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Influence of the Mixed-Valences State on the Magnetic Excitation Spectrum of SmB_6-Based Compounds

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A series of experimental studies of the dynamical magnetic response of Sm in SmB_6-based mixed-valence (MV) systems has been carried out by inelastic neutron scattering on poly- and single-crystalline, double-isotopic (^{154}Sm, ^{11}B), samples. In addition to two strongly damped high-energy peaks associated with the inter-multiplet transitions of Sm^{2+} and Sm^{3+}, pure SmB_6 exhibits a very specific low-energy excitation at 14 meV. These features can be ascribed to the formation of the MV ground state. To study the effect of a variation of the average valence v on the magnetic excitation spectra, solid solutions have been studied in which 2+ or 3+ ions are substituted for Sm. The intensities of the inter-multiplet excitations change roughly in accordance with the variation of v. Systematic changes are observed in the position of the low-energy peak and in the Q and T dependences of its intensity, Further information concerning the energy, anisotropy, and the Q and T dependences of the low-energy excitation was obtained from triple-axis experiments on single crystals of $Sm_{1-x}La_xB_6$ ($x = 0.10$, 0.22) at ambient pressure and SmB_6 at $P = 0.5$ GPa. The transformations observed in the low-energy part of the spectra suggest a relation between the average valence and the degree of delocalization (or hybridization strength) for the "loosely bound" f-electron state formed around the Sm ion, which is a characteristic feature of the MV ground state. © 1997 Academic Press

INTRODUCTION

Mixed- or unstable-valence phenomena are expected to arise in systems where two electronic configurations, corresponding to occupation numbers n and $n-1$ of the lanthanide $4f$ shell, have nearly degenerate energies. The existence of a large hybridization between strongly Coulomb-correlated electron states (the $4f$ orbitals with pronounced atomic character) and itinerant states from the conduction (or sometimes the valence) bands is central to this picture. The term "valence fluctuation" is often used in this context to imply a dynamical character of the valence mixing. Experimentally this assumption is supported by the fact that different spectroscopic methods give qualitatively different pictures of electronic states, e.g., the Mössbauer isomer shift (characteristic time scale $\tau \approx 10^{-8}$ s) yields a single contribution reflecting the average occupation of the $4f$ shell, whereas separate contributions from each configuration are observed in short time scale experiments such as XAS and XPS. From this point of view, inelastic neutron scattering is a very important tool for studying mixed-valence (MV) phenomena (1) because its characteristic time scale is on the order of 10^{-13} s, which is in good correspondence with that of valence fluctuations. Another important advantage of neutron spectroscopy is the possibility to study the atomic vibrations and magnetic moment dynamics of the substance at the microscopic level.

Early in the history of the subject it was realized that some of the most popular MV compounds such as SmS (high-pressure phase), SmB_6, or TmSe display semiconducting behavior when cooled to below room temperature. It was proposed (2, 3) that a very narrow gap in the electronic density of states near the Fermi energy develops as a result of on-site hybridization between the narrow $4f$ band and the broad conduction band. Some authors argued that the above one-particle mixing mechanism cannot be applyed to real MV systems, because strong Coulomb correlations exist among $4f$ electrons, and a many-body theory is thus needed. Alternative approaches have been proposed, such as the "Wigner lattice" model of Kasuya (4), or various ideas related to the concept of excitonic insulating state (5–8). Owing to the small carrier concentration and the resulting poor screening of Coulomb interactions, the electron released from the $4f$ shell is likely to form a local bound state near the MV rare-earth ion rather than being promoted into itinerant conduction band states. In principle, polarized neutron diffraction experiments can provide information about the spatial distribution of the magnetic electrons. However, the first attempt to observe separate contributions from each valence state in the induced magnetic form factor in SmS (gold phase, $P > 0.6$ GPa), where

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about 70% of Sm ions are supposed to be in the 3+ state, gave a puzzling result, namely that the Q dependence of the form factor was essentially identical to that of pure Sm^{2+} (9).

