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Local lattice dynamics and isotope effect in yttrium diboride probed by extended x-ray absorption fine structure spectroscopy

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Abstract. The lattice vibration properties and the boron isotope effect have been studied in YB₂ by using temperature-dependent extended x-ray absorption fine structure (EXAFS). The data show anomalous behavior of the Debye–Waller factor of the Y–B pair due to the superposition of an optical mode associated with the boron sublattice and an acoustic mode corresponding to the yttrium sublattice. We claim that the observed decoupling between metal and boron vibrations is responsible for the lower transition temperature compared to MgB₂. The analysis of the boron isotope effect confirms also that the B–B vibration mode plays a key role in the electron–phonon coupling.

Since the beginning of the new century, two important discoveries have been made in superconductivity research. Two new types of superconductor materials, MgB₂ [1] and iron-based superconductors [2, 3], are now available. The transition temperature (T_c)

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of MgB_2 is close to the McMillan limit [4], while several iron-based superconductors exhibit critical temperatures beyond this limit. Therefore, among the many open questions regarding new superconductors such as MgB_2 and the iron-based superconductors, one concerns their superconductive mechanisms and the possibility of including them within the Bardeen–Cooper–Schrieffer (BCS) framework. Isotopic substitution is a fundamental test of the superconducting nature of a material. For a BCS superconductor, in which the mechanism is mediated by the electron–phonon coupling, the total isotope effect coefficient is about 0.5 [5], while from the experimental data the total isotope effect coefficient of MgB_2 is reduced to 0.32 [6], well below the typical value of a BCS system. This result suggests that the superconductive properties of MgB_2 are more complex in spite of its simple crystal structure. In addition, for the $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ compound, one of the new iron-based superconductors whose T_c is ~ 37 K, experimental data showed an iron isotope effect coefficient of ~ 0.4 [7]. Although without clear agreement, both data suggest that the electron–phonon interaction may play an important role in the superconductive mechanism of both MgB_2 and pnictides superconductors. Isotopic substitution affects the superconductive transition temperature via the dependence of the lattice dynamical properties of a crystal on the isotopic composition. Indeed, it is well known that the lattice dynamics is a key issue of the phonon–electron interaction in a BCS superconductor. Different research works [8]–[10] showed that thanks to its fast timescale and high spatial resolution, extended x-ray absorption fine structure (EXAFS) spectroscopy is an highly valuable tool to probe the local lattice dynamics.

Among the transition-metal diborides that share the same boron-layered structure of MgB_2 , YB_2 is a stimulating and puzzling system because it does not exhibit a comparable critical transition temperature and, in addition, is a useful system to understand how metal atoms affect the electron–phonon interaction by modulating the lattice vibrations. Indeed YB_2 shares a similar electronic structure to MgB_2 in contrast to other AlB_2 -type diborides [11]. In this contribution, we will report an accurate investigation of YB_2 and we will show how EXAFS is a unique technique to probe also the isotope effect and the local lattice dynamics of layered superconductors.

The YB_2 samples were synthesized by the direct reaction method of elemental yttrium and boron ($^{10}\text{B}/^{11}\text{B}$) (Eagle Picher 99% purity). The starting powders were mixed in the stoichiometric ratio and pressed into pellets. The sample pellets were enclosed in tantalum crucibles sealed by arc welding under argon atmosphere, followed by a repeated sintering process around 1000°C . The samples were well characterized for the average structure and phase purity by x-ray diffraction. Samples measured by complex conductivity using the single coil method did not show superconductivity down to 4 K. Temperature-dependent yttrium K-edge absorption measurements on YB_2 compounds were performed with an accuracy of ± 1 K using a Si (111) double crystal monochromator at the XAFS station of the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF). The storage ring was working at 2.2 GeV with an electron current decreasing from 120 to 80 mA in the span time of 12 h. Samples were ground into fine powders and brushed onto tapes that were stacked together to give approximately one x-ray-absorption length at their corresponding metal edges. Data were processed and analyzed using the UWXAFS [12] package of the University of Washington and the FEFF 8.0 [13] package to generate scattering amplitudes and phase shifts starting from the XRD refinement of the investigated samples. Preparation, experimental details of the EXAFS measurements and data analysis are the same as those for other diborides described in [14]–[16].

