Available online at www.sciencedirect.com
ScienceDirect
Journal of Solid State Chemistry 179 (2006) 2858–2861
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Spin-gap magnetic response in (Yb, Lu)B_{12}

E.V. Nefeodova[a,*], P.A. Alekseev[a], J.-M. Mignot[b], K.S. Nemkovski[a], V.N. Lazukov[a], I.P. Sadikov[a], Yu.B. Paderno[c], N.Yu. Shitsevalova[c], R.I. Bewley[d]

[a]*RRC "Kurchatov Institute", 123182 Moscow, Russia*
[b]*Laboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay, 91191 Gif sur Yvette, France*
[c]*Institute of Materials Science, NASU, Kiev, Ukraine*
[d]*Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK*

Received 30 August 2005; received in revised form 26 October 2005; accepted 16 January 2006
Available online 9 February 2006

Abstract

To clarify the role of Yb–Yb correlations in the formation of the gap-like excitation spectrum of YbB_{12}, the spin dynamics of strongly diluted $Yb_{0.25}Lu_{0.75}B_{12}$ have been studied by inelastic neutron scattering in a wide temperature range. The data indicate that the spin gap is not suppressed by the dilution process even for large concentrations of Lu. However, the breaking-down of the Yb-sublattice periodicity leads to a strong smearing of the low-energy features and to a moderate suppression of the high-energy peak in the magnetic spectral response of YbB_{12}. The interrelation of the spin and charge gaps is discussed.

Keywords: Kondo insulator; Inelastic neutron scattering; Spin gap

1. Introduction

The dodecaboride compound YbB_{12} belongs to the class of so-called Kondo insulators. It behaves as a metal or a semimetal with localized magnetic moments at room temperature, but becomes a nonmagnetic semiconductor with a narrow gap at the Fermi energy with decreasing temperature. Inelastic neutron scattering (INS) measurements have revealed that YbB_{12} has a magnetic excitation spectrum unlike other systems with valence instabilities [1,2]. The most intriguing feature in the magnetic response of YbB_{12} is the spin gap like behaviour below $E = 10$ meV at low temperature. Above this level of energy the spectrum consists of three main components: two narrow peaks at $E = 15$ and 20 meV, and a broad peak at 38 meV. Increasing temperature produces drastic changes in the spectral response: (i) the two low-energy excitations are replaced by one peak at about 23 meV; (ii) a substantial quasielastic peak appears, whereas the upper (38 meV) inelastic peak is totally suppressed. These two contrasting forms of the magnetic response at $T \approx 15$ and ~ 100 K can, respectively, be associated with the Kondo-insulator ground state and a single-ion-type state, which is recovered with increasing temperature.

The spin gap value defined from INS is comparable to the energy of the charge gap in the electron density of states determined from transport [3], heat capacity [4], and optical conductivity [5] measurements. The relation between these two gaps is one of the central questions of the Kondo-insulator phenomenon. The theoretical models proposed for Kondo insulators are controversial and consider Yb-sublattice coherence as either essential [6] or irrelevant [7] to the gap formation. In a recent study of the effect of Lu substitution on the magnetic spectral response in YbB_{12} [8], it was concluded that Yb-sublattice coherence is the most important factor affecting the low-energy structure near the gap at low temperatures, but that the spin gap itself may have a primarily incoherent character, as it is still found to exist in the $Yb_{0.75}Lu_{0.25}B_{12}$ spectra. The high-temperature limit of the Yb magnetic spectrum is not influenced by 25% substitution and can be treated as representative of the "single-ion" spin-fluctuation regime. Surprisingly, even for the high concentration of

*Corresponding author. Fax: +7 095 1965973.
E-mail address: elene@isssph.kiae.ru (E.V. Nefeodova).