The first pieces of evidence pointing to the existence of an exciton-like state in MV systems came from a lattice-dynamics study of (Sm, R)S (R = Y, La, Pr, Gd, Tb, Dy, Tm) (10), $Sm_{0.75}Y_{0.25}S$ (11), and, later on, from comprehensive investigations of phonon modes in SmB_6 by neutron scatering (12, 13) in which all acoustic, and the lowest optical, phonon branches in the main symmetry directions have been determined. In addition to a remarkable anomaly in the dispersion curve of LA phonons, two extra vibrational modes without dispersion were found within in the gap between acoustic and optical branches. They exhibit very specific features: the first mode is unpolarized and drowns into the background when temperature is reduced to 100 K, whereas the second is longitudinally polarized, exists only near the Brillouin zone (BZ) boundary, and has an energy which strongly depends on temperature. The vibrational spectra were interpreted on the basis of an excitonic theory of MV semiconductors (8). In the particular model for SmB_6 (and SmS) the spatial extension of the excitonic wave-function proposed for the MV state plays a key role and can account for the most salient features in the phonon dispersion curves. It was shown later (14) that the existence of very soft electronic excitations described by the same wavefunction and connected with valence fluctuations results in a nonadiabatic resonance effect in the lattice dynamics. The consequence of this effect is the appearance, in the lattice vibration spectra, of two extra modes observable by neutrons: one is connected with a self-localized exciton–polaron state populated at high temperature, whereas the other is a coherent vibronic state whose excitation energy is a function of temperature due to the narrow gap in the electronic density of states.

From the above discussion, one sees that the excitonic model is rather successful in explaining lattice-dynamics features of SmB_6. However, the formation of such a "local bound state" should also be reflected directly in the magnetic properties of this system. In particular, specific excitations might occur in the magnetic part of the dynamic response function measured by inelastic neutron scattering. Measurements of a powdered sample of SmB_6 on the time-of-flight spectrometer HET (ISIS) yielded the full spectrum of magnetic excitations (15). Three main features are observed at low temperature ($T \sim 20$ K): two broad "high-energy" peaks and one resolution-limited "low-energy" peak. The former two peaks can be ascribed to inter-multiplet (spin–orbit) transitions corresponding respectively to Sm^{2+} ($^7F_0 \rightarrow {}^7F_1$) and Sm^{3+} ($^6H_{5/2} \rightarrow {}^6H_{7/2}$), observed for the first time simultaneously in a rare-earth compound. Their intensity ratio is in good agreement with the average valence. However, these peaks exhibit considerable broadening as compared to those found in integral-valence substances. The third, low-energy, excitation ($E = 14$ meV) displays quite unusual behavior in comparison with "normal" single-ion magnetic excitations of crystal-field type. Its Q dependence is steep, it vanishes at relatively low temperature $T \sim 100$ K, and its narrow width is in contrast with the strong broadening of the inter-multiplet transition. The properties of the magnetic excitation spectrum seem intimately connected with the nature of the wavefunction of the MV ground state.

More insight into this problem can be expected from single-crystal studies. In addition, a controlled variation of the valence can provide further information about the formation of the ground state. The main goal of this paper is to present the results of a detailed investigation of the ground state wavefunction and excitation spectra of SmB_6, including the effect of a variation of the average valence of Sm. The single-crystal study of the magnetic response of SmB_6-based compounds was aimed at answering a number of questions raised by the time-of-flight results of Ref. (15): is the experimental linewidth of the Sm^{2+}-like inter-multiplet transition due to energy dispersion or intrinsic damping? What is the exact **Q** dependence of the 14 meV peak and can it help us to understand the nature of this excitation? How does the inelastic response change with temperature and valence? Some of these points were the subject of a rather extensive series of experiments described in Ref. (16). Hereafter we recall the most important results and discuss possible interpretations.

