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Lattice dynamics in the Kondo insulator YbB_{12}

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Abstract

The phonon dispersion in the Kondo-insulator YbB_{12} and its structure analogue LuB_{12} has been studied in a wide energy range (up to 55 meV) by means of inelastic neutron scattering. The specific shape of phonon dispersion curves for low-frequency lattice vibrations could be described on the basis of a strong hierarchy suggested for the interactions between boron and rare-earth (RE) atoms: B–B $\gg$ B–RE $\gg$ RE–RE.

Keywords: Kondo insulator; Dodecaborides; Phonons; Inelastic neutron scattering

1. Introduction

YbB_{12} is a typical member of the class of materials broadly known as "Kondo-insulators". This term denotes compounds which are close to valence instability and become semiconducting with a narrow energy gap at low temperature [1]. Understanding the origin of this unconventional insulating ground state is one of the key questions in the physics of strongly correlated electron systems [2]. At low temperatures, the magnetic spectral response of YbB_{12} exhibits a spin gap, which disappears when the Kondo-insulating regime is suppressed by increasing temperature. Various models have been proposed to account for the formation of the spin gap, based on either inter-band transitions in the (coherent) hybridization-gap picture [2], or a local mechanism leading to an array of single-site "Kondo singlets" [3]. These approaches are basically related to the electron subsystem and disregard the possibility of an interplay with lattice vibrations, even though the energy of the near-gap excitations in YbB_{12} as well as the spin-gap itself are known to fall in the range of acoustic and lower optic phonon modes [4,5], and a feedback to the lattice is not unlikely for materials with a valence instability. Therefore, the interesting experimental question is: could the phonons be somehow related to the peculiarities of the excitation spectra and consequently to the formation of the Kondo-insulator ground state in YbB_{12}?

On the other hand, systems based on Kondo-insulators are considered to be perspective candidates for designing high-performance low-temperature thermoelectric materials, and a better understanding of the underlying physical phenomena is important also for this purpose. In particular, studies of the lattice dynamics in these compounds could provide a scientific background for improving the thermal conductivity characteristics of the materials synthesized.

The clearest evidence for a strong electron–phonon interaction in YbB_{12} could be expected to be obtained from the study of the temperature evolution of phonon modes. However, previous inelastic neutron scattering (INS) experiments on powder samples [4,5] did not reveal any temperature dependence of the phonon density of states

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(DOS) in YbB_{12}, and therefore a detailed study of the dispersion curves, and possibly of phonon line widths became necessary. The crystal lattice of YbB_{12} is a variant of the NaCl structure, with B_{12} cuboctahedra instead of chlorine occupying the anion sites. Although the symmetry is quite simple, the primitive cell contains 13 atoms, which means that there are up to 39 different phonon branches. Therefore, the analysis of the measured phonon spectra requires a correct identification of these branches based on a valid model for lattice dynamics.

In this paper, we present a detailed INS study of the low-energy (up to 55 meV) phonon branches in the Kondo-insulator YbB_{12} and its structure analogue LuB_{12} at room temperature. The results are phenomenologically analysed in terms of a Born–von Karman force-constant model, which gives interesting information on inter-atomic interactions, and can account for some peculiarities of the atomic movements in these materials. Preliminary results for YbB_{12} were reported in Ref. [6].

2. Experimental details

High-quality single crystals of YbB_{12} and LuB_{12} were grown by the traveling-solvent floating zone melting technique using ^{11}B isotope (99.5% enrichment) at Hiroshima University (YbB_{12}) and at the NASU Institute for Problems of Materials Science (LuB_{12}). The methods of sample preparation are described in detail in [7,8]. For our measurements we used an assembly of two YbB_{12} crystals (total volume of approximately 0.4 cm^3) aligned to better than 1° with respect to each other, and one large crystal of LuB_{12} ($v \approx 0.4\,cm^3$).

