

## On the study of phase formation and critical current density in superconducting $\text{MgB}_2$

SUCHITRA RAJPUT, SUJEET CHAUDHARY\*, SUBHASH C KASHYAP and PANKAJ SRIVASTAVA

Department of Physics, Indian Institute of Technology Delhi, New Delhi 110 016, India

MS received 2 February 2006

**Abstract.** Superconducting bulk  $\text{MgB}_2$  samples have been synthesized by employing sintering technique without using any additional process steps, generally undertaken in view of the substantial loss of magnesium, during heat treatment. Starting with Mg rich powders having different atomic ratios of Mg : B, as against the nominally required Mg : B = 1 : 2 ratio, we have obtained superconducting  $\text{MgB}_2$  samples of different characteristics. The effect of excess Mg in the starting mixture and processing temperature on the phase-formation, transition temperature ( $T_C$ ) and critical current density ( $J_C$ ) have been investigated by electrical transport and a.c. susceptibility measurements. The X-ray diffraction and X-ray photoelectron spectroscopic analyses of  $\text{MgB}_2$  bulk samples have been carried out to understand the role of excess Mg and the effect of processing temperature. It is established that  $\text{MgB}_2$  samples with high critical current density can be synthesized from a Mg rich powder having Mg : B in 2 : 2 ratio, at temperatures around 790°C. Critical current density has been found to vary systematically with processing temperature.

**Keywords.**  $\text{MgB}_2$ ; transition temperature; X-ray photoelectron spectroscopy.

### 1. Introduction

The observation of superconductivity at high transition temperature ( $T_C$ ) of 39 K (which is nearly twice the highest  $T_C$  recorded for any intermetallic compound) in  $\text{MgB}_2$ , in 2001 (Nagamatsu *et al* 2001), had sparked renewed interest in the study of superconductivity in non-cuprate materials. Potential large scale applications of  $\text{MgB}_2$  in different morphologies, including bulk (Kumakura *et al* 2001; Botta *et al* 2002; Bud'ko *et al* 2002; Cardwell *et al* 2002), single crystal, wires, tapes (Cardwell *et al* 2002) and thin films (Buzae and Yamashita 2001), are envisaged primarily due to its relatively high transition temperature, better mechanical properties (Feng *et al* 2004), weak-link free grain boundaries (Jin *et al* 2001), high transport critical current density,  $J_C$  (Buzae and Yamashita 2001; Canfield *et al* 2001), large coherence lengths (Welp *et al* 2003) and simple crystal structure (King *et al* 2002; Cava *et al* 2003).

In spite of the chemical and structural simplicity, the synthesis of stoichiometric  $\text{MgB}_2$  has so far proved to be very difficult. The vapourization of Mg and its affinity for oxygen is the main difficulty encountered in the synthesis of  $\text{MgB}_2$ . Liu *et al* (2001) found that the  $\text{MgB}_2$  phase is thermodynamically stable only under high Mg partial pressure. If the Mg overpressure is too low, the decom-

position of  $\text{MgB}_2$  is thermodynamically favoured, whereas if it is too high, Mg condenses on  $\text{MgB}_2$  itself. It is reported that superconducting bulk  $\text{MgB}_2$  samples are synthesized by sintering a compressed pellet of Mg and B powders either in vacuum or in Ar atmosphere (Cardwell *et al* 2002). A few groups have synthesized superconducting  $\text{MgB}_2$  either by hot-press sintering a stoichiometric mixture of Mg and B powders (Shen *et al* 2003; Drozd *et al* 2004), or by covering the starting powder mixture in Ta foil followed by sealing in a quartz or Nb-lined stainless steel container (Kumakura *et al* 2001; Botta *et al* 2002; Cardwell *et al* 2002). Since the above researchers have employed additional steps to arrest the evaporation of Mg, hence an approach, which compensates for the vapourization of Mg, and leads to the formation of  $\text{MgB}_2$  with improved superconducting properties should be attempted. Both from technical and scientific point of view, it becomes important to study the effect of various synthesis parameters and starting composition on the  $\text{MgB}_2$  phase formation and the critical current density. The use of excess Mg (only in the limited range) on superconducting properties of  $\text{MgB}_2$  has been investigated (Ribeiro *et al* 2003). In this paper, we report the preparation of  $\text{MgB}_2$  bulk samples in a single step without involving cumbersome steps of evacuation of ampoule or high pressure sintering, etc. The transition temperature is determined from both the magnetic a.c. susceptibility measurement as well as electrical transport measurement.