INTER-MULTIPLET TRANSITION

Energy spectra for SmB_6 were measured for a number of different **Q** values in reciprocal space, in particular at equivalent points in different Brillouin zones (zone center and zone boundary along principal symmetry directions), corresponding to different momentum transfers $Q \equiv |\mathbf{Q}|$. In all cases the peak corresponding to the inter-multiplet transition was observed with its maximum near 36 meV and a half-width $\Gamma/2 \approx 14$ meV (fit by a Lorentzian lineshape) even at temperatures as low as 2 K. Spectra obtained at this temperature for two different scattering vectors $\mathbf{Q} = (q, q, q)$ ($q = 0.76$ and 1.25), corresponding to equivalent BZ points along [111], are shown in Figs. 1b and 1c. The linewidth is much larger than the instrumental resolution, which can be estimated as 4 meV (FWHM) in this energy range. Therefore, the physical origin of the line broadening is clearly intrinsic. The intensity of this peak depends on the momentum transfer Q and follows with good accuracy the Q dependence of the inelastic structure factor calculated for this transition. Thus, one can conclude that the excitation observed here corresponds to a single-ion-like state with short lifetime $\tau_f \approx 3 \times 10^{-13}$ s estimated from the linewidth Γ, which agrees quite reasonably with typical valence

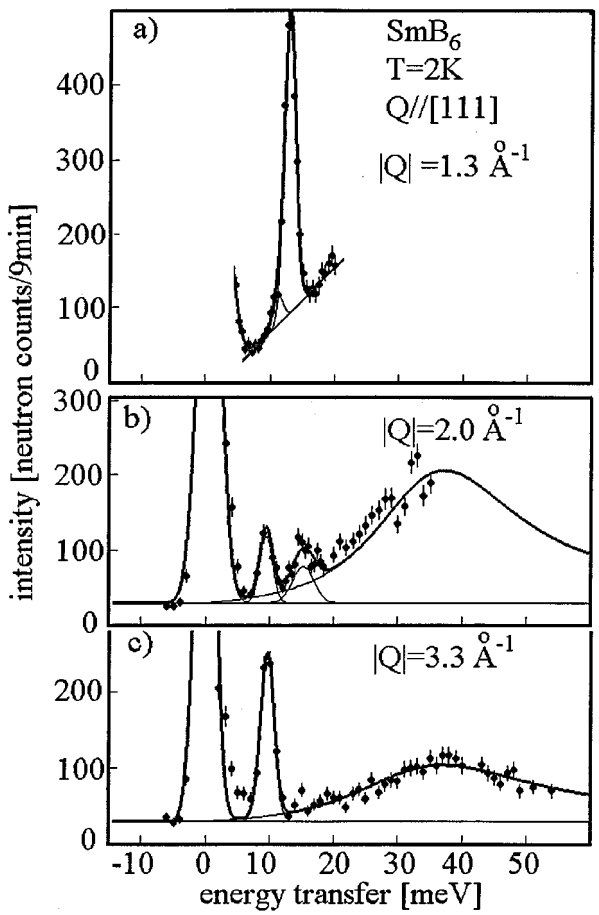

FIG. 1. Neutron scattering spectra of single-crystal SmB_6 at $T = 2$ K measured in the constant k_f mode ($E_f = 30.5$ meV) at fixed scattering vector $\mathbf{Q} = (q, q, q)$: (a) $q = 0.5$; (b) $q = 0.76$; (c) $q = 1.25$. The peak at 10 meV is a LA phonon mode (fitted by a Gaussian). Optical phonon contaminations at higher energies have been subtracted out. The solid line through the high-energy peak is a fit by a Lorentzian with $\Gamma/2 = 14$ meV, $E_0 = 34.5$ meV. Its intensity was scaled from frame (c) to frame (b) by use of the Sm^{2+} form-factor calculated for this transition. Energy ranges are limited due to restrictions in the scattering geometry. The magnetic excitation at 14 meV is fitted by a Gaussian with a width (FWHM) of 2.1 meV (resolution-limited).

fluctuation times derived from other types of experiments. The measurements of Ref. (17) performed on powder samples (La, Ba or Ca substitution of Sm) in a wide energy range have shown a clear correlation between the average valence and the relative spectral weights of the inter-multiplet transitions corresponding to each Sm ion configuration, f^5 or f^6.

