts the hybridization-gap interpretation for that system and supports the single-ion interpretation.[15,16] We note that $YbAl_3$ (as well as $CeSn_3$) remains paramagnetic at all temperatures and shows Fermi-liquid properties[5,6] at low temperatures.

In conclusion, the present measurements of the paramagnetic spectral response in $YbAl_3$ give the clearest evidence from neutron-scattering studies of an excitation across a hybridization gap in the f band at low temperatures. Interpretations based on single-ion models can be excluded because of the extremely pronounced thermal smearing and softening effects, as well as the fact that disorder within the rare-earth sublattice produced by dilution with Lu completely wipes out all inelastic structure in $\chi''(Q,\omega)$ yielding one broad quasielastic distribution.

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