Title
Evidence for a subtle structural symmetry breaking in EuB6

Permalink
https://escholarship.org/uc/item/5xt5782m

Journal
Journal of Physics Condensed Matter, 21(45)

ISSN
0953-8984

Authors
Martinho, H
Rettori, C
Dalpian, GM
et al.

Publication Date
2009-12-31

DOI
10.1088/0953-8984/21/45/456007

License
CC BY 4.0

Peer reviewed
Evidence for a subtle structural symmetry breaking in EuB6

H Martinho1, C Rettori2, G M Dalpian1, J L F da Silva3, Z Fisk4 and S B Oseroff5,6

1 Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Rua Santa Adélia 166, 09210-170, Santo André, São Paulo, Brazil
2 Instituto de Física ‘Gleb Wataghin’, UNICAMP, 13083-970, Campinas, São Paulo, Brazil
3 National Renewable Energy Laboratory, Golden, CO 80401, USA
4 Department of Physics, University of California, Davis, CA 95616, USA
5 San Diego State University, San Diego, CA 92182, USA
6 Instituto de Ciencias Basicas, Universidad Nacional de Cuyo, Mendoza, Argentina

E-mail: herculano.martinho@ufabc.edu.br

Received 8 August 2009, in final form 22 September 2009
Published 23 October 2009
Online at stacks.iop.org/JPhysCM/21/456007

Abstract

This work presents a systematic Raman scattering study and first-principles calculations for the EuB6 system. Evidence for the presence of an incipient (∼1 × 10−4 Å) tetragonal symmetry break of its crystalline structure was found. Forbidden Raman modes at ωRm(1) ∼ 1170 cm−1, ωRm(2) ∼ 1400 cm−1, and ωRm(3) ∼ 1500 cm−1 were observed. The tetragonal symmetry of ωRm(2) and ωRm(3) together with spin-polarized first-principles simulations of the structural and magnetic properties fully support such a break of symmetry. Our data and calculations explain the occurrence of ferromagnetism in Eu hexaborides, previously reported.

1. Introduction

The hexaborides RB6 (R = alkaline-earth metal) are one of the most intensively studied groups of intermetallic compounds due to their large variety of physical ground states [1]. In particular, the family R1−xAxB6 (A = magnetic rare earth) has attracted considerable interest due to the intriguing connections between their magnetic [2], transport [3], and optical properties [4, 5]. The available crystallographic data indicate that these compounds are cubic with the unit cell surrounded by eight B6 octahedra, at each vertex [6].

EuB6 is a ferromagnetic (FM) metal, characterized by a quite small effective carrier density at high T (∼10−3 per unit cell) [7–11, 3, 12]. Actually, the physical processes occurring below T ≲ 16 K are a matter of debate. Súllow et al [7] have shown that EuB6 presents a FM transition at TC1 = 15.3 K where the spins order parallel to the [100] direction. A drop of an order of magnitude in its resistivity was also observed at this temperature and magnetic polaron overlap had been invoked to account for these features [8]. Andreev reflection spectroscopy combined with Hall effect and magnetoresistivity data indicated that EuB6 has a semimetallic band structure with a fully spin-polarized hole band and an unpolarized electron band [9]. Eu-derived conduction band splitting due to coupling to core electrons at each Eu site was found to be the origin of the phase transition at TC1 [10]. The intimate correlation between magnetism and transport properties is believed to originate from the strong exchange interaction among spins of charge carriers and local f electrons [8]. At TC2 = 12.5 K spins undergo a reorientation transition to the [111] direction [7]. Below TC2 all Eu2+ spins participate in the long-range FM order [7, 13, 14]. Ferromagnetism in this case was found to arise from the half-filled 4f shell of Eu2+ ions, whose localized spins account for the measured magnetic moment of ∼7 µB/f.u. [7, 11, 3].

Evidence for the occurrence of these two magnetic transitions below T ≲ 16 K was found from muon spin rotation microscopic measurements by Brooks et al [15]. They concluded that the ferromagnetic state of EuB6 is reached via two magnetic transitions at 15.5 K and 12.6 K, respectively. Two distinct components were resolved in the muon data, one oscillatory and one non-oscillatory, which arose from different kinds of magnetic environments [15].
The transition temperatures decrease with Ca content [3, 16] and are completely suppressed for $x \lesssim 0.30$ [17]. Electron microscopy data indicate the coexistence of insulating Ca-rich and metallic Eu-rich regions that percolate at $x \approx 0.30$ [17]. Moreover, Urbano et al. [18] recently analyzed the behavior of the Eu$^{2+}$ electron spin resonance (ESR) linewidth and concluded that the percolation of the impurity bound states has already started at $x \approx 0.15$, i.e., involving next to nearest neighbors.