LOW-ENERGY EXITATION AT 14 meV

In Figs. 1a and 1b, one can see a narrow peak at 14 meV, the intensity of which strongly decreases with increasing Q. This peak is resolution limited at $T = 2$ K, a quite remarkable feature in comparison with the strongly damped inter-multiplet transition. It demonstrates a weak dispersion along the [111] direction within the limits of 1 meV. The intensity was studied extensively as a function of **Q**. A strong dependence was indeed found, but no correlation was found between the intensity and the orientation of the reduced wavevector **q** with respect to the scattering vector. Furthermore, the excitation does not exist in reciprocal space if $Q > 2$ Å^{-1}. A three-dimensional "map" of the intensity of the peak in the scattering plane of the experiment is shown in Fig. 2. The striking results are (i) a very strong anisotropy of the signal, whose intensity is largest for **Q** along [111] and almost zero along [100], and (ii) a very steep decrease with increasing Q, much steeper than for a normal f-electron form-factor. The above features are clearly incompatible with a single-ion crystal-field excitation associated with either valence state of the Sm ion. It is also difficult to invoke a mixed magnetic–lattice mode since the excitation lies within the gap between acoustic and optical modes. On the other hand, the results can be understood naturally by assuming that the excitation is magnetic in origin and takes place within the extended electronic state around the samarium ion. From the Q dependence of the inelastic form factor, the maximum of the electronic density in real space can be deduced to lie at a distance from the origin of about three times the radius of the $4f$ shell. The directions for which the intensity is largest are those going from the Sm site to the center of the near-neighbor B_6 "molecules," suggesting that the boron p orbitals are involved in the construction of the extended state.

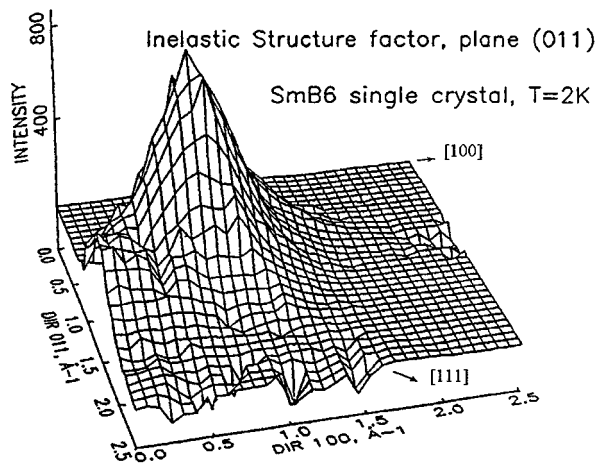

FIG. 2. **Q** profile of the integrated intensity of the 14 meV peak from the neutron scattering spectra of the SmB_6 single crystal at 2 K. All three main symmetry directions are in the scattering plane.

SOLID SOLUTIONS AND HIGH-PRESSURE EFFECTS

Further experimental information was obtained by varying the Sm valence and observing the changes produced in specific features of the magnetic excitation spectra. The measurements were performed on La-substituted single crystals of $Sm_{1-x}La_xB_6$, as well as on the pure single crystal of SmB_6 under an external pressure. From L_{III}-edge spectroscopy, it is known that La substitution gradually shifts the valence to 2 + (18, 19), whereas hydrostatic pressure favors the 3 + state. Of course, substitution not only changes the average valence but also produces disorder on the rare-earth sublattice, a potentially important effect if the formation of the ground state involves coherence phenomena among the Sm sites. The data for the $Sm_{1-x}La_xB_6$ samples with $x = 0.1$ and 0.22 are presented in Figs. 3 and 4. The experimental conditions for both samples were the same as in the measurements of SmB_6, apart from the use of a closed-cycle refrigerator instead of a cryostat. Sample volumes were 0.1 and 0.2 cm^3, respectively.

