ANISOTROPIC THERMAL EXPANSION IN DIBORIDES
AS A FUNCTION OF MICRO-STRAIN

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Thermal expansion of diborides (AB₂), with different intercalated atoms (A) is studied as a function of temperature in the range of 100-370 K by high-resolution x-ray powder diffraction. The results indicate a well-defined relationship between the anisotropy of the thermal expansion and the micro-strain of the boron layers, εₓ=(a-α₀)/α₀ (where α₀=c/1.08 is the equilibrium a-axis for an unstrained AB₂ system), determined by the atomic radius of the intercalated atoms. The thermal expansion is isotropic at εₓ=0 (i.e., near c/α₀=1.08) while the AB₂ system is unstrained, and it gets anisotropic away from the equilibrium. The anisotropy increases with increasing micro-strain in both directions (positive or negative, i.e. tensile or compressive) suggesting that the micro-strain is a key variable to define the state of diborides. As a matter of fact, the MgB₂ with the highest T_c shows a tensile micro-strain, εₓ=6% and a large thermal expansion anisotropy.

1 Introduction

In the layered superconductors the superconducting transition temperature T_c depends not only on the charge density but also on the elastic micro-strain due to the lattice mismatch existing between the different layers. In fact, the superconductivity appears near a critical region of charge density and micro-strain of the CuO₂ plane [1]. Recently the high T_c superconductivity is observed in a rather simpler layered structure, the magnesium diboride, with a T_c of 39 K [2]. This latest finding throttles the research activities to explore special case of this system to be high T_c superconductor among the diborides [3]. The AB₂ diborides have a C32 structure where boron monolayers with honeycomb lattice like graphite are intercalated with a metallic monolayer with hexagonal close-packed lattice. Between the boron planes and the metallic monolayer there is a mismatch that induced a micro-strain in the boron layers [4]. However, the question of fundamental importance is to understand which is the parameter that could be used to describes the micro-strain in the boron layers, which are behind the fundamental electronic structure of the diboride systems [5-7]. Here we will show how one can determine this key parameter through a study of the thermal expansion of the diborides for different intercalated metal ions.
Thermal expansion of diborides was previously studied by Loennberg [8] providing an indication that the thermal expansion in diborides depends on metal radius of the intercalated atoms. However the study was limited to the transition metal diborides with a small $c/a$ ratio. In this paper we have extended the investigation of the thermal expansion to the diborides with larger $c/a$ ratio, as the case of the high $T_c$ superconducting MgB$_2$. Using high-resolution x-ray diffraction, we show that anisotropy of the thermal expansion has an interesting parabolic behaviour as function of the $c/a$ ratio and the AB$_2$ structure is nearly isotropic at $c/a=1.075$. The results suggest that the thermal expansion is intimately related with the micro-strain of the boron layers, defined as $\varepsilon=(a-a_0)/a_0$ where $a_0=c/1.08$ is the expected equilibrium a-axis for an unstrained AB$_2$ system. The outcome is consistent with the recent findings [9] in which the diboride superconductivity has been found to follow the phase diagram with micro-strain $\varepsilon_a$ and the charge density in the boron planes as two variables.

2 Experiments

Several samples of diborides are studied, including the commercially available AB$_2$ compounds with different transition metal atoms A of the Group IVB (A=Ti and Zr) from Alfa-Aesar and AlMgB$_4$, Al$_2$MgB$_6$ and MgB$_2$ grown by the direct reaction method [10]. The starting materials of elemental magnesium and aluminum (rod, 99.9 mass% nominal purity) and boron (99.5 % pure <60 mesh powder) were used for the synthesis of the AlMgB$_4$, Al$_2$MgB$_6$ and MgB$_2$ in the direct reaction method. The elements in a stoichiometric ratio were enclosed in tantalum crucibles sealed by arc welding under argon atmosphere. The tantalum crucibles were then sealed in heavy iron cylinder and heated for one hour at 800 °C and two hours a 950 °C in a furnace. The important improvement in the synthesis process was to avoid use of quartz tube (unlike the Ref. 11 where quartz was used), for preparation of the diborides, since the Mg gas at high temperature reacts with quartz and induces MgO impurities phases in the final compound. The samples were characterized for their superconducting properties by the temperature dependence of the complex conductivity using the single-coil inductance method [12] showing $T_c=4+2$ K, 24±3 K, 39±0.5 K in AlMgB$_4$, Al$_2$MgB$_6$ and MgB$_2$ respectively [4, 10]. No superconductivity was found in TiB$_2$ and ZrB$_2$ down to 0.3 K.