INS experiments were performed at room temperature on the thermal-beam triple-axis spectrometer 2T at the LLB (Saclay). The samples were oriented with a $\langle 110 \rangle$ crystal axis normal to the scattering plane. For YbB_{12}, neutron spectra were recorded at fixed final energy using a Cu 1 1 1 vertical-focusing monochromator, a PG 002 horizontal-focusing analyzer, and a graphite filter placed in the scattered beam to remove higher-order contamination. With the selected final energy of $E_f = 30.5$ meV, the resolution at zero energy transfer was approximately 2 meV (FWHM). We have measured the acoustic branches for the three main symmetry directions, along with several optic branches. The results of a first treatment of these data were published in [6]. However, after a more detailed analysis of the obtained data, it was found that the energy and momentum resolutions were not high enough, especially for identifying the optic branches.

A second series of measurements was thus undertaken using a PG 002 monochromator at a final energy of $E_f = 14.7$ meV yielding an energy resolution at zero energy transfer of approximately 0.8 meV. Unfortunately, this had the effect of restricting the accessible range of momentum transfer Q to smaller values, which turned out to be critical for validating a lattice dynamics model. The reason is that for this purpose, it is necessary to measure the same phonons at equivalent points near different Brillouin zone centers and to compare their intensities with calculated phonon structure factors. Decreasing the accessible Q range hampers this procedure because, at small Q, it is difficult to reliably separate the phonon and magnetic contributions to the scattering function. To circumvent this problem, we have performed separate measurements on LuB_{12}, which is isostructural to YbB_{12} but gives no magnetic contribution to the neutron scattering spectra. Previous powder data [4,5] had indicated that the phonon DOS in YbB_{12} and LuB_{12} have the same overall structure and are predominantly determined by boron vibrations, apart from differences at low energies, which are due to the different nuclear scattering lengths of Yb and Lu. Apparently, the structure of the phonon DOS is common to all rare-earth (RE) dodecaborides, and the study of LuB_{12} could also be relevant to the lattice dynamics in other dodecaborides. In our case, the phonon dispersion curves of YbB_{12} and LuB_{12} can be expected to be very similar, unless specific electron–phonon interaction effects arise from the unstable *f*-shell and Kondo-insulator state in Yb at *low temperature*. Since initially [6] the number of low-energy optic branches was not correctly determined because of limited resolution, we have repeated the fitting procedure of the YbB_{12} spectra taking into account the high-resolution data for LuB_{12}.

3. Results and discussion

Fig. 1 shows the experimental results for YbB_{12} and LuB_{12} along the three main symmetry directions, together with the dispersion curves obtained by fitting the data to the model discussed hereafter. One can see that, in agreement with our expectations from DOS measurements, the observed phonons have the same energies for both samples within experimental accuracy. One of the most interesting features is that the optic branches are separated from the acoustic ones by a gap of about 5 meV, and just near the gap edge a weak-dispersive optic branch exists close to 20 meV. We emphasize that this weakly dispersive branch, along with the acoustic ones, are the most plausible candidates for interplay with two magnetic excitations observed at about 20 and 15 meV, respectively [9]. Another important feature is that acoustic branches have a large dispersionless part. In the region of weak dispersion, longitudinal and transverse acoustic branches are almost degenerate. In powder experiments [4,5] Q-space averaging of the dispersionless parts of the acoustic branches resulted in a pronounced peak at 15 meV in the phonon DOS, which was attributed to the vibration of the RE atoms. It is known from the theory of lattice dynamics (see e.g. [10]) that such a shape of the dispersion curves indicates a weak bonding of the RE atoms with the boron sublattice.

For an interpretation of the results, we applied a simple Born–von Karman force-constant model using the UNISOFT software package [11]. One usually starts to develop a phenomenological model for lattice dynamics from the