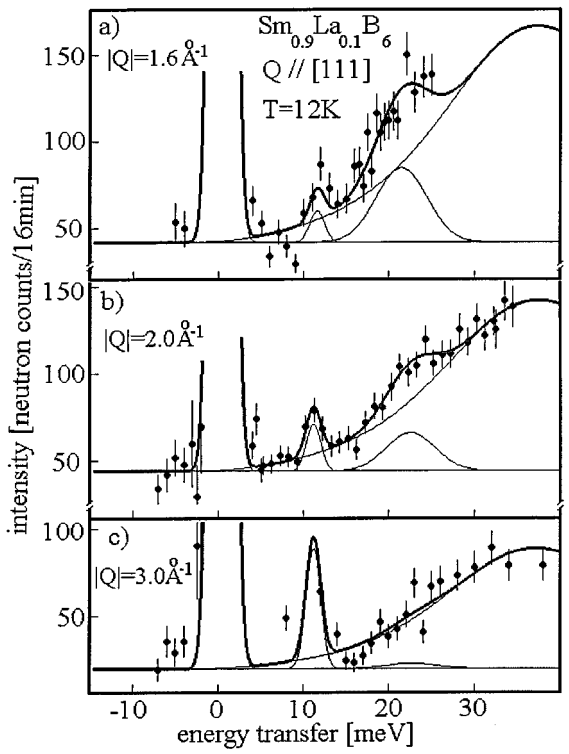

FIG. 3. Neutron scattering spectra of single-crystal $Sm_{0.9}La_{0.1}B_6$ at $T = 12$ K measured in the constant k_f mode ($E_f = 30.5$ meV) at fixed scattering vector $\mathbf{Q} = (q, q, q)$: (a) $q = 0.615$, $Q = 1.6$ Å^{-1}; (b) $q = 0.76$, $Q = 2.0$ Å^{-1}; (c) $q = 1.18$, $Q = 3.0$ Å^{-1}. The peak at 11 meV is a LA phonon mode (fitted by a Gaussian). The high-energy peaks are fitted by a Lorentzian with parameters $\Gamma/2$ and E_0 close to those used in Fig. 1 and scaled from (c) to (b) and (a) using the calculated form-factor of the inter-multiplet transition. The magnetic excitation at 21.5 meV is fitted by a Gaussian with a width (FWHM) of ≈ 6 meV, larger than the resolution.

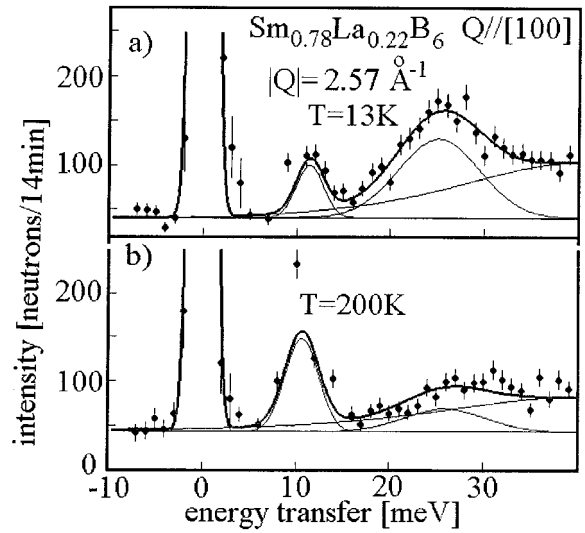

FIG. 4. Neutron scattering spectra of single-crystal $Sm_{0.78}La_{0.22}B_6$ at $T = 13$K (a) and $T = 200$ K (b), measured in the constant k_f mode ($E_f = 30.5$ meV) at fixed scattering vector $\mathbf{Q} = (1.7, 0, 0)$, $Q = 2.57$ Å^{-1}. The peak at 11 meV is a LA phonon mode (fitted by a Gaussian). The high-energy peak is fitted by a Lorentzian with parameters close to those used in Figs. 1 and 3 and scaled from (b) to (a) using the calculated form factor of the inter-multiplet transition. The magnetic excitation at 25 meV is fitted by a Gaussian with a width (FWHM) of ≈ 9 meV.

From Fig. 3 it can be seen that a magnetic peak exists in $Sm_{0.9}La_{0.1}B_6$ at an energy transfer of 21 meV, superimposed on the tail of a broad peak with maximum at approximately 37 meV. The latter obviously corresponds to the inter-multiplet transition, whereas the former replaces the 14 meV excitation which is no longer observed. The phonon peak is unchanged. For the 21 meV excitation, the Q dependence, anisotropy (at fixed $Q = 1.95$ Å^{-1}), and temperature variation were also studied. The anisotropy is much less pronounced, and the Q dependence along [111] less steep, than for the 14 meV excitation in pure SmB_6, as shown in Fig. 6. However, the peak almost completely disappears at $Q = 3$ Å^{-1}. This is indeed a problem for neutron scattering experiments because the conditions imposed by energy and momentum conservation strongly limit the range of energy transfers accessible for small Q values.