The structural properties of the samples were determined by powder x-ray diffraction using synchrotron radiation at the Elettra storage ring (Trieste), operated at 2 Gev and 170 mA. The diffraction patterns were measured at XRD beam line using synchrotron light emitted by a Wiggler source and monochromatized by a double crystal Si (111) monochromator and focused on the sample by a Pt coated silicon mirror. A CCD detector of diameter 165 mm with 2048x2048 pixels per frame, from Mar-research, was used to record the diffraction patterns. Diffraction pattern of Si was measured in the same experimental conditions to ensure the calibration with respect to any non-orthogonality of the detector to the direct beam (tilt), and the direct beam center on the detector.

3 Results and Discussion

Figure 1 shows the x-ray powder diffraction (XRD) patterns of different diborides, measured at low temperature (T=100 K). While the patterns of the AlMgB$_4$, AlMg$_2$B$_6$
and MgB$_2$ are displayed in the upper panel, the lower panel of the figure shows the patterns measured on the ZrB$_2$, MgB$_2$ and TiB$_2$ compound. It should be observed that the diffraction peaks in the patterns of AlMgB$_4$ and AlMg$_2$B$_6$ are broader, compared to the one for the MgB$_2$ system, presumably due to presence of domains of non uniform distribution of Al/Mg ions in the earlier. It should be recalled that such a lattice disorder was found to induce a broadening of the superconducting transition, however, with a minor effect on the $T_c$ value [4,10]. The powder diffraction patterns were analysed by standard least-squares refinement to determine the temperature dependence of the lattice parameters $a$ and $c$.

![Diffraction patterns](image)

**Figure 1.** X-ray powder diffraction patterns measured on several diborides at low temperature ($T=100$ K); the patterns of AlMgB$_4$, Al$_2$MgB$_6$ and MgB$_2$ are displayed in the upper panel while the patterns of TiB$_2$, MgB$_2$ and ZrB$_2$ are plotted in the lower panel.

Figure 2 shows relative thermal expansion of magnesium diborides with variable Mg contents (Mg$_x$Al$_{1-x}$B$_2$ with $y=0.98$, 0.67, 0.5) in the temperature range of 100-300 K. The left panel shows the relative thermal expansion along the $a$-axis while the right panel shows the one along the $c$-axis. The increase of magnesium increases the thermal...
expansion along the $c$-axis, with a relatively smaller decreases in the $a$-axis. Thus it is clear that the magnesium doping produce a higher anisotropy of thermal expansion.

Let us now compare the thermal expansion of the magnesium diboride with that of others. Figure 3 shows the thermal relative thermal expansion of the MgB$_2$ with titanium and zirconium diborides, along the $a$-axis (left panel) and the $c$-axis (right panel). The thermal expansion exhibits a pronounced anisotropy, with the $c$-axis response substantially higher than along the $a$-axis. The lattice parameter along the $c$-axis increases twice compared to the lattice parameters along the $a$-axis at the same temperature, in agreement with the neutron diffraction data by Jorgensen et al [13]. It could be seen that the thermal expansion of magnesium diboride is significantly higher than the one for the zirconium and titanium diborides.