\*Author for correspondence (sujetc@physics.iitd.ernet.in)

## 2. Experimental

Four sets of polycrystalline bulk samples of  $\text{MgB}_2$  were prepared by heat treating the pellets formed from different mixtures of magnesium (99.8%, Strem chemicals) and boron (99.9%, Cerac) powders with starting composition equivalent to  $\text{Mg}_x\text{B}_2$ , where  $x = 1.25, 1.5, 1.75$  and  $2.0$  (named as MB1, MB2, MB3 and MB4, respectively).

Thoroughly ground mixture of Mg and B was compressed uniaxially at a pressure of  $\approx 750$  MPa to form pellets of 5 mm diameter. These pellets were kept on the alumina plates and buried under a heap of Mg powder before subjecting to heat treatment. The pellets of each set were heat treated at various temperatures under Ar atmosphere. A ramping rate of  $5^\circ\text{C}/\text{min}$  was maintained using a programmable box-furnace (Model-K1252, Heraeus) for increasing the temperature to the hold temperature,  $T_h$ , at which the samples were maintained for 1 h in all the cases. The hold temperature was varied in the range  $500$ – $920^\circ\text{C}$ . The samples were then quenched in air. The a.c. susceptibility ( $\mathbf{c}_{\text{a.c.}} = \mathbf{c}'_{\text{a.c.}} + i\mathbf{c}''_{\text{a.c.}}$ ) measurement was carried out at different temperatures by a very sensitive (home-made) a.c. susceptometer in an a.c. field of  $\sim 250$  mOe (unless otherwise stated) at 540 Hz using a closed cycle He-cryostat and a lock-in-amplifier which separated the in-phase and out-of-phase signals of the complex  $\mathbf{c}_{\text{a.c.}}(T)$ . Both the  $\mathbf{c}_{\text{a.c.}}-T$  and  $\mathbf{r}-T$  data were recorded while warming the samples at a slow rate of  $0.25$  K/min to ensure thermal equilibrium between the sample and the sensor. The X-ray diffraction data on these samples were acquired by employing a 12 kW rotating anode, Rigaku X-ray diffractometer. The X-ray photoelectron spectra were recorded on a Thermo VG Scientific MultiLab 2000 X-ray photoelectron spectrophotometer, using Mg  $K\alpha$  (1253.6 eV) as an excitation source.

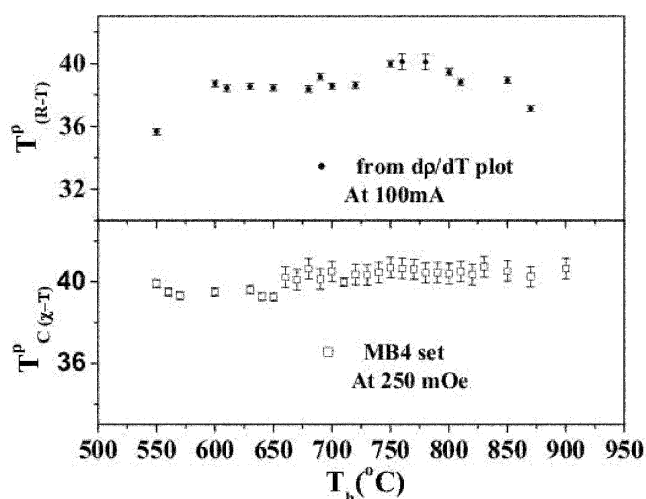
## 3. Results and discussion

In view of the high volatility of Mg during the synthesis of  $\text{MgB}_2$ , existence of a finite window for thermodynamically stable  $\text{MgB}_2$  in the phase diagram when Mg overpressure is high, and the fact that among the known compounds of the Mg–B system i.e.  $\text{MgB}_2$ ,  $\text{MgB}_4$ ,  $\text{MgB}_6$ ,  $\text{MgB}_7$  and  $\text{MgB}_{12}$ ,  $\text{MgB}_2$  is clearly the most Mg-rich (binary) compound (Massalski 1990), it was decided to take Mg in excess of stoichiometric requirement (33.33%) in the starting mixture of Mg and B powders. The MB1–MB4 samples were therefore prepared by having monotonically increasing amount of excess Mg in the starting mixture (from 38.5 a/o to 50 a/o). Furthermore, the pellets were buried under a heap of Mg powder.