The intriguing fact concerning EuB$_6$ is that symmetry constraints prevent the occurrence of FM order in the cubic $O_h$ space group [19, 7]. Lattice symmetry must be lowered to one of the $O_h$ tetragonal subgroups to allow ferromagnetism [7, 19]. High resolution $T$-dependent x-ray diffraction measurements by Süllow et al. [7] failed to observe direct evidence of this symmetry breaking. However, they had observed an anisotropic intensity distribution of the Bragg peaks in all $hl$, $hk$, and $kl$ planes that presented four symmetrically arranged wings around each peak. Strain at the sample surface, lattice disorder, vacancies or an incipient structural distortion were enumerated as possible origins for the wings but were not conclusively assigned. ESR $g$-value measurements on the $Ca_{1-x}EuB_{6}$ series suggested that the crystal symmetry may be lower than cubic [20].

The purpose of this work is to find a possible symmetry breaking in the crystal structure of EuB$_6$ that could explain the appearance of the FM ordering reported. For this reason we carefully studied the polarization and temperature dependence of the Raman scattering (RS) spectra of EuB$_6$ single crystals and performed ab initio calculations.

### 2. Experimental details

Single-crystalline samples of EuB$_6$ were grown in a flux of 99.999% pure Al, using the starting elements of Eu and B with purities of 99.95% and 99.99%, respectively [6]. Magnetic and transport characterization data can be found in [20]. The crystal’s shapes were plate-like with typical dimensions of $0.5 \times 4 \times 6$ mm$^2$. Raman measurements were carried out using a triple spectrometer equipped with a LN$_2$ CCD detector. Each spectrum was corrected by the spectrometer response as a function of the excitation source. The laser power was kept below 12 mW on a spot of diameter of about $100 \mu$m. All measurements were made in a near-backscattering configuration.

For the cubic $O_h$ RB$_6$ unit cell, the zone-center $T_{2g}$, $E_g$, and $A_{1g}$ phonons are Raman active. These modes correspond to internal displacement of B atoms in the B$_6$ octahedron [21]. Previous RS works [21–29] have reported these modes at $\sim 780$ ($T_{2g}$), $\sim 1150$ ($E_g$), and $\sim 1260$ ($A_{1g}$) cm$^{-1}$. Besides these phonons, additional modes at $\sim 200$ and $\sim 1400$ cm$^{-1}$ were also reported. The former was conclusively assigned to two-phonon RS [26] and the latter has had no clear assignment yet.

![Figure 1](image_url)

**Figure 1.** Room temperature unpolarized RS of EuB$_6$, showing the expected phonons of the $O_h$ cubic structure as well as the forbidden ones. (This figure is in colour only in the electronic version)

### 3. Results and discussion

Figure 1 presents the EuB$_6$ RS spectrum taken at 300 K. It shows the $T_{2g}$, $E_g$, and $A_{1g}$ phonons of the cubic phase at 775, 1137 and 1264 cm$^{-1}$, respectively. Also, extra broad modes at $\sim 1170$, $\sim 1400$, and $\sim 1500$ cm$^{-1}$ were observed. To verify the phononic origin of these extra modes we used another laser line (488.0 nm) to excite the sample. All modes were observed at the same Raman shift. The spectral intensity response was five times larger when the excitation was the $514.5$ nm, indicating a possible resonant behavior. We shall label these extra modes as forbidden Raman modes $fRm(1)$, $fRm(2)$, and $fRm(3)$, respectively. The other compounds of the $Ca_{1-x}Eu_xB_6$ series showed similar spectra. The intensity of the $fRms$ appeared larger for $x = 0.10$. For $x = 1$ and $x \geq 0.30$ a shoulder close to the $E_g$ phonon was observed (not shown). This shoulder was always $\sim 25$ cm$^{-1}$ above the $E_g$ phonon frequency. For CaB$_6$ and EuB$_6$ it was attributed to the charge imbalance arising in the boron octahedron [21, 22, 27]. It is worth mentioning that the $E_g$ peak had a symmetric shape for $x = 0.05$ and 0.10.