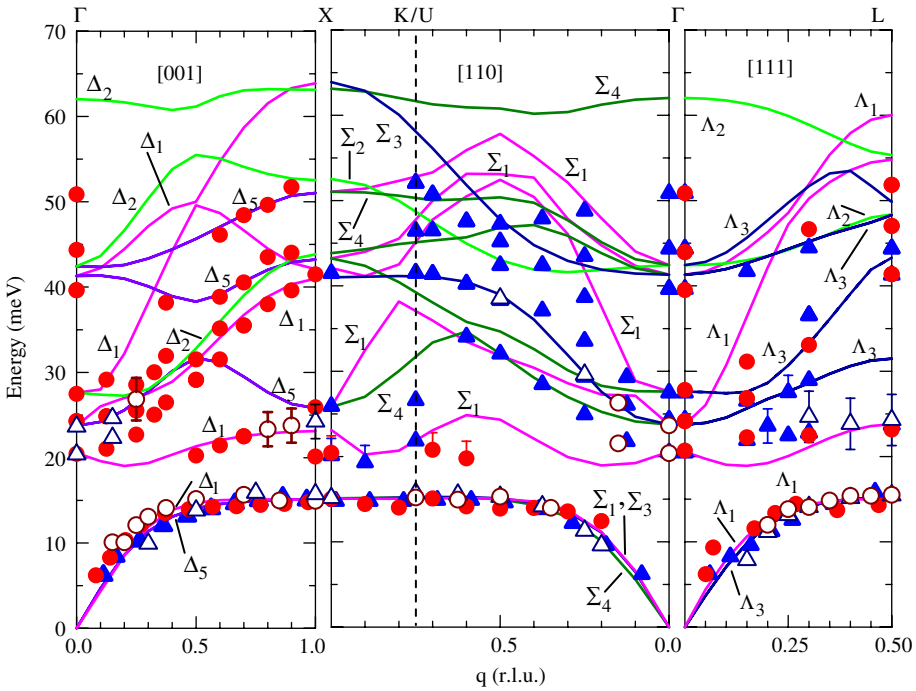

Fig. 1. Energy dispersion of phonons in YbB_{12} (open symbols) and LuB_{12} (closed symbols). Circles: longitudinal branches; diamonds: transverse branches. Lines represent the result of the UNISOFT model calculation. Irreducible representations of phonon branches are given in the Bouckaert–Smoluchowski–Wigner notation [12].

group-theoretical analysis of phonons in a wide enough energy range using data measured in a large number of different Brillouin zone centers, which gives the phonon symmetry. Based on this, one can determine a first set of model parameters consistent both with energies at the Γ point and with symmetry for all observed phonons. Some further variation of model parameters then allows the dispersion curves to be described satisfactorily within the entire Brillouin zone. In our case, the realization of this scheme was strongly hampered because the number of phonon branches (39) is quite high and the phonon spectrum extends up to energies of about 130 meV [5]. On the other hand, the analysis of the low-energy part of the spectrum only is also not simple because the symmetry of the corresponding phonon branches is not known in advance. In order to determine phonon symmetry, we performed measurements near several Brillouin zone centers chosen on the basis of our previous model calculations [6]. We have found a set of model parameters for which the number of calculated branches below 55 meV was sufficient to qualitatively describe the experimental points. Then we checked the symmetry of the corresponding calculated branches by comparing calculated dynamical structure factors with experimental phonon intensities for all studied Brillouin zones. Finally, we fitted the calculated dispersion curves to the experimental data placing emphasis on the low-energy part of the phonon spectrum. Since UNISOFT does not include a fitting option, one can only calculate the dispersion curves, structure factors, etc. for some particular values of the inter-atomic potential.

Table 1
Atomic positions in the primitive cell of REB_{12}

Atom	Atomic position
RE	(0, 0, 0)
B_a	(0.50, 0.67, 0.67)
B_b	(0.50, 0.33, 0.33)
B_c	(0.67, 0.50, 0.33)
B_d	(0.33, 0.50, 0.67)
B_e	(0.67, 0.50, 0.67)
B_f	(0.33, 0.50, 0.33)
B_g	(0.33, 0.67, 0.50)
B_h	(0.67, 0.33, 0.50)
B_i	(0.67, 0.67, 0.50)
B_j	(0.33, 0.33, 0.50)
B_k	(0.50, 0.33, 0.67)
B_l	(0.50, 0.33, 0.33)

Different boron atoms are labelled by the indices *a* to *l*.