0022-4596/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2006.01.029

non-magnetic defects (90%) the spin gap does not seem to disappear, i.e. the $Yb_{0.1}Lu_{0.9}B_{12}$ magnetic excitation spectrum does not show any observable quasi-elastic signal at low temperature. The spectrum is dominated by the broad peak centred around 38 meV, whereas the components become undetectable at 15 and 20 meV. Unfortunately, the measured intensity of the magnetic signal in $Yb_{0.1}Lu_{0.9}B_{12}$ was rather weak because of the low Yb concentration. Furthermore, the whole magnetic scattering cross-section is located in the broad peak, making the information obtained difficult to treat quantitatively. Finding clear evidence for the spin gap in a strongly diluted compound remains a major point for discussing this feature in general, and for selecting the correct approach to analysing the experimental spectra.

In this paper, we present results of a detailed INS study of the magnetic response and its temperature dependence in strongly diluted $Yb_{0.25}Lu_{0.75}{}^{11}B_{12}$. This concentration can still be assumed to represent a predominantly single-site behaviour for the Yb spin dynamics, while providing a substantial improvement in the statistical accuracy in comparison with $Yb_{0.1}Lu_{0.9}B_{12}$. We will discuss the evolution of the spin gap as a function of temperature and Lu concentration, and compare it to the corresponding evolution of the charge gap obtained from optical spectroscopy [5].

2. Experiment

Powder samples of $Yb_{0.25}Lu_{0.75}{}^{11}B_{12}$ ($m\sim10$ g) and of the reference compound $Lu^{11}B_{12}$ ($m = 5.85$ g) were prepared at NASU Institute for Problems of Materials Science (Kiev, Ukraine) by borothermal reduction at 1700 °C under vacuum. To reduce the neutron absorption, samples were prepared using ^{11}B isotope with 99.5% enrichment. The neutron scattering experiment was performed on the time-of-flight spectrometer HET (ISIS, RAL) with two incident neutron energies $E_0 = 80$ or 50 meV, which provide resolutions (full-width at half-maximum of the elastic line in vanadium) of 3.6 and 2.0 meV, respectively. Measurements were taken at three temperatures: 10, 70, and 120 K. The experimentally defined transmission of the $Yb_{0.25}Lu_{0.75}{}^{11}B_{12}$ sample was 80% for $E_0 = 80$ meV. The $Lu^{11}B_{12}$ sample was used for estimating the phonon contribution. The magnetic part of the $Yb_{0.25}Lu_{0.75}{}^{11}B_{12}$ spectra was determined by the standard procedure using the ratio of $Lu^{11}B_{12}$ spectra for low and high scattering angles [9]. Absolute calibration was effected by normalization to a vanadium standard.

3. Results and discussion

Fig. 1 presents magnetic scattering functions for $Yb_{0.25}Lu_{0.75}B_{12}$ at the two limiting temperatures, $T = 10$ and 120 K. Data from Ref. [8] for YbB_{12} and $Yb_{0.75}Lu_{0.25}B_{12}$ are shown for comparison.