The polarized RS experiments were performed on the $ab$ and $ac$ planes at room $T$ (figure 2). The $a, b$ and $c$ axes correspond to the [001], [010], and [100] crystallographic cubic directions [6]. The smaller crystal thickness determines the $c$ axis (see the inset of figure 2(b)). The expected selection rules are summarized in table 1. It was found that $A_{1g}$, $E_g$, and $T_{2g}$ phonons had the expected selection rules for the $O_h$ space group. Analysis concerning the $fRms$ is shown in table 2. Thus, the $fRm(1)$ has a cubic $A_{1g}$ symmetry. Instead, $fRm(2)$ and $fRm(3)$ did not appear on the $T_{2g}$ channel probed with the $(a, b)$ configuration (figure 2(b)) but were clearly observed on the same channel in the $(c, a)$ case (figure 2(d)). Thus, we concluded that the symmetry of $fRm(2)$ and $fRm(3)$ is $A$, of a non-cubic group. The above, is strong evidence of an incipient breaking of the cubic symmetry. It is possible to consider that:

---

2
Figure 2. Room temperature polarized RS spectra for EuB₆ in the configurations listed in table 1. The inset of (b) shows the typical crystal shape and the $a$, $b$ and $c$ axes.

(i) the fRm(1) is a doublet of the $A_{1g}$ phonon originating from the charge imbalance arising in the $B_6$ octahedron, resembling the $E_g$ doublet, and

(ii) the fRm(2) and fRm(3) are bands activated by the subtle non-cubic symmetry of the lattice.

The temperature dependence of the RS spectra is displayed in figure 3. The fRm(1) kept its intensity almost constant while the fRm(2) and fRm(3) modes presented a strong intensity increase at low temperatures, $T \lesssim 20$ K. The total integrated area of fRm(2) and fRm(3) increased nearly 6 times between 400 and 14 K. For $T > 400$ K, the peak’s intensities were nearly constant.

Ogita et al [27] observed a broad peak at \(~1400~\text{cm}^{-1}\), probably due to the superposition of fRm(2) and fRm(3) bands. These authors assigned it to an overtone of the $T_{2g}$ phonon. This interpretation is incorrect for the following reasons: (i) the energy of this broad mode is smaller than twice the $T_{2g}$ phonon frequency; (ii) the selection rule for this mode is incompatible with any combination of the $O_h$ irreducible representations (IR), contrary to what was expected from the direct product $T_{2g} \otimes T_{2g} = A_{1g} + E_g + T_{1g} + T_{2g}$ [30]; and (iii) the temperature dependence is incompatible with a two-phonon RS process. These authors also observed a low frequency mode at \(~200~\text{cm}^{-1}\), in agreement with other authors [22, 25, 26]. Since this mode was conclusively assigned to two-phonon RS [25] its selection rules will not be explored in this work.

Another scenario corresponds to considering the fRms as disorder-activated infrared-active phonons or combinations of Raman-active and infrared-active modes. Yahia et al [23] measured the RS and infrared reflectivity for several hexaborides. Comparing the frequencies of their infrared-active modes with the frequencies of the fRms, one concludes that there are no infrared modes, or possible combinations, that could be assigned to the fRm peaks. Thus, this assumption should also be disregarded. The cubic symmetry breaking proposed here is the straightforward scenario.

Notice that the $A_{1g}, E_g, T_{2g}$ and fRm(1) phonons still have cubic symmetry. This suggests that the overall crystal distortion may be very small, which explains the difficulties of bulk techniques that explains x-ray diffraction studies in resolving large scale subtle symmetry changes.

Currently, high resolution synchrotron x-ray diffraction experiments (see, e.g., the work of Yang and Ren [31]) have shown that typical cubic ferromagnets like DyCo₂, CoFe₂O₄, and Terfenol-D experience a tiny structural change \((c - a)/a \lesssim -1.0 \times 10^{-3}\) to a non-cubic symmetry at $T_C$. A similar subtle deviation of the cubic structure is probably appearing in

---

**Table 2.** Experimentally observed selection rules for the fRms.

<table>
<thead>
<tr>
<th></th>
<th>fRm(1)</th>
<th>fRm(2)</th>
<th>fRm(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g} + E_g + T_{2g}$</td>
<td>$\times$</td>
<td>$\times$</td>
<td>$\times$</td>
</tr>
<tr>
<td>$A_{1g} + E_g$</td>
<td>$\times$</td>
<td>$\times$</td>
<td></td>
</tr>
<tr>
<td>$T_{2g}$ ($a, b$)</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$E_g + T_{2g}$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$T_{2g}$ ($c, a$)</td>
<td>$-$</td>
<td>$\times$</td>
<td>$\times$</td>
</tr>
</tbody>
</table>
the hexaborides. However, the results presented here show that the crystallographic structure is non-cubic in the 14 and 780 K probed ranges. The intensity increase of fRm(2) + fRm(3) below 20 K is probably related to the enhancement of the \((c-a)/a\) ratio near to the magnetic transition driven by magnetoelastic coupling. This symmetry breaking may also allow the FM in this system.

