Inelastic neutron scattering study of the Kondo semiconductor YbB_{12}

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Time-of-flight inelastic neutron scattering experiments on the archetype Kondo-insulator compound YbB_{12} are reported. At the minimum temperature of $T=15$ K, the magnetic response clearly shows a spin-gaplike behavior below 10 meV. Above this energy, the spectrum consists of three main components at 15, 20, and 38 meV. Above 40 K, substantial quasielastic scattering is recovered whereas the upper peak is rapidly suppressed. An extra intensity remains visible in the 20 meV region up to $T=159$ K. These results reflect the formation of a singlet Kondo-insulator ground state, but an additional mechanism is needed to explain the complex structure of the magnetic response. One possibility is an interplay between hybridization and crystal-field effects. [S0163-1829(99)05743-4]

I. INTRODUCTION

Mixed-valence (MV) semiconductors and Kondo insulators form a fascinating class of materials, which behave as metals or semimetals near room temperature, but develop unconventional semiconducting properties when they are cooled to low temperatures. The formation of a narrow electronic gap (or pseudogap) in these systems cannot be explained by the single-electron band structure, but likely results from complex correlation effects, involving *f*-electron quasiparticles hybridized with conduction-band states. The best-known members of this family are SmB_6 and $Ce_3Bi_4Pt_3$, but the compound YbB_{12}, which has not been studied so extensively in the past, also exhibits typical Kondo-insulator properties. Its crystal structure can be conveniently described as a variant of the NaCl type ($Fm3m$) in which boron atoms, forming tightly bound dodecahedra, replace the anion. Accordingly, the lattice spacing is relatively large $a_0 = 7.469$ Å. One salient physical property of YbB_{12} is the non-integral population of the Yb $4f$ shell (MV state). This was inferred from an analysis of the high-temperature magnetic susceptibility (estimated valence $\nu=2.85$),[1,2] of x-ray photoemission (XPS) spectra at $T=300$ K ($\nu=2.9$),[3] and photoemission results at $T=30$ K ($\nu=2.86\pm0.06$).[4] All these values are consistent and do not suggest a significant temperature dependence of the Yb $4f$-shell occupancy. The metallic, local-moment properties existing at high temperature undergo dramatic changes as temperature decreases. The magnetic susceptibility follows a Curie-Weiss behavior above 170 K but, around 75 K, it shows a broad maximum then rapidly decreases to reach a constant value[2] characteristic for nonmagnetic ground state. The low-temperature behavior of the electrical resistivity and of the electronic term in the specific heat are explained by the opening of a narrow gap, $E_g/k_B \approx 140$ K, around the Fermi energy in the electronic density of states.[5,6] From this point of view, YbB_{12} is quite similar to the archetype MV system SmB_6, in which neutron[7,8] and Raman[9] experiments have recently revealed unexpected characteristics of the spectral response. Both systems have similar electronic properties: $R^{3+}B_6$ and $R^{3+}B_{12}$ are metals with one free electron per formula unit.[10] However, there are significant differences in the formation of their ground states. In the case of Sm, one deals with a competition between two unfilled *f*-shell states, mediated by the hybridization with conduction-band states. In YbB_{12}, on the other hand, the hybridization causes a partial localization of one extra electron from the conduction band to form a closed-shell $4f^{14}$ configuration carrying no magnetic moment. This situation may be more closely related to that occurring in Ce MV compounds, where the $4f^1$ state of Ce^{3+} is admixed with the empty-shell configuration (electron-hole symmetry). From heat-capacity data and entropy calculations, it was concluded that crystal-field (CF) effects split the lower multiplet $J=7/2$ of Yb^{3+} into one quartet ground state Γ_8 and two doublets Γ_7 and Γ_6 (Refs. 2 and 6), with a total splitting of more than 300 K.[6] From theoretical considerations on the *f*-electron excitation spectra, an upper limit of this splitting, of about 60 meV, has even been suggested.[11] However, this picture most likely applies only for temperatures larger than ~240 K (i.e., $T \geqslant T_K$) (Refs. 2 and 4) since

the appearance of the low-temperature Kondo-insulator state is believed to reflect the formation of a nonmagnetic many-body singlet state. Therefore, a detailed study of the magnetic excitation spectra in YbB_{12} by inelastic neutron scattering is essential to clarify the exact nature of the ground state.

A previous neutron time-of-flight experiment was carried out by Bouvet[11] at the end of the 1980s, using a powder sample of $Yb^{11}B_{12}$ with 98% ^{11}B enrichment. These results were subsequently discussed in several theoretical publications by Kasuya (e.g., in Ref. 12). The original data have been published recently,[13] together with an improved analysis of the phonon correction. In the meantime, we had undertaken new experiments using a powder sample with a higher ^{11}B enrichment (99.5%).[14] The results are described in the present paper. It is of particular interest to compare measurements performed on different specimens using different spectrometers, because the synthesis of good-quality YbB_{12} is known to be difficult, and several aspects of the analysis of the neutron spectra are not straightforward within the limits of experimental accuracy. The experiments reported in Ref. 13 had been realized on the spectrometers IN4 (ILL) and DN6 (CEA/Grenoble) with incident neutron energies of less than 70 meV and a resolution (full width at half maximum) of about 5 meV at zero energy transfer. It will be shown in the following that the use of the time-of-flight spectrometer HET, located on the ISIS neutron spallation source, at incident neutron energies of 80 and 200 meV, together with the substantial reduction of the sample absorption, provide both improved instrumental resolution and higher counting statistics. This turns out to be critical for correctly assessing the nature and temperature dependence of the various components of the magnetic response.