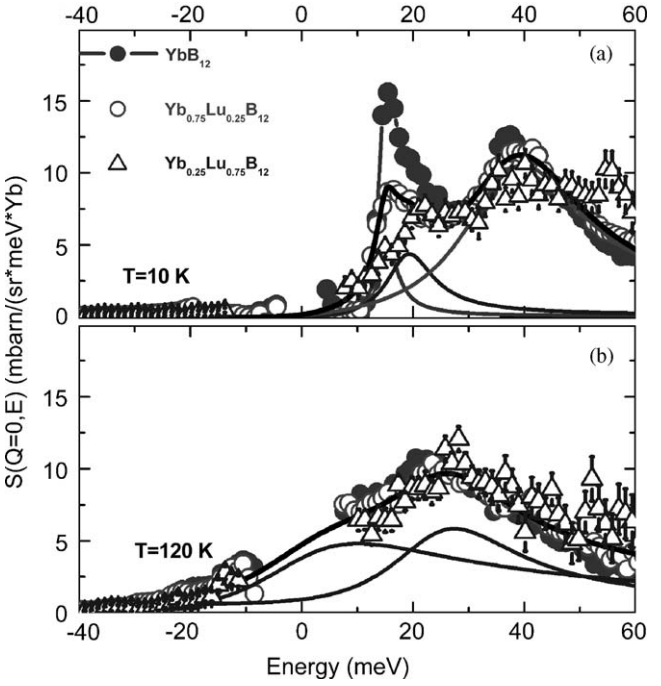

Fig. 1. Magnetic excitation spectra of $Yb_{1-x}Lu_xB_{12}$ at $T = 10$ K (a) and 120 K (b); the YbB_{12} (solid circles) and $Yb_{0.75}Lu_{0.25}B_{12}$ (open circles) spectra were measured with the incident energy $E_0 = 80$ meV [8]; the $Yb_{0.25}Lu_{0.75}B_{12}$ (triangles) spectrum was obtained as a combination of magnetic scattering spectra measured at $E_0 = 50$ and 80 meV. Lines represent a fit of the $Yb_{0.75}Lu_{0.25}B_{12}$ spectrum by the inelastic and quasi-elastic Lorentzian peaks.

The important experimental factor (Fig. 1a) is the clear evidence for the absence (or at least the strong suppression) of the magnetic signal at low temperature within the energy range of the gap regardless of Lu concentration. The three-peak structure observed in the YbB_{12} magnetic spectrum is retained in the case of $Yb_{0.75}Lu_{0.25}B_{12}$. The increase of the Lu concentration in $Yb_{1-x}Lu_xB_{12}$ from $x = 0.25$ to 0.75 results in a further broadening and a strong suppression of the near-gap low-energy peaks. This confirms that the low-energy part of the YbB_{12} inelastic magnetic spectral response at low temperature depends strongly on the concentration of non-magnetic defects.

In comparison with these near-gap components, the broad 38-meV peak appears to be much more robust with respect to the substitution (Fig. 1a). There was some indication, in the results of Ref. [8] for $x = 0.25$, of a limited change in the 38-meV peak. This peak had a shoulder at 42 meV for $x = 0$, which was not observed for $x = 0.25$. The intensity change, on the other hand, was small enough and remained within the limits of experimental accuracy. For $x = 0.75$ significant broadening is observed (Fig. 1a), and the peak shape becomes more symmetric, while its amplitude is clearly reduced.

Therefore, the breakdown of periodicity on the Yb-sublattice leads to a strong suppression of the low-energy features and a moderate change in the high-energy peak of the YbB_{12} magnetic spectral response. The important point is that no quasi-elastic scattering is observed even for

samples with high Lu concentration, implying that the spin gap itself exists over a large range of concentrations of non-magnetic "defects".

Increasing the temperature to $T \approx 120\,\mathrm{K}$ drastically changes the spectral shape of the $Yb_{0.25}Lu_{0.75}B_{12}$ magnetic response. The effect is analogous to that observed in pure YbB_{12}. Quite remarkably, all spectra measured in this regime have almost identical profiles irrespective of the Lu concentration, which means that the same limiting behaviour is achieved with increasing temperature independently of the presence of non-magnetic defects on the Yb-sublattice. This result supports the assumption, made previously for pure YbB_{12}, that the high-temperature regime is dominated by single-site magnetic fluctuations. Two main contributions to the spectral function can be identified: a broad quasi-elastic peak, and an inelastic peak at energy $\approx 23\,\mathrm{meV}$ (Fig. 1b). The latter component is associated with the deviation of the magnetic susceptibility in this compound from a Curie law occurring at relatively high temperature as shown in Ref. [2].

It should be noted that Lu substitution and temperature affect the spin gap of YbB_{12} in different ways. Lu substitution has a relatively weak effect, whereas increasing temperature suppresses the spin gap drastically for all concentrations of Lu.