In $Sm_{0.78}La_{0.22}B_6$, the magnetic peak (see Fig. 4) is observed at 25 meV, and its Q dependence is even smoother than in the previous sample (see Fig. 6). When temperature is increased, some weak, but still detectable, signal exists even at 200 K. For 14 meV excitation of SmB_6 (16) intensity goes down rapidly when T only increases up to 50 K and it almost disappears at 100 K, therefore, substitution makes T dependence more "single-ion-like"; i.e., the decrease of peak intensity becomes more similar to the behavior of singlet–triplet transition with the corresponding energy.

The anisotropy, studied for $Sm_{0.78}La_{0.22}B_6$ at $Q = 1.97$ Å^{-1}, appears to be rather weak and of opposite character in comparison with SmB_6. Concerning the inter-multiplet transition, it can be noted that no appreciable change occurs in its energy position and linewidth with respect to the pure compound. Since the Sm^{3+} excitation lies beyond the upper energy limit of the present measurements, and a reliable absolutization of the intensities is not possible, no information regarding the change in the average valence of the system can be extracted from the data.

The above results indicate a general tendency of the low-energy signal in the magnetic excitation spectrum to become more single-ion-like when La is substituted for Sm. As the concentration x increases, the Q and T dependences of its intensity become more similar to the normal f-electron behavior. The energy of the peak increases nonlinearly with La concentration. We have no precise information about the valence of samarium in the low-concentration region; from existing data in the literature (18, 19) it can be assumed to be approximately a linear function of x.

The application of an external pressure on SmB_6 changes its valence in the opposite direction to La substitution, making Sm more trivalent. We estimate the effect of an applied pressure of 0.5 GPa on the valence as $\Delta v \approx +0.05$ with respect to SmB_6. The experimental data for SmB_6 (same single crystal as in Ref. (16)) under a pressure of 0.5 GPa at $T = 12$ K are shown in Fig. 5. A peak is clearly observed at 7.5 meV for $Q = 1.3$ Å^{-1}, and its magnetic origin is proved by the Q and T dependences of its intensity. The peak almost disappears when Q increases to ≈ 1.7 Å^{-1} (see Fig. 6) or the temperature is raised to about 30 K. Releasing the pressure results in the suppression of this peak, whereas the original one reappears at approximately 13 meV. The energy difference of about 1 meV with respect to the previous measurements at ambient pressure may result from residual stresses, because the helium pressure was released without heating the pressure cell. Unfortunately, we could not study the anisotropy in detail due to low intensity of the signal, but it follows from the experimental data that the anisotropy is changed qualitatively with respect to SmB_6. The general trends of the pressure effect are opposite to those observed with La substitution: the energy of the peak becomes lower, and the Q dependence seems even steeper than in SmB_6 at ambient pressure.

The influence of the valence variation on the Q dependence of the intensity of the low-energy excitation is summarized in Fig. 6 for the different samples discussed above. The form factor of the inter-multiplet $J = 0 \rightarrow J = 1$ transition for the Sm^{2+} state (the lowest possible valence) with energy 36 meV is also shown in Fig. 6. Systematic changes are clearly observed for samples $Sm_{1-x}La_xB_6$ where an increase in x leads to the decrease in the Sm-average valence (18, 19). For these samples a lower valence results in a smoother Q dependence. This effect can be interpreted as the result of changing the extent of the spatial distribution of the electronic density associated with the