II. EXPERIMENTS

Powder samples of $Yb^{11}B_{12}$ and of the reference compound $Lu^{11}B_{12}$ were prepared at the Institute for Problems of Materials Science NASU (Kiev, Ukraine) by borothermal reduction at 1700 °C under vacuum. Starting constituents were Yb oxide Yb_2O_3, Lu_2O_3, and elemental ^{11}B (99.5% enrichment). The ^{11}B isotope was selected in order to decrease the absorption cross-section of the sample. X-ray diffraction measurements confirmed that both materials have the cubic $Fm3m$ structure, and no impurity phase was detected. The room-temperature lattice parameters are 7.4634(2) Å for $Lu^{11}B_{12}$ and 7.4684(2) Å for $Yb^{11}B_{12}$. The powder samples of YbB_{12} (8.6 g) and LuB_{12} (5.85 g) were placed in a flat square-shaped aluminum container with dimensions 42 $\times$ 42 mm and thicknesses of 2.0 ± 0.3 mm and 1.4 ± 0.3 mm, respectively.

The neutron scattering experiments were performed on the time-of-flight spectrometer HET (ISIS, RAL) with two incident energies $E_i = 200$ and 80 meV. These incident energies make it possible to explore a wide interval of momentum transfers ($0.5\,\text{Å}^{-1} \leqslant Q \leqslant 11\,\text{Å}^{-1}$ for $E_i = 80$ meV, and $1.2\,\text{Å}^{-1} \leqslant Q \leqslant 24\,\text{Å}^{-1}$ for $E_i = 200$ meV) in the positive energy transfer range. The measured transmission of the YbB_{12} sample was 0.85 at the incident energy $E_i = 200$ meV, 0.82 at $E_i = 80$ meV, and 0.79 at $E_i = 50$ meV. The $Yb^{11}B_{12}$ measurements were performed at temperatures of $T = 15$, 37, 55, 75, 105, and 159 K for $E_i = 80$ meV, and at $T = 15$ K for $E_i = 200$ meV. $Lu^{11}B_{12}$ was studied at $T = 15$ K for both incident energies, and only at $T = 159$ K for $E_i = 80$ meV. Absolute calibration of the measured cross sections was achieved by normalization to a vanadium standard. The detectors were grouped into seven banks with average scattering angles $\langle 2\theta \rangle$ of 5°, 11.5°, 16.5°, 21.5°, 26.5°, 115°, and 130°. The flight path to the detectors was 4 m at $\langle 2\theta \rangle = 5°$ and 115°, 2.5 m at $\langle 2\theta \rangle = 11.5°$ to 26.5° and 130°. The resulting energy resolutions (full width at half maximum of the elastic peak in vanadium) for incident neutron energies of $E_i = 80$ meV (200 meV) were 2.15 meV (5.7 meV) for $\langle 2\theta \rangle = 5°$, and 3 meV (8 meV) for $\langle 2\theta \rangle = 11.5$ to 26.5°. Spectra were typically recorded with a total proton current of 1000 μAh.

III. RESULTS

A. Subtraction of phonon scattering

Before analyzing the magnetic spectral response of $Yb^{11}B_{12}$, it is essential to achieve a proper separation of the magnetic and nuclear components in the experimental spectra. In the earlier work of Bouvet,[11] it had been found that a strong phonon excitation exists at $E = 16$ meV, almost exactly superimposed on one of the magnetic peaks of interest, which made the determination of the magnetic signal in this region questionable. Subsequently, the same data were reanalyzed[13] by considering the B_{12} and rare-earth contributions to the phonon density of states separately. In the present measurements, a more direct approach was made possible by the use of a higher incident energy with a better experimental resolution. The method is similar to that described in Ref. 15, and consists in deriving the nuclear contribution at low scattering angles ($2\theta_L$) from that measured at high scattering angles ($2\theta_H$) by means of an energy-dependent scaling factor $r(E, 2\theta_L, 2\theta_H)$. This factor is determined from independent measurements of an appropriate nonmagnetic reference material. This procedure is based on two main assumptions. The first one is that magnetic scattering makes a negligible contribution to the high-angle spectra, because of the markedly different wave-vector dependencies of the magnetic (form-factor decrease) and phonon (approximately $\propto Q^2$) signals. In the case of Yb^{3+} ions, this is realized for momentum transfers $Q \geqslant 9\,\text{Å}^{-1}$. The second requirement is that the scaling functions (high angle to small angle) for the phonon component of the spectra should be the same for YbB_{12} and the non-magnetic reference compound LuB_{12}. The validity of this assumption mainly relies on the equivalence of multiple-scattering contaminations in the two materials. In the present case, both have a relatively strong residual absorption for thermal neutrons ($\approx$270 barns per YbB_{12} formula unit), which results in a strong suppression of multiple-scattering effects because the transmission along the sample is much lower than perpendicular to its surface (i.e., in the direction of the incident beam). Therefore, the scaling function $r(E, 2\theta_L, 2\theta_H)$ derived from LuB_{12} should be applicable to YbB_{12}.