From the  $\mathbf{c}_{\text{a.c.}}-T$  measurement carried out on these samples prepared at different hold temperatures, it was found that none of the samples of MB1 and MB2 sets, having starting compositions of  $\text{Mg}:\text{B} = 1.25:2$  (i.e. 38.5 a/o) and

$\text{Mg}:\text{B} = 1.5:2$  (i.e. 42.8 a/o), respectively, were superconducting. On further increase in the Mg ratio (i.e. 46.6 a/o ( $\text{Mg}:\text{B} = 1.75:2$ ) in MB3 set), only those samples which were prepared at a hold temperature lying in the range  $650$ – $760^\circ\text{C}$  exhibited superconducting transition. The samples of MB4 set having 50 a/o of Mg (most Mg rich, i.e.  $\text{Mg}:\text{B} = 2:2$ ) are superconducting (see figure 1) even when synthesized over a wider range of hold temperature i.e.  $T_h = 550$ – $900^\circ\text{C}$  with  $T_{\text{C}(c-T)}^{\text{p}}$  lying in the range of  $39.2 \pm 0.2$ – $40.7 \pm 0.5$  K, with a transition width ( $\Delta T$ ) of  $\leq 1.0$  K. Here,  $T_{\text{C}(c-T)}^{\text{p}}$  is defined as the temperature at which  $\mathbf{c}''(T)$  exhibits a maximum. When the processing temperature was kept below  $550^\circ\text{C}$ , no superconductivity was observed down to the lowest investigated temperature of  $\approx 15$  K, in MB4 samples. On the higher side of hold temperature i.e.  $T_h > 900^\circ\text{C}$ , the resulting samples were mechanically too crumbly to make any measurement. This is in agreement with the observation of Jin *et al* (2001) who reported the formation of porous samples (and the loss of 60% of Mg) at  $900^\circ\text{C}$ . It is thus evident that the 100% increase of excess Mg in the starting mixture (set MB4) led to superconducting samples when sintered over a wider range of  $550$ – $900^\circ\text{C}$ .

The critical current density ( $J_c$ ) of the samples of set MB4, sintered at different temperatures, has been calculated using modified Bean's critical state model (Beans 1962; Chen *et al* 1989; Clem 1994). Figure 2 shows  $J_c(T)$  behaviour of the  $\text{MgB}_2$  samples synthesized at  $T_h$  of 550, 790, 850 and  $870^\circ\text{C}$  with the estimated transition temperature,  $T_p$ . For all the samples, the estimated/extrapolated  $J_c$  at 37.5 K is more than  $10^7$  A/m<sup>2</sup>. Further, the sample synthesized at  $790^\circ\text{C}$  exhibited highest  $J_c$  of  $1.5 \times 10^7$  A/m<sup>2</sup> at 39.6 K. It is, therefore, noted that  $790^\circ\text{C}$  is the most suitable synthesis temperature for preparing  $\text{MgB}_2$  from a starting mixture having 100% excess of Mg.

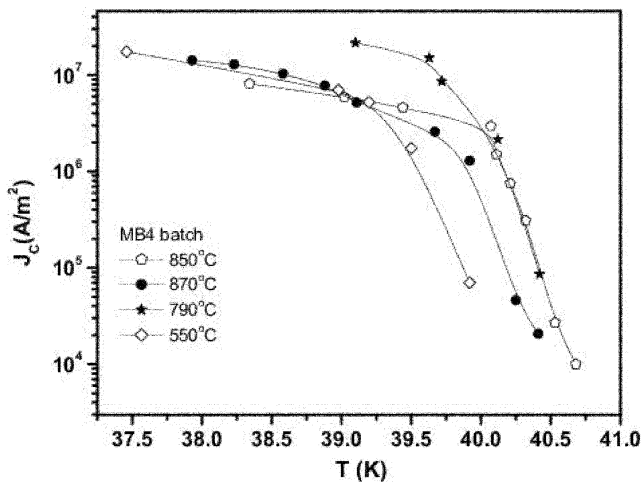


**Figure 1.** Variation of  $T_{\text{C}(R-T)}^{\text{p}}$  (upper panel) and  $T_{\text{C}(c-T)}^{\text{p}}$  (lower panel) with sintering temperature for the  $\text{MgB}_2$  samples from MB4 batch ( $\text{Mg}_{2-x}\text{B}_2$ ,  $x = 0$ ). All these samples are quenched to room temperature after a hold time of 1 h.