We also performed spin-polarized first-principles calculations to corroborate these findings. Calculations were based on the all-electron projector augmented wave (PAW) method and density functional theory (DFT) within the local density approximation as implemented in VASP [32, 33]. Similar computational calculation methodology was recently employed by Kim et al [34] to successfully explain the optical conductivity of EuB6.

In order to get the correct correlation among spin orientations and crystal structure optimization, the spin–orbit coupling was taken into account in a fully self-consistent way. The structural equilibrium volume for the [111] and [100] spin orientations was obtained by optimizing the structural forces and stress without taking the symmetry into account, i.e., all possible cell shapes were allowed. An energy cutoff of 500 eV was employed. A \((10 \times 10 \times 10)\) grid yielding 1000 k-points was used for the Brillouin zone interaction. Due to the small energy differences between spin orientations, the energy and force convergence criteria were set to \(1 \times 10^{-6}\) eV and 0.01 eV/Å, respectively. We have also performed LDA + U calculations [35]. As the Eu f levels are very localized, the results obtained with LDA + U were almost the same without the U parameters. Thus, in the following, only the LDA results will be presented.

It was found that the [111] spin configuration is 3.2 meV/EuB6 lower in energy than the [100] one, in agreement with the magnetic characterization data from the literature [7].

In all cases, a small lattice distortion along the spin direction was observed. Although small, it was enough to break the cubic symmetry of the unit cell, allowing the occurrence of FM. For the Eu spin in the [111] direction, the unit cell lattice vectors obtained were

\[
\vec{a} = 4.134\ 43\ \hat{x} + 0.001\ 24\ \hat{y} + 0.001\ 24\ \hat{z};
\]

\[
\vec{b} = 0.001\ 24\ \hat{x} + 4.134\ 43\ \hat{y} + 0.001\ 24\ \hat{z};
\]

\[
\vec{c} = 0.001\ 24\ \hat{x} + 0.001\ 24\ \hat{y} + 4.134\ 43\ \hat{z}.
\]

The resulting non-cubic unit cell had the boron octahedra slightly distorted in the spin direction. The values obtained for the lattice parameters are in excellent agreement with experimental findings (agreement better than 1.5%).

The [100] spin orientation leads to a slightly non-cubic structure of tetrahedral symmetry, i.e., \(\vec{a} \neq \vec{b} = \vec{c}\). The optimized lattice vectors were

\[
\vec{a} = 4.121\ 78\ \hat{x}; \quad \vec{b} = 4.121\ 71\ \hat{y}; \quad \vec{c} = 4.121\ 71\ \hat{z}.
\]

Furthermore, a distortion in the boron octahedron structure was also observed. For example, the \(u\) parameter, defined as the distance between the center of the unit cell and the B atoms, is smaller in the [100] direction than in the others: \(u_{100} = 1.2350\ \text{Å}\) and \(u_{010} = u_{001} = 1.2351\ \text{Å}\). Although small (\(\sim 1 \times 10^{-3}\) Å), these distortions were consistent with the lower symmetry observed by means of Raman scattering.

The local magnetic moments, the shape of the Eu f wavefunction and the local density of states for the two configurations were very similar, and almost spin orientation independent. Figure 4 shows the projected density of states (DOS) relative to the Eu f levels for the two spin directions with magnetization along [100] (upper panel) and [111] (lower panel) directions. The DOS are very similar, with an exchange splitting of 4–5 eV. The dashed lines indicate the Fermi level. The most noticeable difference concerns the level splitting. Along the magnetization direction with the highest crystal symmetry ([111]) the levels are sharper than the tetragonal one ([100]). The [100] direction appeared more delocalized and had more peaks. That is probably due to crystal electric field effects. The computational simulations clearly show that the unit cell symmetry should be non-cubic in both configurations, in order to enable a net magnetic moment to be present in the unit cell.

4. Conclusions

In conclusion, the experimental results showed the appearance of three fRms in EuB6 that do not belong to the expected set of Raman-active phonons of the \(O_h\) cubic group. After analyzing different possibilities it was concluded that fRm(1) is a doublet of the \(A_{1g}\) phonon, caused by a charge imbalance in the \(B_6\) octahedron, similar to the \(E_g\) doublet. Also, the fRm(2) and fRm(3) bands arise from the cubic symmetry breaking that induces a non-cubic environment in the \(B_6\) octahedron. First-principles calculations of magnetic and structural properties corroborated this symmetry breaking.

Acknowledgments

This work was supported by the Brazilian Agencies CNPq and FAPESP. SBO was partially supported by Raices 2009, Argentina.
References