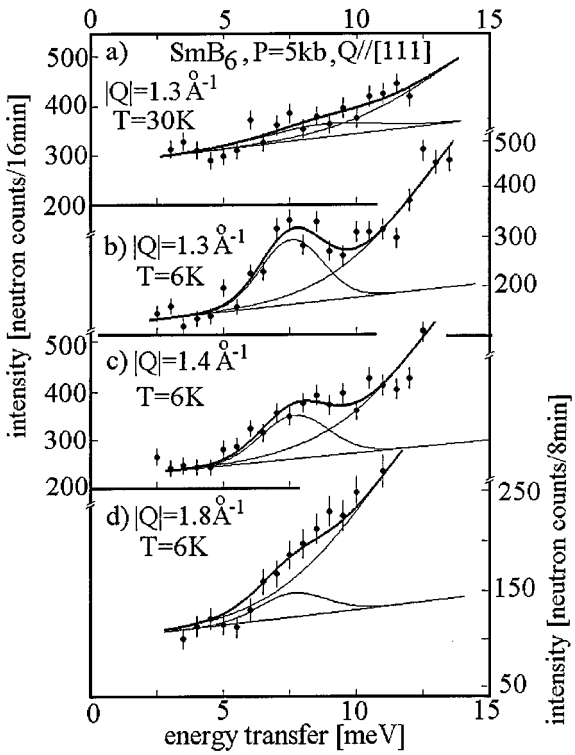

FIG. 5. Neutron scattering spectra of single crystal SmB_6 under the pressure $P = 0.5$ GPa measured in the constant k_f mode ($E_f = 14.7$ meV) fixed scattering vector $\mathbf{Q} = (q, q, q)$: (a) $T = 30$ K, $q = 0.5$, $Q = 1.3$ Å^{-1}; (b) $T = 6$ K, $q = 0.5$, $Q = 1.3$ Å^{-1}; (c) $T = 6$ K, $q = 0.54$, $Q = 1.4$ Å^{-1}; (d) $T = 6$ K, $q = 0.70$, $Q = 1.8$ Å^{-1}. The magnetic excitation at 7.5 meV is fitted by a Gaussian.

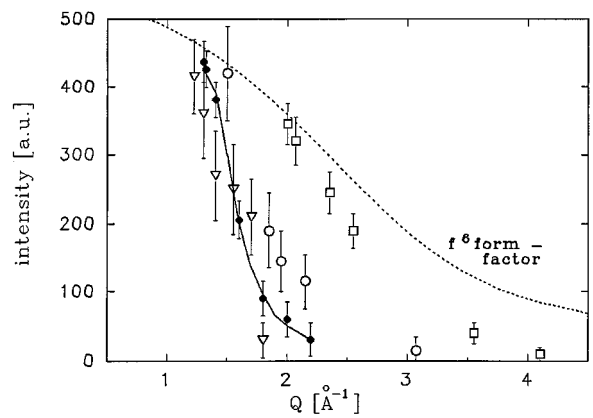

FIG. 6. Integrated intensity of the low-energy excitation as a function of the momentum transfer Q; □, $Sm_{0.78}La_{0.22}B_6$; ○, $Sm_{0.9}La_{0.1}B_6$; ▽, SmB_6. $P = 0.5$ GPa; solid line and points, SmB_6, $P = 0$, experimental data from (16); dashed line, calculated f^6 form factor.

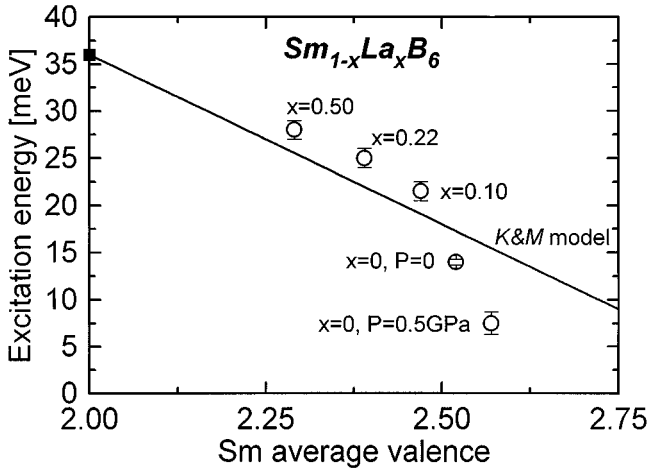

FIG. 7. Dependence of the magnetic excitation energy (lower peak) on the Sm valence in $Sm_{1-x}La_xB_6$; circles, these experiments; square, energy of the inter-multiplet transition for the f^6 configuration of Sm^{2+}; line, calculation for the model of Ref. (20).