In our experiments, the spectra for YbB_{12} and LuB_{12} were measured under identical conditions. Both materials have almost equal transmissions and, as noted above, the contributions from multiple scattering should be very similar and

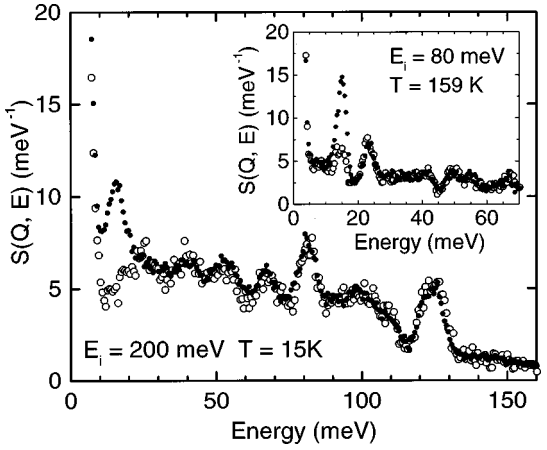

FIG. 1. Energy spectra of LuB_{12} (open circles) and YbB_{12} (black dots) at $T=15\,\mathrm{K}$, measured with the incident neutron energy $E_i=200\,\mathrm{meV}$ at a scattering angle $\langle 2\theta\rangle=130°$. The spectra are normalized with respect to the intensity of the peak at 125 meV. Inset: energy spectra at $T=159\,\mathrm{K}$ for $\langle 2\theta\rangle=130°$ and $E_i=80\,\mathrm{meV}$; the two spectra have been normalized in the high-energy region ($E=60-70\,\mathrm{meV}$).

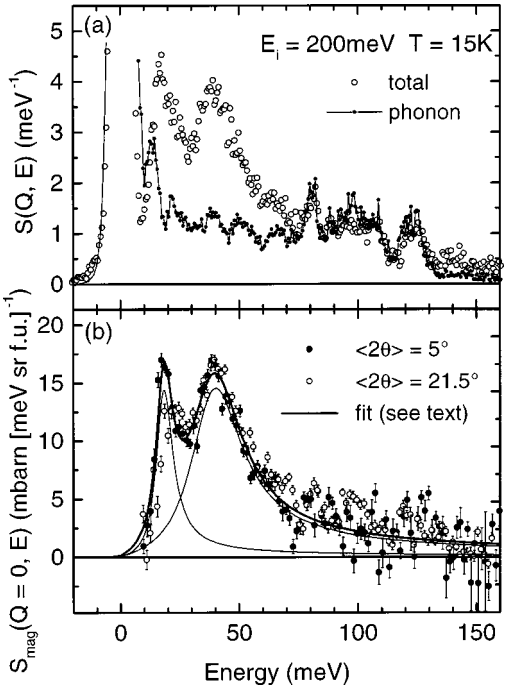

FIG. 2. Energy spectra of YbB_{12} at $T=15\,\mathrm{K}$ measured with the incident neutron energy $E_i=200\,\mathrm{meV}$. (a) total scattering intensity (open circles) and phonon contribution (dots) for the lowest scattering angle $\langle 2\theta\rangle=5°$. (b) Comparison of the magnetic spectra for two different scattering angles. Intensities have been scaled to $Q=0$ using the Yb^{3+} form factor. Lines represent a fit to a spectral function consisting of two Lorentzian peaks.

relatively small. Moreover, since the Yb and Lu elements have comparable atomic masses, and YbB_{12} and LuB_{12} have similar electronic band structures, one can expect the phonon densities of states to be nearly identical. Coherent effects may exist at low energy transfers and small scattering angles because of the large coherent cross section, but this effect is partly compensated by the relatively small size of the Brillouin zone in RB_{12} systems, which produces substantial averaging in the powder spectra. From our data, it can be concluded that coherent effects are notable only in the foot of elastic line, and this limited energy range was therefore excluded from the following analysis.

The scattering functions $S(Q,E)=(k_i/k_f)(d^2\sigma/dEd\Omega)$ of YbB_{12} and LuB_{12} obtained for a scattering angle of $\langle 2\theta\rangle=130°$ are shown in Fig. 1. Here, Q is larger than $13\,\mathrm{Å}^{-1}$ for all energies and only phonon scattering can be expected to contribute. Both spectra exhibit several phonon peaks up to 130 meV, as in the case of SmB_6.[16] In the low-resolution measurements ($E_i=200\,\mathrm{meV}$), it can be noted that the low-energy part of the phonon spectra, below 30 meV, is strongly modified upon replacing Lu by Yb. At higher energy transfers, the spectra are identical in the limits of experimental accuracy. In the spectra measured with better resolution ($E_i=80\,\mathrm{meV}$), one sees that the intensity of the peak centered at $E\approx 15\,\mathrm{meV}$ is larger by a factor of 3.1 ± 0.1 in YbB_{12} than in LuB_{12} (inset in Fig. 1), whereas the signal at higher energies is the same in both compounds. These results clearly indicate that the peak at 15 meV arises from the vibration modes of the rare-earth ions: indeed, the ratio of the total nuclear scattering cross sections of Yb and Lu is 23.4/7.2 $=3.25$, in good agreement with the experimental value. The scattering observed at higher energies, in particular the pronounced peak above 20 meV, which is essentially independent of the rare-earth element, can be ascribed to the vibration modes of boron. This distinction is the basis of the analysis performed in Ref. 13.

LuB_{12} spectra for different scattering angles have been measured at 15 and 159 K, and the scaling functions $r(E,2\theta_L,2\theta_H)$ determined at these two temperatures were found to coincide within experimental accuracy. The values obtained at $T=159\,\mathrm{K}$ were used for the treatment of the YbB_{12} spectra because the statistics at low energy was better at this temperature.