Several series of trial runs were thus made to find a set of force constants parameters providing the best quantitative description for acoustic branches along the main symmetry direction and for three lower groups of optic branches at the Γ point.

The main idea of the model was suggested in our previous work [6]. Based on specifics of the dodecaboride structure, we assumed that the YbB_{12} lattice can be considered as Yb atoms embedded in a boron "skeleton". This means that boron atoms interact more strongly with one another than with ytterbium, and that interactions between ytterbium atoms are mainly mediated by boron

Table 2
Force constant parameters for $Yb(Lu)B_{12}$

Coordination sphere number	Interaction									
	RE–RE			RE–B			B–B			
	Inter-atomic distance (Å)	L (N/m)	T (N/m)	Inter-atomic distance (Å)	L (N/m)	T (N/m)	Inter-atomic distance (Å)	Interacting pair	L (N/m)	T (N/m)
1	5.28	−0.5	−0.5	2.78	2.5	5	1.76	B_a–B_b	3	0
								B_a–B_d	−1.2	3.5
2				4.13	4	2	2.49	B_a–B_k	0.5	130
3							3.05	B_a–B_c	−0.15	0
4							3.52	B_a–B_b	0	0
								B_a–B_d	0	0
5							3.93	B_a–B_k	15	−3
6							4.31	B_a–B_c	34	0
7							4.66	B_a–B_b	3	−0.7
								B_a–B_d	0	0
8							5.28	B_a–B_a	0	0
								B_a–B_c	−0.25	0
9							5.56	B_a–B_b	40	0
								B_a–B_d	−1.7	0

L and T denote longitudinal and transverse force constants, respectively.

atoms, the direct interaction between ytterbium atoms being the weakest. This supposition is in good agreement with the above-mentioned features of the acoustic phonon branches. However, the model suggested in [6] fails to describe the large number of low-energy optic branches, as well as the small splitting of longitudinal and transverse acoustic branches. The boron sublattice appeared to be too rigid and there were not enough degrees of freedom for the realization of low-energy boron vibrations.

In our improved model, we have taken into account a larger number of coordination spheres. It was found that in order to achieve reasonably good agreement between the calculation and the experimental data for the dispersion curves and the dynamical structure factors, it is necessary to include one coordination sphere for Yb–Yb interactions, two for Yb–B interactions and nine for B–B interactions. We also emphasize that, in our model, force constants are anisotropic. Although all boron positions are equivalent, the atoms are different from the point of view of the positional relationships and hence of the interactions among them. As a result, it is necessary for the presentation of the model to label boron atoms within the primitive cell. The atom types in UNISOFT notation and their positions are listed in Table 1. The model parameters derived from the above analysis are listed in Table 2.

In Fig. 1, one can see that the calculated dispersion curves shown as solid lines are quite close to the experimental data points. The model simultaneously provides a quantitative description of the acoustic branches, a semi-quantitative description of the dispersion for the low-energy optic phonons, and a qualitative description of the upper part of the measured energy range. Interestingly, the above-mentioned low-energy optic modes arise predominantly from movements and "breathing" of B_{12} cuboctahedra. It is also worth noting that the cut-off energy of the phonon spectrum in our model is 128 meV, which is is very close to the experimental value of 130 meV [5].

4. Conclusion

The lattice dynamics in the Kondo-insulator YbB_{12} and its structure analogue LuB_{12} was studied by means of INS. It was found that there is a strong hierarchy in the strength of inter-atomic interactions in these compounds: the B–B interaction is stronger than the B–RE interaction, which itself is stronger than the RE–RE interaction. As a result, vibrations of rare-earth atoms can be regarded as "rattling" modes, very much like those observed in filled skutterudites [13], whereas the lower optic branches correspond mainly to vibrations and "breathing" of B_{12} nano-clusters. These optic phonons, as well as the acoustic modes, fall within the energy region of the magnetic excitations in YbB_{12}. In principle, due to symmetry they might be involved in sizable electron–phonon interaction and therefore play a role in the formation of the unusual magnetic excitation spectrum. Evidence, however, remains to be produced for the existence of such an effect.

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