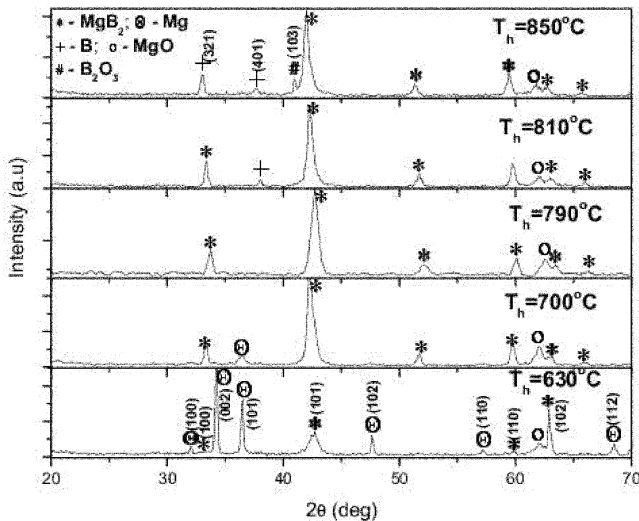
The X-ray diffractograms (XRD) of various  $\text{MgB}_2$  samples from MB4 set have been analysed for correlating the formation of various phases with the increase in processing temperature. For the sake of brevity, we show in figure 3, diffractograms of the samples synthesized at 630, 700, 790, 810 and 850°C. It may be noted that the samples prepared at 630 and 700°C possess additional phases, viz. Mg and MgO. This could be due to the excess Mg taken in the starting powder mixture. The absence of peaks corresponding to Mg in the diffractograms of the samples sintered at 790°C and up to ~870°C reveals the complete consumption of Mg in the formation of the diboride phase. The presence of peaks corresponding to the rem-

nant B in the XRD patterns of samples prepared at 810 and 850°C clearly support this view. These results indicate that at higher  $T_h$ , all the Mg is consumed in the formation of  $\text{MgB}_2$  besides its vapourization (m.p. of Mg, 650°C). The sample prepared at 790°C has maximum fraction of  $\text{MgB}_2$  with MgO as the only additional phase, and none of the constituents is detected in the elemental form. All these diffractograms reveal the formation of MgO too. This is understandable as the heating process was carried out in flowing Ar (without vacuum sealing). These MgO particles act as effective pinning centres, since the average particle size of MgO was estimated to lie between 70–150 Å using Debye-Scherrer formula, which is comparable to the coherence length in  $\text{MgB}_2$  [~100 Å, (Welp *et al* 2003)].

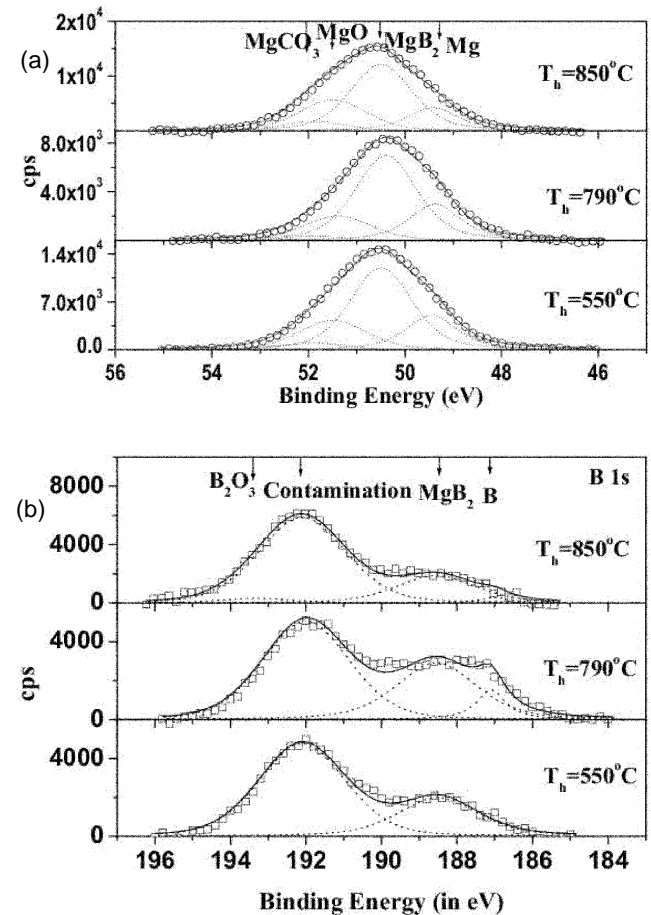
XPS analysis has also been undertaken for the samples of MB4 batch to strengthen the qualitative phase analysis drawn from XRD. The core level Mg-2p and B-1s XPS spectra, recorded for a few representative  $\text{MgB}_2$  samples