B. Magnetic response

Magnetic spectra of YbB_{12} for different scattering angles and temperatures have been obtained by subtracting out the calculated nuclear component. This procedure is illustrated in Fig. 2(a), which represents the neutron spectrum for $\langle 2\theta\rangle=5°$, measured at $T=15\,\mathrm{K}$ with an incident neutron energy of 200 meV. Data points in the range $-5\,\mathrm{meV}\leqslant E\leqslant 5\,\mathrm{meV}$ have been discarded because of the large statistical error caused by the strong nuclear elastic contribution. Figure 2(b) shows the high-energy ($E_i=200\,\mathrm{meV}$) magnetic spectra for two different scattering angles, $\langle 2\theta\rangle=5°$ and 21.5°, normalized with respect to a vanadium standard, corrected for self-screening, and scaled to $Q=0$ according to the calculated magnetic form factor of Yb^{3+} (Ref. 17). It can first be noted that, at least for energies larger than 20 meV, the two data sets coincide within error bars. A similar agreement was found for other magnetic spectra measured at low scattering angles (5°–26.5°), lending strong support to the procedure applied above to estimate the phonon term. With this resolution, the magnetic response of YbB_{12} appears to contain only two spectral components centered around 20 and 40 meV, which can be well fitted by assuming simple Lorentzian spectral functions with half widths $\Gamma_i/2$ [thin

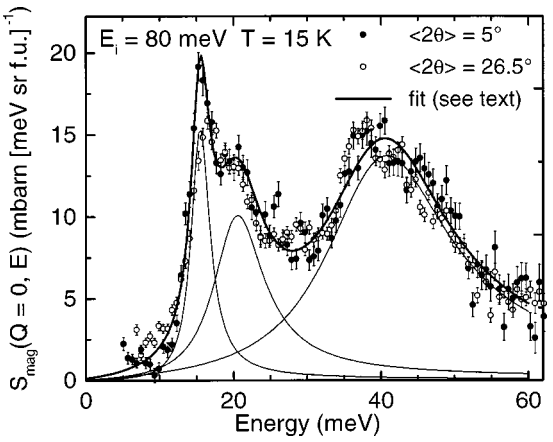

FIG. 3. Magnetic energy spectra of YbB_{12} at $T=15\,\mathrm{K}$, measured with the incident neutron energy $E_i=80\,\mathrm{meV}$, for two different scattering angles. Intensities have been scaled to $Q=0$ using the Yb^{3+} form factor. Lines represent a fit to a spectral function consisting of three Lorentzian peaks.

lines in Fig. 2(b)] and representing the scattering function by the usual phenomenological expression

$$S_{\mathrm{mag}}(E,T)\propto \frac{E}{1-\exp(-E/k_BT)} \times\sum_i \chi_i'(T)\,\frac{\Gamma_i(T)/2}{(\Gamma_i(T)/2)^2+(E-E_i)^2}. \quad (1)$$

No significant additional intensity is detected up to 150 meV. The low-energy part of the spectra, measured with a better resolution at $E_i=80\,\mathrm{meV}$, is shown in Fig. 3 for two different scattering angles $\langle 2\theta\rangle=5°$ and 26.5°. Again, the agreement between the two sets of data is quite good. In comparison to the low-resolution data, the spectra shown in Fig. 3 reveal that the lower peak actually consists of two components at $E=15$ and 20 meV. This explains incidentally why the two spectra shown in Fig. 2(b) were found to deviate at low energies: the different scattering angles correspond to different flight paths and resolutions, and the effect becomes significant in the case of peaks with small line widths. The upper peak is broader and centered at $E=38\,\mathrm{meV}$. The most remarkable feature is the absence of any detectable magnetic intensity below 10 meV at this temperature ($T=15\,\mathrm{K}$). In particular, we do not observe any evidence of quasielastic scattering. More precisely, if such a signal exists, it has to be either very narrow ($\Gamma/2<4\,\mathrm{meV}$) or very broad with a low intensity. We will see below that both possibilities are rather unlikely. The experimental spectrum was fitted by three Lorentzians. The same analysis was performed for all spectra measured at different scattering angles. The integrated intensities are plotted in Fig. 4 as a function of the momentum transfer Q. We recall that, since all experimental spectra have been scaled to $Q=0$ (see above), the data plotted in Fig. 4 are already corrected for the Q dependence of the magnetic form factor. Therefore, the fact that the intensities of the peaks at 20 and 38 meV do not vary appreciably with Q indicates that these excitations follow the form factor of Yb^{3+}. On the other hand, it is clear that the intensity of the lower peak at 15 meV decreases much more steeply.

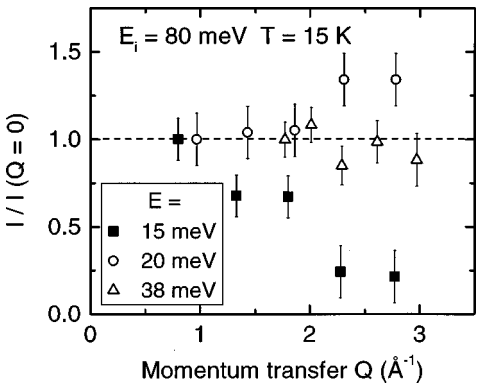

FIG. 4. Normalized Q dependence of the integrated intensities of the different magnetic spectral components of YbB_{12} at $T=15\,\mathrm{K}$ (incident energy $E_i=80\,\mathrm{meV}$).