It is interesting to compare the effects of Lu substitution and temperature on the magnetic and optical spectra. As shown in [5] from reflectivity measurements, a well-developed charge gap is observed at low temperature only for a nearly perfect lattice of Yb ions, in strong contrast to our observations regarding the spin gap. However, both the charge and spin gaps are found to vanish with increasing temperature at all studied Lu concentrations. The fact that these two peculiar features form simultaneously below 70 K suggests that they are closely related.

One possible mechanism for the occurrence of a charge gap Δ_c was introduced in [10] in connection with optical measurements on the Kondo insulator $Ce_3Bi_4Pt_3$. It was argued that the charge gap formation in that material is a consequence of the local Kondo coupling of the charge carriers to the Ce 4*f* magnetic moments. In this model the opening of the charge gap, i.e. the localization of conduction electrons, is due to the *d* electrons becoming involved in the singlet formation, and the suppression of charge carriers is thus expected to scale with the number of quenched Ce magnetic moments, as was observed experimentally in $Ce_3Bi_4Pt_3$.

A similar analysis can be carried out in the case of YbB_{12}. The effective density of localizing carriers is calculated from the optical conductivity [5] using the optical sum rule

$$N_{\mathrm{eff}} = \frac{\Delta n(T)}{m^*} \sim \int_0^{\Delta_c} \sigma(\omega, T)\,\mathrm{d}\omega - \int_0^{\Delta_c} \sigma(\omega, 300\ \mathrm{K})\,\mathrm{d}\omega. \quad (1)$$

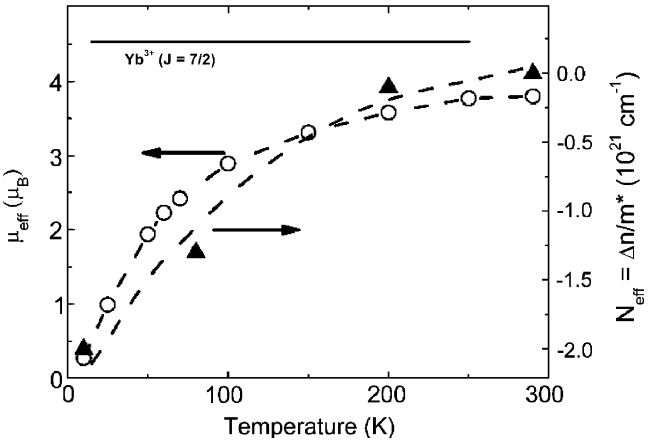

Fig. 2. Temperature dependence of the effective Yb magnetic moment μ_{eff} in YbB_{12} (left axis), and the number of localized charge carriers N_{eff} (right axis); the solid line is the Hund's rule value for Yb^{3+}; dashed lines are guides for the eye.

The notation is that of [10], with $\sigma(\omega)$ being the optical conductivity, n the carrier density, m^* the effective mass in units of the free electron mass m_0. The effective magnetic moment μ_{eff} is derived from the measured local magnetic susceptibility [2]:

$$\chi = \mu_{\mathrm{eff}}^2(T)/3k_{\mathrm{B}}T \quad (2)$$

assuming a Curie law for the ionic 4*f* states. The resulting effective magnetic moment per Yb ion and effective carrier density are plotted in Fig. 2 as a function of temperature.

One notices that both quantities decrease on cooling, and that the suppression of charge carriers approximately follows the reduction of the local Yb 4*f* magnetic moment. This observation suggests that the charge gap is not a one-electron band structure effect, but is governed by the formation of the Kondo singlet, in analogy with $Ce_3Bi_4Pt_3$. In this sense, the charge and spin gaps can be regarded as the consequence of a common physical mechanism.