excitation. The correlation between the position of the low-energy peak and the average valence is presented in Fig. 7. The low-temperature value of the Sm valence was estimated to be 2.52 for SmB_6, ≈ 2.47 for $x = 0.1$, and ≈ 2.39 for $x = 0.22$, with an accuracy of 0.02. In the same graph, the data from Ref. (17) for the polycrystalline $Sm_{0.5}La_{0.5}B_6$ sample are also shown. From this plot it is tempting to speculate that, on further decreasing the valence to the limiting value $v = 2$, the energy of the peak would tend toward the value of 36 meV corresponding to the stable $4f^6$ shell. This conclusion is supported by the analysis of the Q dependences, as the change of the valence to more 2+ results in a more localized electronic distribution with a form factor getting closer to that of a stable $4f^6$ shell. It can be remarked that, both in SmB_6 under pressure and for small La substitution ($x = 0.1$), the parameters of the low energy peak change more rapidly with the valence that in the solid solutions that contain a higher concentration of impurity ions in the Sm sublattice.

DISCUSSION

We shall now discuss possible theoretical descriptions of the Sm mixed-valence ground state which may be relevant to the present experimental results. The model elaborated by Kikoin and Mishchenko (20) is based on the same representation of the MV wavefunction that they used in their previous calculations of phonon anomalies. Essential to this model is the existence of two components (local 4*f*-like, and extended) in the total wavefunction. The local part is sensitive to interactions localized in the core of the ion, in particular to the spin–orbit coupling which defines the energy spectrum of the magnetic excitations from this ground state wavefunction. The excitation energy is directly related to the relative weight of the localized part and can thus be expected to increase gradually as the valence state of Sm becomes closer to 2+. In Fig. 7 the straight line shows how the excitation energy should depend on the valence according to Ref. (20). This model basically does not take into account any correlation in the Sm sublattice, and effects such as the small energy dispersion have to be explained by a weak overlap of the tails of the extended part of the MV wavefunction. A different approach has been proposed by Kasuya (21) in the context of a general discussion of Kondo insulators. In contrast to the previous model, this theory is essentially based on an inhomogeneous description of the MV state (i.e., Sm^{2+} and Sm^{3+} ions located at different sites), with the low-energy excitation arising from "Kondo" bound electron states occurring at the trivalent sites. Its energy is defined as the energy difference between two different electronic bound states of f and s symmetry. In such a picture, the variation of the average valence corresponds to a change in the number of Sm^{2+} sites and is not expected to produce a strong change in the energy of the excitation. In the case of solid solutions, it has been argued (22) that the low-energy peak observed in solid solutions is different in nature from that of pure SmB_6 and could arise from a local CEF state occurring at distorted Sm sites possessing La neighbors. However, this picture does not explain so far the anomalous Q dependence of the intensity in the alloy systems nor why one does not observe distinct several peaks corresponding to different La/Sm occupations of the Sm coordination shell with comparable probabilities.

Both models can explain the **Q** dependence of the intensity for the 14 meV peak in SmB_6. The smooth variation of the low-energy excitation properties with the valence is more consistent with the excitonic model of Refs. (14) and (20), but we have already noted that the exact dependence of the excitation energy is not a simple linear function of the valence, as suggested by the model. The strongest difference between the predicted and experimentally observed dependences takes place in the region where the Sm sublattice is almost fully occupied, and only in the highly diluted state, in the vicinity of $x = 0.5$, does the character of the valence-induced changes become close to the predictions. This suggests that the interaction between different Sm sites may contribute to the formation of this excitation and has to be taken into account in a more realistic model. We will not discuss here the temperature effects at any length because they are not treated quantitatively in the above models, which simply ascribe them to a destabilization of the excitonic state (see also Ref. (3)). Let us emphasize, however, the following important experimental features: (i) the temperature variation is steep and depends on the valence (ii) inelastic spectral weight is transferred to the quasielastic region when temperature increases.

In this survey, we have tried to show that after the burst of interest in MV materials during the 1970–1980s and the subsequent shift of activity toward other strongly correlated systems, some fundamental questions have been left unsettled. In the case of SmB_6, some of them can be revisited based on a new generation of experimental studies, especially using inelastic neutron scattering. Interesting, and quite unexpected, results have been obtained, stimulating in turn new theoretical ideas as to the nature of the quantum ground state in MV compounds with a narrow gap. The existence of a local electronic bound state in Sm systems is now well-substantiated by results of lattice and magnetic dynamics, but its exact origin is still open to discussion.

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