Next, the evolution of the magnetic excitation spectrum in YbB_{12} was investigated as a function of temperature. Quite remarkably, increasing temperature up to only 159 K produces drastic changes in the entire spectral response between 0 and 50 meV. A selection of spectra for different temperatures $T=15$, 55, 75, and 159 K is shown in Fig. 5. At $T=75\,\mathrm{K}$ [Fig. 5(c)] the peak at 38 meV has its intensity reduced almost by a factor of two, without substantially shifting its position. Moreover, a quasielastic component appears at low energy. The two inelastic peaks at 15 and 20 meV are clearly observed for $T<100\,\mathrm{K}$. At the highest temperature,

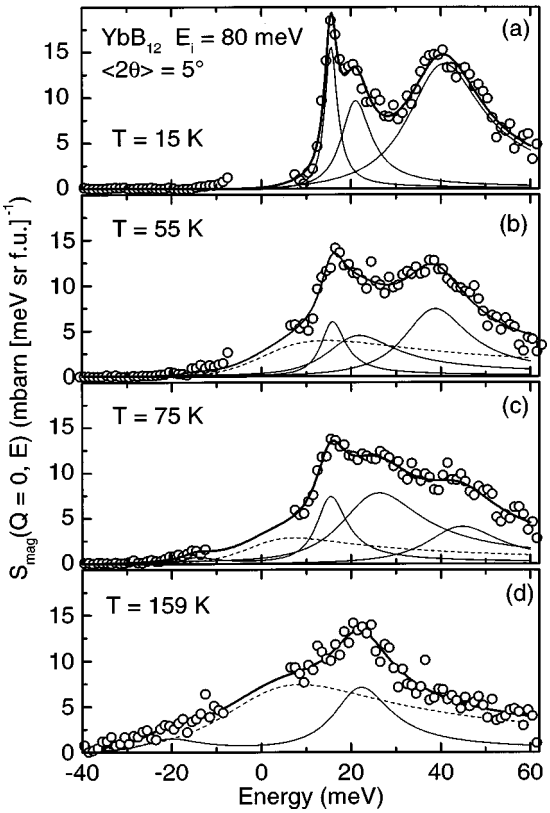

FIG. 5. Magnetic energy spectra, $S_{\mathrm{mag}}(Q=0,E)$, of YbB_{12} at four different temperatures, measured at the lowest scattering angle $\langle 2\theta\rangle=5°$ with the incident energy $E_i=80\,\mathrm{meV}$. The lines represent a fit to a spectral function consisting of inelastic (thin lines) and quasielastic (dashed line) Lorentzian peaks.

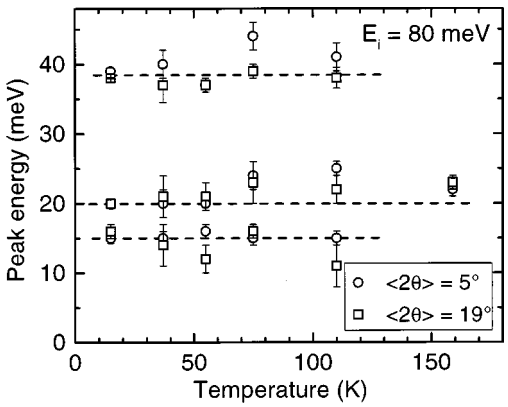

FIG. 6. Temperature dependence of the magnetic peak positions in YbB_{12} in spectra measured for two different scattering angles. The values for $\langle 2\theta \rangle \approx 19°$ were obtained by averaging the spectra over the angular range $11° \leqslant 2\theta \leqslant 26.5°$ prior to fitting. The dashed lines correspond to the constant energies $E = 15$, 20, and 38 meV.

$T = 159$ K, they are replaced by one broad peak centered at about $E = 23$ meV. Simultaneously, the peak at 38 meV disappears completely and the quasielastic contribution becomes dominant. In Fig. 5(d), one sees that the spectrum at $T = 159$ K could be fitted using only the quasielastic peak and one inelastic peak, both with Lorentzian line shapes. The parameters obtained from the different fits are summarized in Fig. 6 (peak positions) and Fig. 7 (integrated intensities). In the latter figure, the values corresponding to the quasielastic peak have been calculated as $\int (1/E)(1 - \exp(-E/k_BT))S_{\mathrm{mag}}(Q=0,E)dE$ to correct the results for the effect of the temperature factor. On the other hand, the intensities of the inelastic peaks have been obtained as $\int S_{\mathrm{mag}}(Q=0,E)dE$, which corresponds, in the case of CF excitations, to the usual product of the Boltzmann population factor by the squared transition matrix element. The experimental half widths of the peaks at 15, 20, and 38 meV are $\Gamma/2 = 2.5 \pm 1$, 5 ± 2, and 10 ± 3 meV, respectively, and $\Gamma/2 = 15 \pm 5$ meV for the quasielastic peak. The T dependencies of the line widths have not been plotted because their variations were not considered significant. It can only be noted that the widths of the peaks at 15 and 20 meV are systematically smaller at 15 K than at higher temperatures.

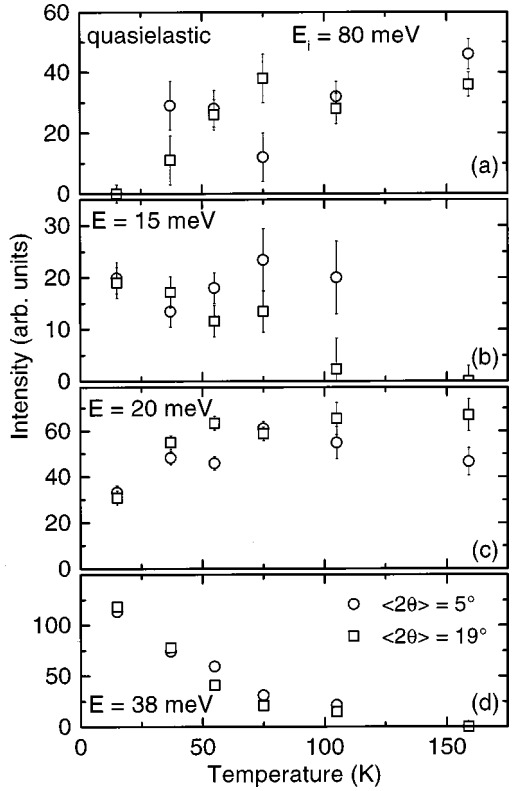

FIG. 7. Temperature dependence of the integrated intensities for (a) the quasielastic peak, and the inelastic peaks at (b) 15, (c) 20, and (d) 38 meV. Two sets of points correspond to different average scattering angles and different resolution conditions.