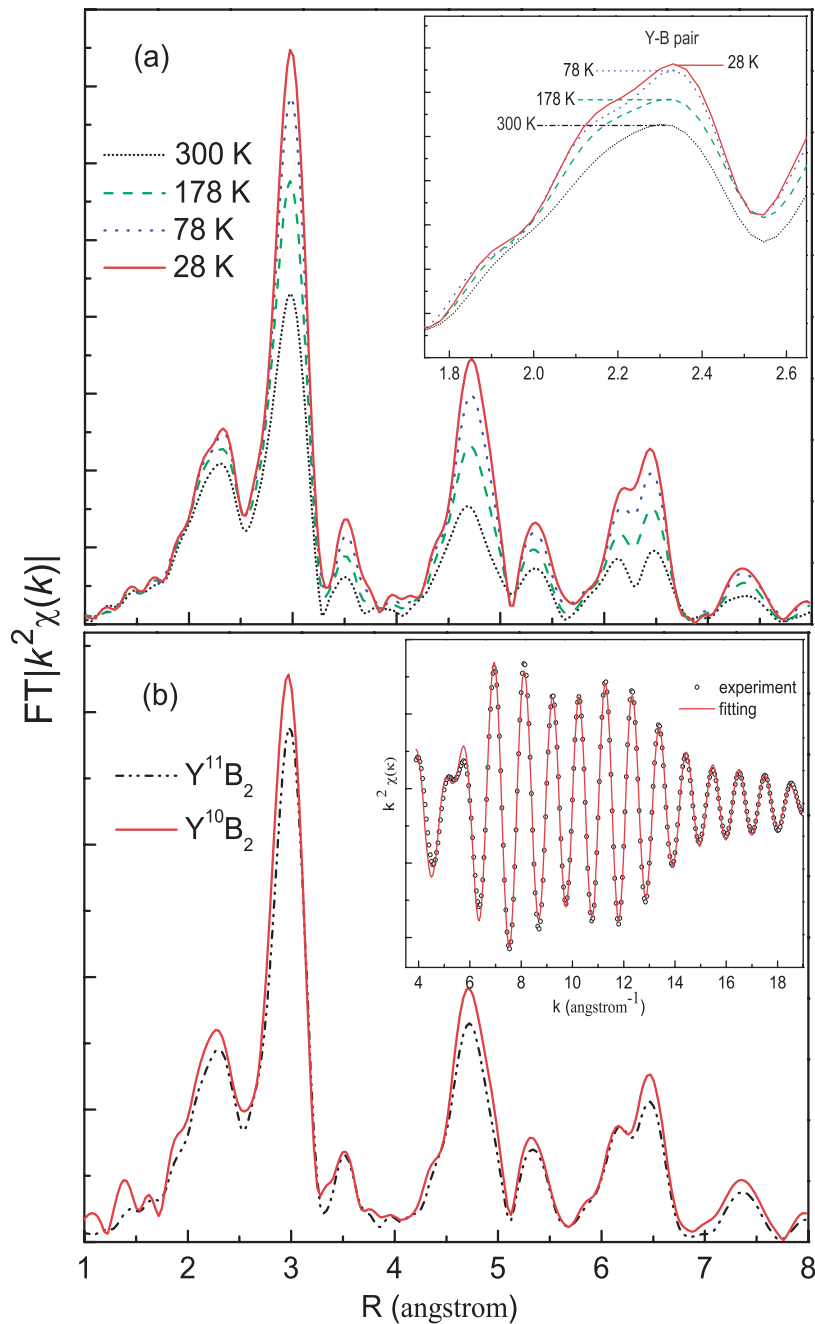


Figure 1. (a) Moduli of Fourier transforms for $Y^{11}B_2$ at several temperatures (the inset is a magnification of the Y–B peak), and (b) comparison of Fourier transforms between $Y^{10}B_2$ and $Y^{11}B_2$ at 128 K (the inset shows a comparison of the experimental and fit EXAFS oscillations for the Y–B and Y–Y shells of $Y^{11}B_2$ at 128 K).