One of the possible reasons why the effect of alloying on the charge and spin gaps in YbB_{12} may be different is that the suppression of the charge gap by Lu substitution obtained from optical and bulk properties is sensitive to the formation of impurity states near the bottom of the conduction band. This assumption is consistent with the remark made in [5] that the gap in $\sigma(\omega)$ is suppressed "by filling in from the bottom, rather than by narrowing". In diluted samples, the charge gap becomes a "pseudo-gap" and can exist over a wide range of Lu concentrations as observed here also for the spin gap.

4. Conclusion

The role of Yb–Yb correlations in the Kondo insulator YbB_{12} was studied by means of INS on a $Yb_{0.25}Lu_{0.75}{}^{11}B_{12}$ powder sample. The spin gap is still observable at this composition, which corresponds to the strongly diluted limit of the YbB_{12} Kondo insulator. Therefore, the

formation of a spin gap in the magnetic excitation spectra of YbB_{12} appears to be the result of single-site (local) processes. On the other hand, the low-energy structure near the gap edge and, to some extent, the 38 meV peak at low temperature are affected by the disruption of periodicity on the Yb-sublattice or by magnetic (''inter-site'') correlations. At $T > 100$ K, 4*f*-electron correlations are suppressed and the magnetic excitation spectrum corresponds to the spin-fluctuation response of uncorrelated Yb ions regardless of the Lu concentration. It has been shown that the formation of the gap in the charge density of states is directly related to the suppression of local magnetic moments, lending support to the assumption that the Kondo coupling is the basic mechanism responsible for the formation of both the charge and spin gaps in YbB_{12}.

Acknowledgments

P.A.A. and E.V.N. are grateful to ISIS facilities for financial support and hospitality during their stay at RAL for the measurement. The work was supported by INTAS Grant no. 03-51-3036, RFBR Grant no. 05-02-16426, and Grant HIII-2037.2003.2.

References

[1] A. Bouvet, T. Kasuya, M. Bonnet, L.P. Regnault, J. Rossat-Mignod, F. Iga, B. Fåk, A. Severing, J. Phys.: Condens. Mater. 10 (1998) 5667–5677.
[2] E.V. Nefeodova, P.A. Alekseev, J.-M. Mignot, V.N. Lazukov, I.P. Sadikov, Yu.B. Paderno, N. Yu. Shitsevalova, R.S. Eccleston, Phys. Rev. B 60 (1999) 13507–13514.
[3] F. Iga, N. Shimizu, T. Takabatake, J. Magn. Magn. Mater. 177–181 (1998) 337–338.
[4] F. Iga, S. Hiura, J. Klijn, N. Shimizu, T. Takabatake, M. Ito, Y. Matsumoto, F. Masaki, T. Suzuki, T. Fujita, Physica B 259–261 (1999) 312–314.
[5] H. Okamura, M. Matsunami, T. Inaoka, T. Nanba, S. Kimura, F. Iga, S. Hiura, J. Klijn, T. Takabatake, Phys. Rev. B 62 (2000) R13265–R13269;
H. Okamura, M. Matsunami, T. Inaoka, S. Kimura, T. Nanba, F. Iga, S. Hiura, T. Takabatake, J. Phys. Soc. Jpn. 71 (2002) 303–305.
[6] P.S. Riseborough, Adv. Phys. 49 (2000) 257–320.
[7] S.H. Liu, Phys. Rev. B 63 (2001) 115108-1-115108-6.
[8] P.A. Alekseev, J.-M. Mignot, K.S. Nemkovski, E.V. Nefeodova, N.Yu. Shitsevalova, Yu.B. Paderno, R.I. Bewley, R.S. Eccleston, E.S. Clementyev, I.P. Sadikov, N.N. Tiden, J. Phys.: Condens. Mater. 16 (2004) 2631–2646.
[9] A.P. Murani, Phys. Rev. B 50 (1994) 9882–9892.
[10] B. Bucher, Z. Schlesinger, P.C. Canfield, Z. Fisk, Phys. Rev. Lett. 72 (1994) 522–525.