The main effects of temperature can be summarized as follows. The peak at 38 meV does not appear to shift significantly with increasing temperature (Fig. 6), but its intensity is strongly reduced between 15 and 55 K, then decreases more slowly [Fig. 7(d)]. This very steep temperature dependence cannot be explained by thermal population effects for any realistic CF scheme. It rather seems to correlate with the emergence of the quasielastic peak, which is observed above $T = 37$ K. This signal grows rapidly with increasing temperature up to 75 K [Fig. 7(a)]. For higher temperatures its intensity increases more gradually. On the other hand, the peaks at lower energies seem to be related to each other. The peak at 20 meV increases with temperature, while the peak at 15 meV peak decreases [Figs. 7(b) and 7(c)]. The latter peak could be traced up to 105 K and its energy does not change. The position of the 20 meV peak shifts slightly up to $E \approx 23$ meV at $T = 159$ K.

IV. DISCUSSION

The unusual magnetic excitation spectrum of YbB_{12}, as well as its pronounced temperature dependence, clearly reflect the formation of the Kondo-insulator state at low temperature. At $T = 15$ K, three main components are found to exist: one narrow peak at $E = 15$ meV, whose intensity varies with Q faster than the Yb^{3+} form factor, and two broader ones at 20 meV and 38 meV. Most remarkable is the absence of appreciable magnetic scattering at low energies, which proves that a gap Δ_m of about 10 meV exists at this temperature in the magnetic excitation spectrum of YbB_{12}. These results are in line with those reported recently by Bouvet *et al.*[13] In view of the various experimental problems to be overcome (difficult sample preparation, absorbing material, coincidence of magnetic, and lattice excitations), it is satisfying that data obtained on different specimens, using different spectrometers, and treated by different procedures, lead to a consistent description of the low-temperature magnetic response in YbB_{12}.

One advantage of the present measurements is that the spectra could be calibrated in absolute units. Therefore, the total magnetic cross section was estimated, at a given temperature, by integrating the experimental scattering function over the energy,

$$\sigma_M = 4\pi \int_{-\infty}^{+\infty} S(Q=0,E)dE, \tag{2}$$

with S in (barn meV^{-1} sr^{-1}/Yb).

Because of the limited energy range of our experimental data, the values of the scattering function near $E=0$ and for $E>E_i$ were approximated by the same analytical expressions (Lorentzian) that were used for the fits in the preceding section. The resulting total magnetic cross sections at $T=15\,\mathrm{K}$ are 8.8 ± 0.8 barn for $E_i=80\,\mathrm{meV}$ and 11 ± 1 barn for $E_i=200\,\mathrm{meV}$ (with an integration cutoff of 500 meV). These values are somewhat smaller than the cross section calculated for the Yb^{3+} ion ground-state multiplet $J=7/2$ ($\sigma_M=12.6$ barn). The difference between the results obtained for different values of E_i may indicate that our extrapolations of the scattering functions to high energy transfers are not sufficiently accurate, especially in the case of the lower incident energy where the experimental range is more limited. On the other hand, the missing cross section for $E_i=200\,\mathrm{meV}$ can be roughly accounted for by the ''substitution'' of 10% of the Yb^{3+} by nonmagnetic Yb^{2+}. Therefore, if we assume a valence of 2.8 to 2.9,[1,3] the experimental magnetic cross section measured at $T=15\,\mathrm{K}$ implies that other components of the spectrum that might have been overlooked in the above analysis (for instance quasielastic scattering with a very small line width) represent *less than* 15% of the total spectral weight.

As noted in the Introduction, there is strong experimental evidence that the magnetic properties of YbB_{12} are dominated by the Kondo effect, both in the pure compound and its solid solutions $Yb_{1-x}Lu_xB_{12}$, with Kondo temperatures estimated to be on the order of 250–300 K over a wide range of concentrations.[2] For normal metallic Kondo systems with moderate T_K, the magnetic excitation spectrum at low temperature is expected to contain one quasielastic component originating from the many-body ground state, and well-defined inelastic peaks related to the ionic CF scheme. It is easy to see that our data are not amenable to such a description. For an Yb^{3+} ion at a cubic site, the ground state $J=\frac{7}{2}$ splits into one quartet Γ_8 and two doublets Γ_7 and Γ_6. All wave functions and transition-matrix elements are fixed in this case.[18] If the ground state is Γ_8, as suggested by previous studies,[2,12] the spectrum at low temperature $k_BT\ll\Delta_{\mathrm{CF}}$ should consist of one quasielastic and two inelastic lines with intensity ratios 7.2:6.0:7.8.[19] In other words, the quasielastic signal should amount to more than 50% of the sum of the inelastic components, in complete contradiction with the experimental result. For other choices of the ground state, either Γ_6 or Γ_7, only *one* excitation would exist at low temperature because the transition to the other doublet has its matrix element equal to zero, but an additional peak should appear when T becomes of the order of the crystal field. Therefore, it is evident that the low-temperature magnetic response of YbB_{12} is deeply altered by the formation of the Kondo-insulator ground state accompanied by the opening of a gap in the electronic density of states, and that it cannot be interpreted in terms of a single-ion (Kondo+CF) picture. The data indicate that the local magnetic moment in the ground state is strongly reduced, or possibly cancelled, which is consistent with the recent susceptibility results.[2]