A clear temperature dependence and isotope-effect evidence for YB_2 were shown on the magnitude of the Fourier transforms (FTs), which directly correlates with the Debye–Waller factors (DWFs), as shown in figure 1. To quantitatively obtain further insight into the vibration

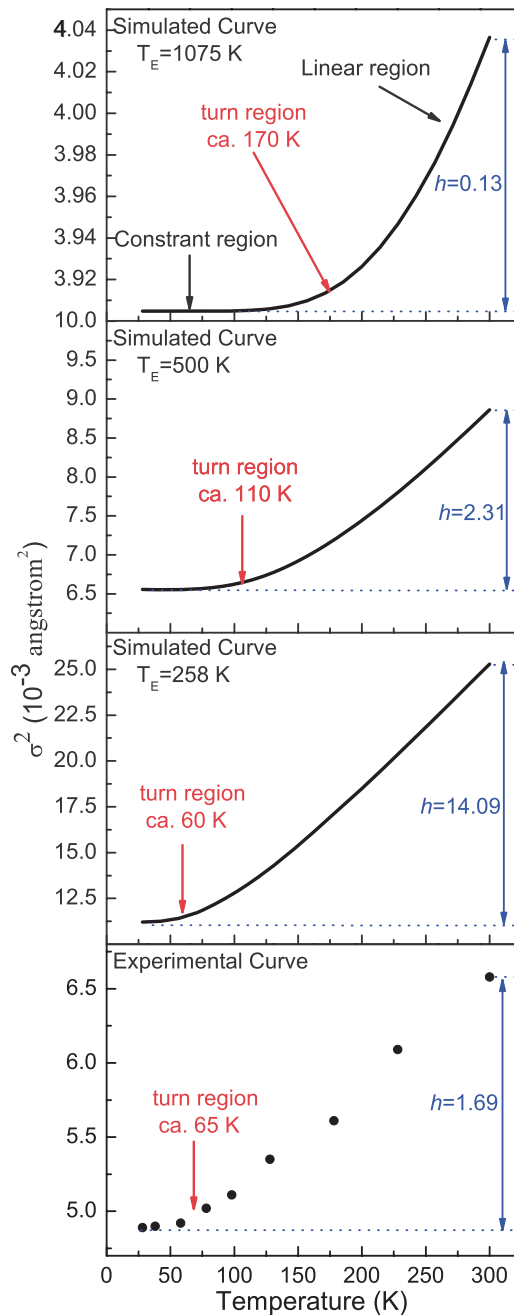


Figure 2. Comparison between experimental Y–B DW factors and simulations of the $Y^{11}B_2$ system using an Einstein model with different characteristic temperatures.

behavior, we extracted the DWFs of the Y–B pair by fitting the EXAFS signals of Y–B and Y–Y pairs, the quality of which is shown in, for example, the inset of figure 1(b) for $Y^{11}B_2$ at 128 K. Lattice dynamics information is contained in the temperature dependence of the DWFs, which is flat at low temperature and begins to increase monotonically from about 50 K, as shown in figure 2 (symbols). In order to illustrate the anomalous vibration behavior of the Y–B bond,