![Graphs showing thermal expansion of MgB$_2$ and other diborides](image)

**Figure 2.** Relative thermal expansion of the $a$-axis (left) and the $c$-axis (right) for Mg$_{y}$Al$_{1-y}$B$_2$ with different magnesium content. The error bars are smaller than the symbols. The solid curve is a polynomial fit.

Now we wish to discuss evolution of the thermal expansion in different diborides. Figure 4 shows the room temperature anisotropy of thermal expansion, determined for several diborides, as a function of the $c/a$ ratio. The thermal expansion anisotropy is defined by the ratio of thermal expansion coefficients along the $c$ and $a$-axis, i.e. $\alpha_c/\alpha_a$. The thermal coefficients, $\alpha_c$ and $\alpha_a$, are calculated from the derivative of the polynomial fit to the temperature dependence of the lattice parameters determined by x-ray diffraction. The value of the $\alpha_c/\alpha_a$, determined in the present work (filled symbols) are plotted with the one measured by Loennberg [8] for comparison (open symbols). In the earlier work, Loennberg [8] rightly observed that the thermal expansion anisotropy decreases with increasing the radius of the metal atom, however, as evident from the data, the study was limited to the group IV-VII transition metal diborides and not the diborides with larger $c/a$ ratio (e.g. MgB$_2$). As a matter of fact, a clear minimum in the thermal expansion anisotropy is observed at 1.075, where the system is nearly isotropic ($\alpha_c/\alpha_a$=1). If metal ions with larger or smaller radius are introduced the thermal expansion anisotropy increases.
Figure 3. Relative thermal expansion of the \(a\)-axis (left) and the \(c\)-axis (right) for the TiB\(_2\) and ZrB\(_2\), compared with the one for the MgB\(_2\). The error bars are smaller than the symbols. The solid curve is a polynomial fit.

Figure 4. Anisotropy of the thermal expansion at room temperature for the diborides with AlB\(_2\)-structure, plotted as a function of the \(c/a\) ratio. AlMgB\(_4\) and Al\(_2\)MgB\(_6\) are indicated with 114 and 126 respectively. The half-width of the symbols error indicates the experimental error. The dotted curve is only a guide to the eye.

From the present results it is clear that at a particular value of the \(c/a\) ratio, the diboride structure is unstrained. This particular result permits us to define the micro-strain of the boron layers along the \(a\)-axis as \(\varepsilon_a=(a-a_0)/a_0\) where \(a_0=c/1.075\) is the expected \(a\)-axis for an unstrained AB\(_2\) structure. A positive or negative boron micro-strain, \(\varepsilon_a\), indicates that the boron layers are under tensile or compressive strain. The thermal expansion anisotropy increases with increasing micro-strain in both directions suggesting that the micro-strain is an important variable to define the state of diborides with AlB\(_2\)-structure.
With this observation, it is possible to describe all diborides with a phase diagram characterised by two variables, the micro-strain and the charge density in the boron planes. This recalls recently reported phase diagram for the cuprates [1], where superconductivity appears near a critical region of charge density and micro-strain of the CuO$_2$ plane. Analogously a critical region is found for the diborides where MgB$_2$, having the highest T$_c$, shows a tensile micro-strain $\varepsilon_a$=6% and a large thermal expansion anisotropy.

4 Summary and Conclusions

In summary, we have investigated diborides with different intercalated atoms between the boron layers by high resolution x-ray diffraction measurements to explore a structural parameter that could describes the state of diborides with AlB$_2$-like structure. We find a well-defined relation between the anisotropy of thermal expansion and the micro-strain in diborides. The results suggest that the thermal expansion is nearly isotropic when the system is unstrained and an increasing thermal expansion anisotropy appears while the boron layers are under tensile or compressive stress. In fact, it is the intercalated ion which determines the micro-strain in the electronically active boron layers in the diborides. These results are consistent with the hypothesis that the phase diagram of diborides is determined by micro-strain and charge density in the boron planes, and provide another experimental feed-back to support intimate relationship between the high T$_c$ superconductivity and electron-lattice interactions.

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