The appearance of a gap in the magnetic excitation spectrum of a Kondo insulator at low temperature was reported previously for the compound $Ce_3Bi_4Pt_3$ ($\Delta_m=12\,\mathrm{meV}$).[20] In that case, the gap started to fill when the system was heated to a temperature of about 50 K, and a damped, quasielastic-like response was recovered at $T\approx150\,\mathrm{K}$. A simple model was proposed, in which the magnetic response at low temperature was ascribed to interband spin-flip transitions across a hybridization gap, and the temperature dependence to a rapid closing of this gap between 50 and 100 K. In the case of YbB_{12}, a more detailed analysis is possible because several distinct components could be singled out in the experimental spectra. The influence of temperature on the magnetic response is of particular interest as these components exhibit contrasted behaviors in the temperature range ($T\approx70\,\mathrm{K}$) where the gaplike behavior appears. On several important points, our analysis of the evolution of the different spectral components is at variance with that reported in the work of Bouvet *et al.*[13] In our data, the main effects of increasing temperature are the recovery of a quasielastic component above 50 K, accompanied by the suppression of the peak at 38 meV with no substantial shift in its energy position. From the sequence of spectra presented in Fig. 5, it is clear that (i) the peak at 23 meV observed at $T=159\,\mathrm{K}$ is *not* the result of a gradual shift of the 38-meV peak to lower energies as claimed in Ref. 13, and (ii) the appearance of the quasielastic signal correlates with the suppression of the 38 meV peak rather than with a softening of the excitation at 20 meV. Both measurements agree, however, on the remarkable observation that the original signal at 38 meV is strongly suppressed by heating to a temperature of 100 K, even though its excitation energy is much larger (by a factor of about 4) than the corresponding thermal energy. The rapid transfer of spectral weight from this inelastic signal to a quasielastic response as temperature increases indeed corresponds to what was observed for $Ce_3Bi_4Pt_3$, and can be ascribed to the collapse of the electronic gap. Interestingly, recent optical conductivity experiments on YbB_{12} single crystal[21] have revealed the existence of a peak at ~40 meV for $T=20\,\mathrm{K}$, which disappears, together with the gap, when temperature is raised to above 70 K. One should be careful, however, in comparing optical and magnetic spectra because the latter correspond to excitations with spin reversal but no charge transfer.

The origin of the two peaks at 15 and 20 meV in YbB_{12} deserves special attention because such structures were not detected in $Ce_3Bi_4Pt_3$. On the other hand, a narrow peak at about 14 meV, ascribed to an excitonlike bound state,[7,8] has been reported for SmB_6. From our data, it seems that the two spectral components in YbB_{12} change gradually to a single-broadened excitation at about 23 meV, which is clearly visible in the spectrum for $T=159\,\mathrm{K}$. At this temperature, the intensity of the quasielastic signal is comparable to, or even stronger than, that of the latter inelastic peak. Therefore, if a single-ion regime is considered to be recovered at this temperature, as demonstrated in Ref. 2, it is reasonable to ascribe the inelastic peak to a CF-like excitation, with an estimated splitting of the order of 20 meV (at least the total splitting should not exceed twice this value for the case of an equidistant level scheme).

In several respects, the spectral structure of YbB_{12} displays interesting similarities with that reported recently for CeNi.[22,23] Although the latter material is not a semiconductor like YbB_{12}, but a rather conventional intermetallic mixed valence compound, it demonstrates a spin gap of the order of 15 meV, a nonmagnetic ground state, narrow peaks just

above the gap edge, and a broad response centered at about 60 meV, which somehow transforms to a quasielastic peak upon a moderate increase in temperature to $T \sim 100-200$ K. It was estimated[24] that CF effects can produce a splitting of the Ce^{3+} energy levels roughly compatible with the energies of the peaks near the spin gap. These peaks, which demonstrate some collective character, were thus tentatively ascribed to former CF excitations modified by hybridization effects. In the case of YbB_{12}, the occurrence of a doublet structure at low temperature could result from Yb-Yb correlations. This point requires further investigations, especially experiments on single-crystals. Measurements on solid solutions with an Yb valence closer to 3+ would also be useful to clarify the CF structure.

An alternative interpretation of the spectral response in YbB_{12} may be suggested based on a comparison with SmB_6. Indeed, the behavior of the 15 meV excitation in YbB_{12} is reminiscent of the ''exciton'' peak found at 14 meV in the latter compound,[7] as its intensity drops more steeply at increasing Q than the magnetic form factor. However, it has to be noted that this effect is far less pronounced here than in SmB_6. The double structure at 15 and 20 meV in YbB_{12}, in contrast to the single peak in SmB_6, also implies that the two systems are not strictly equivalent. In the interpretation of Refs. 12 and 13, the two peaks are attributed to distinct mechanisms, and the upper one is assumed to be too weak in SmB_6 to be detected by inelastic neutron scattering. On the other hand, these two peaks might result from a mixed collective excitation arising from the interaction of two dispersive magnetic modes, or possibly of one magnetic and one phonon mode. The latter effect, which has been reported previously[25] for the compound $CeAl_2$ is not unlikely in the case of YbB_{12} because the magnetic excitations nearly coincide with strong peaks in the phonon density of states at 15 and 22 meV.