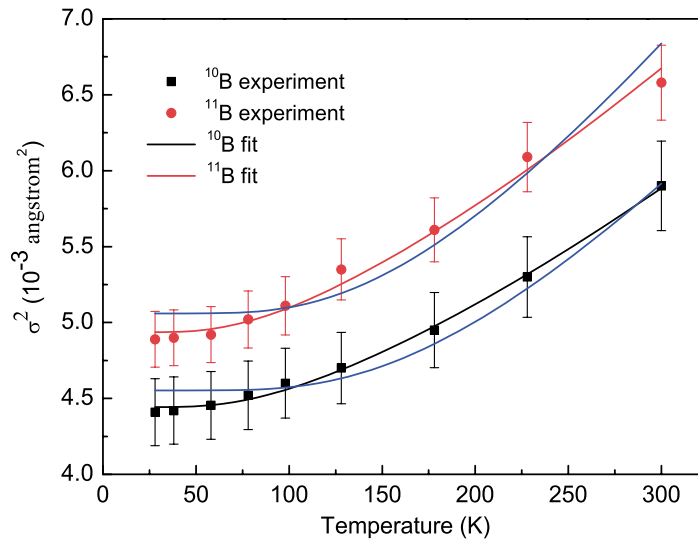


Figure 3. Comparison between experimental DW factors (symbols) and calculations (continuous lines) for the Y–B in different yttrium diborides using a modified Einstein model with two vibration frequencies. Blue curves in the simulations refer to the normal Einstein model with temperatures of 606 and 544 K for the $Y^{10}B_2$ and the $Y^{11}B_2$, respectively.

we compare in figure 2 the experimental DWF curve (symbols) with simulations within the framework of an Einstein model with different Einstein temperatures. Usually, a DW curve presents three distinct temperature regimes: a constant region at low temperature; a ‘turning region’ in the intermediate range and a linear region at high temperature. Therefore, the DW behavior versus temperature may be described with two parameters, the first associated with the turning point in the intermediate range and the second associated with the height (h) of the curve as outlined in figure 2. The two parameters are determined only by the vibration frequency, e.g. the Einstein temperature of a given atomic pair. The turning point of the curve shifts towards low temperature with decreasing Einstein temperature. With an Einstein temperature of 258 K the simulation is close to the experimental behavior and strongly suggests that the low-frequency vibration mixes with the Y–B pair vibration, a high-frequency mode that should behave as an optical mode. Such behavior is confirmed by the fact that the height of the simulated curve is much larger than in the experimental data. By increasing the vibration frequency, the height value decreases and the high-frequency vibration mixes with the Y–B pair vibration. In figure 3, we compare the Y–B (symbol curves) experimental Debye–Waller factors of the $Y^{10}B_2$ and $Y^{11}B_2$ compounds and their fits (blue line) using the Einstein model with the temperatures of 606 and 544 K, respectively. Looking at these curves it is evident that the model fails to describe the DW factors for the Y–B pair. In order to reproduce the experimental data, we introduce a modified Einstein model with two temperatures described as

$$\sigma_{\text{vib}}^2 = \sigma_{\text{stat}}^2 + a \frac{\hbar^2}{2k\mu} \frac{1}{T_{E1}} \coth \left[\frac{T_{E1}}{2T} \right] + (1 - a) \frac{\hbar^2}{2k\mu} \frac{1}{T_{E2}} \coth \left[\frac{T_{E2}}{2T} \right],$$

where a is a parameter describing the degree of decoupling of the Y–B pair and μ is the reduced mass of the Y and B atoms. Using this modified Einstein framework, we obtained for the Y–B

Table 1. Values of the static displacements, Einstein temperatures and vibration frequencies ($\nu' = kT_E/e$) associated with the Y–B shell of $Y^{10}B_2$ and $Y^{11}B_2$.

Compounds	Bond	R (Å)	σ_{stat}^2 (Å ²)	T_E (K)	ν' (meV)
$Y^{10}B_2$	Y–B	2.72	0.0013	1125 ± 40	97.0 ± 3.4
				277 ± 10	23.9 ± 0.8
$Y^{11}B_2$	Y–B	2.72	0.0016	1075 ± 40	92.7 ± 3.4
				258 ± 10	22.2 ± 0.8

pair the two temperatures listed in table 1. Comparison between this second fit and experiments is given in figure 3. As expected, the fit yields one large and a second small Einstein frequency associated with the vibration of the B atoms inside the boron layer and with the vibration of the Y atoms, respectively. Because of their large mass difference, we associate the high frequency mode with B, while Y atoms are associated with the smaller vibration frequencies. The decoupling of the Y and B vibration mode, in contrast to the strong coupling of the Mg and B vibration mode in MgB_2 , could be responsible for the different superconducting behavior exhibited by YB_2 and MgB_2 .

Moreover, a complete decoupling of the vibration of the Y–B pair is possible, as shown by the parameter a , which is 0.895. We also obtain the values of μ/a and $\mu/(1-a)$, which are 10.76 and 91.71, and are very close to the values of the B and Y atom mass, labeled m_B and m_Y , respectively. This means that the behavior of the Y–B vibration can be described by the superposition of the boron and yttrium vibrations, that is

$$\sigma_{\text{vib}}^2 = \sigma_{\text{stat}}^2 + \frac{\hbar^2}{2km_B} \frac{1}{T_{E1}} \coth \left[\frac{T_{E1}}{2T} \right] + \frac{\hbar^2}{2km_Y} \frac{1}{T_{E2}} \coth \left[\frac{T_{E2}}{2T} \right].$$

In order to better understand the role played by phonons in the superconductive mechanism of diborides, we also analyzed the effect of B isotope substitution on the lattice vibration. Table 1 reports the vibration frequencies of the Y–B of the two isotopic compounds obtained by temperature-dependent EXAFS measurements analyzed with the modified Einstein model introduced above. In the high-frequency optical mode corresponding to the B vibration, we observed a frequency shift of about 4.3 meV. These data are in agreement with the shift predicted by Osborn *et al* [17] for the MgB_2 compound, and hence similar lattice vibrations in both YB_2 and MgB_2 may occur.

In a multi-component system, the isotope effect coefficient for the component i is defined as $a_i = d \ln T_c / d \ln M_i$, where M_i is the atomic mass. For a phonon-mediated BCS type superconductor, the superconductive transition temperature is proportional to the characteristic phonon energy ω_{in} and therefore the estimated B isotope effect coefficient is $a_B = d \ln \omega_{\text{in}} / d \ln M_B$. Previous theoretical investigations assigned to the B–B vibration in MgB_2 a dominant role in the electron–phonon coupling [18]. To verify the claim, we chose YB_2 in order to evaluate the B isotope effect coefficient and considered the B–B vibration frequency as the characteristic phonon frequency. If the vibration mode is relevant for the superconductive mechanism, according to the BCS theory the isotope effect coefficient should be about 0.5. Actually, the transition temperature in YB_2 is less than 4 K, and this compound is a BCS superconductor [19]. From temperature-dependent EXAFS data, the Einstein frequencies of

the B–B bond in $Y^{10}B_2$ and $Y^{11}B_2$ are 97.0 and 92.7 meV, respectively, and the corresponding B isotope effect coefficient α_B is 0.48, a value really close to the BCS prediction. As a consequence, these data strongly support the hypothesis that the B–B vibration plays an important role in the superconductive mechanism in transition-metal diborides. The case of MgB_2 remains an open question since data for the boron isotope effect in this compound report a value of 0.30 [6].

Summarizing, the local lattice vibration properties and the B isotope effect in YB_2 have been investigated by temperature-dependent EXAFS experiments. The EXAFS signals are characterized by anomalous behavior of the DWF of the Y–B pair, which was described by a modified Einstein model. The analysis allows correlating the lattice vibration with the superconductive mechanism in metal diborides: (a) the vibration decoupling between metal and B atoms is probably the mechanism that leads to the strong decrease of the superconducting critical temperature for YB_2 compared to MgB_2 ; (b) the B–B vibration mode plays a key role in the electron–phonon coupling. The analysis presented here could also be extended to the newly discovered iron-based superconductors and high- T_c cuprate superconductors.

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