In the preceding discussion, it has been suggested that magnetic correlations among Yb ions might play an important role at low temperature (for instance by causing some dispersion in the low-energy magnetic excitations). This assumption can be substantiated by comparing the bulk magnetic susceptibility $\chi_{\text{bulk}}(T)$ to the local susceptibility $\chi_{\text{st}}(T)$ derived from the neutron magnetic response. Here, we apply the standard Kramers-Kronig relation

$$\chi_{\text{st}}(T) = K \int_{-\infty}^{+\infty} (1/E) S(Q=0,E,T)[1-\exp(-E/k_B T)]dE \tag{3}$$

to the data obtained by extrapolating our experimental spectra to $Q=0$. In Eq. (3), the numerical value of the prefactor K is 0.22 if S is expressed in units of barn $[\text{meVsr f.u.}]^{-1}$, and χ_{st} in emu/mole.

The temperature dependence of the static magnetic susceptibility calculated using this expression is plotted in Fig. 8, together with the bulk susceptibility from Ref. 2. The agreement between the neutron and bulk measurements is quite good at high temperatures. However, the two curves start to deviate for $T \leqslant 50$ K, and the difference exceeds a factor of two at the lowest temperature. In Ref. 1, the high-temperature part of the data was described by a Curie-Weiss law with a reduced value of the local moment $p_{\text{loc}} = 0.9 p_{\text{loc}}(Yb^{3+}) = 4.09\,\mu_B$, and a paramagnetic Curie temperature $\theta_P = -79$ K. From the magnetic neutron spectrum, it can be suggested that this rather large value results, at least partly, from a Van-Vleck term in $\chi(T)$ connected with the inelastic peak at $E = 20$ meV, which produces deviations from the simple Curie law for temperatures in the range 100–300 K.

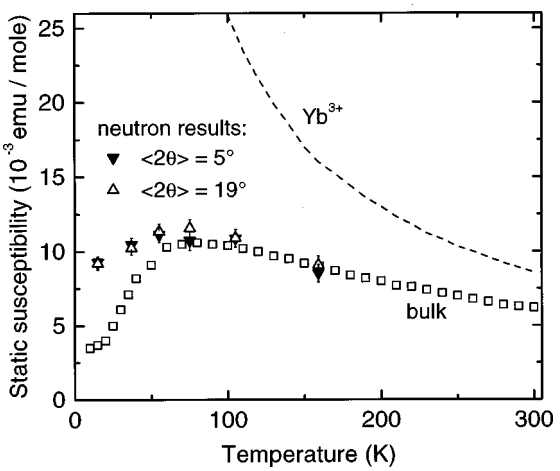

FIG. 8. Temperature dependence of the static magnetic susceptibility. △, ▼: data derived from the neutron spectra for two different average scattering angles (error bars denote the estimated uncertainty in the absolute normalization of the data); □: bulk susceptibility from Ref. 2; dashed line: static susceptibility calculated as $\chi_{\text{st}}(T) = p_{\text{loc}}^2 \mu_B^2 / 3k_B T$, with $p_{\text{loc}} = 4.54$ for Yb^{3+}.

The discrepancy between χ_{bulk} and χ_{st} below 50 K is unlikely to result from an artifact in the calculation of χ_{st} using equation (3). For $T < 50$ K, χ_{st} becomes sensitive to the spectral weight existing at energies below a few millielectronvolts, but this part of the spectrum cannot be responsible for the decrease in $\chi_{\text{st}}(T)$ on cooling simply because the magnetic intensity is found to be negligible in this energy range. Alternatively, to obtain a decrease in χ_{st} of the same magnitude as in χ_{bulk} from the higher-energy region (10 to 20 meV), one should suppose that the real intensity there is only one half of that estimated from the fit to the experimental spectra, which is totally unrealistic. We thus believe that the difference between the neutron and the bulk results has a physical origin, namely that the low-Q dependence of the magnetic signal for $T < 50$ K does not follow the single-ion form factor of Yb^{3+}, as was assumed in our extrapolation to $Q=0$ of the experimental values of $S(Q,E,T)$ (most of which were measured with $Q > 0.7$ Å^{-1}). A reduced intensity at $Q=0$, as compared to that derived from finite Q values, typically indicates that antiferromagnetic correlations exist between near-neighbor Yb ions, making the Q dependence nonmonotonic. Other mechanisms might in principle produce the same effect (for instance a change in the Yb form factor associated with the formation of the hybridized many-body ground state) but no experimental information is available to support such speculations.

V. CONCLUSION

The magnetic response of the Kondo-insulator compound YbB_{12} in a wide range of energies has been determined from time-of-flight inelastic neutron scattering measurements, tak-

ing special care to accurately separate the superimposed phonon contribution. Magnetic excitations were observed up to $E=40$ meV, and their spectrum strongly transforms as a function of temperature. At $T=15$ K, no evidence of either quasielastic or inelastic magnetic scattering was found below 10 meV. This result clearly shows that the formation of the Kondo-insulator state at low temperature is accompanied by the opening of a gap in the magnetic excitation spectrum. As temperature increases, a strong and broad quasielastic response is recovered, while the inelastic peak that existed initially at about 38 meV becomes smeared out. Narrower peaks at 15 and 20 meV, which were well resolved at the lowest temperature, merge gradually into a single component at about 23 meV. It is suggested that these excitations are related to CF effects in Yb^{3+}. The total magnetic cross-section derived by integrating the experimental intensities is consistent with an Yb valence of the order of 2.8–2.9. The calculated static magnetic susceptibility agrees well with the bulk measurements for $T>50$ K, but it deviates strongly at lower temperatures, suggesting that Yb-Yb correlations become significant.

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