**Figure 2.**  $J_c$  vs  $T$  curves for  $\text{MgB}_2$  samples from MB4 set sintered at 550, 790, 850, and 870°C.



**Figure 3.** X-ray diffraction patterns for the  $\text{MgB}_2$  pellets sintered at 630, 700, 790, 810 and 850°C. The sample sintered at 790°C is found to have lesser impurities than those sintered at lower and higher temperatures.



**Figure 4.** Core level spectra of the observed (a) Mg-2p and (b) B-1s peaks together with the fitted curves having both the gaussian and Lorentzian components, for samples sintered at 550°C, 790°C and 850°C from MB4 batch (whereas the symbols represent the experimental spectrum, the dotted lines indicate the component-peak used for overall curve fitting of the resulting peak shown by the solid line. The various peak-locations have been appropriately indicated by vertical-arrows).

**Table 1.** Observed and reported binding energies of Mg-2*p* and B-1*s* electrons in Mg, MgB<sub>2</sub>, MgO, contamination and other oxides in B, and B<sub>2</sub>O<sub>3</sub> for samples synthesized from MB4 set at 550°C, 790°C and 850°C, respectively.

Core level	Source/compound	Reported BE (eV)	Observed BE (eV)
Mg-2 <i>p</i>	Mg	49.2–49.9 (Wagner <i>et al</i> 1979)	49.4–49.5
	MgB <sub>2</sub>	50.54 (Wagner <i>et al</i> 1979)	50.4–50.6
	MgO	51.5 (Jariwala <i>et al</i> 2003)	51.4–51.6
	MgCO <sub>3</sub>	51.9 (Crist 1999)	51.9
B-1 <i>s</i>	B	186.9–187.5 (Wagner <i>et al</i> 1979)	187.0–18.1
	MgB <sub>2</sub>	188.2 (Garg <i>et al</i> 2004)	188.5–188.55
	Other contamination	191.4, 193.2 (Aswal <i>et al</i> 2002)	192.1–192.2
	B <sub>2</sub> O <sub>3</sub>	193.3 (Aswal <i>et al</i> 2002)	193.3

(two at the extreme ends and one in the middle of the processing temperature) are presented in figure 4. The core level spectrum of a multivalent element in a sample will generally exhibit a broad peak, which can be deconvoluted to identify different chemical states of the element in question. The observed Mg-2*p* peaks in various spectra have been resolved into four peaks (table 1) with their maxima at 49.4–49.5, 50.4–50.6, 51.4–51.6 and 51.9 eV. The peak at 49.4 eV corresponds to 2*p*-electrons in metallic magnesium (Wagner *et al* 1979), while the other three peaks at higher BE values i.e. at 50.4–50.6, 51.4–51.6 and 51.9 eV, can be attributed to the presence of MgB<sub>2</sub>, MgO and MgCO<sub>3</sub> (Crist 1999; Jariwala *et al* 2003), respectively. Likewise a broad B-1*s* peak in the XP spectra (figure 4b) has been deconvoluted into a number of peaks appearing at 187–187.1, 188.5–188.55, 192.1–192.2 and 193.3 eV, respectively. These peaks correspond to unreacted B, MgB<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and other contaminants of B (Wagner *et al* 1979; Aswal *et al* 2002; Garg *et al* 2004), respectively. McGuinness *et al* (2001) also reported two additional peaks at 191.4 and 193.2, besides the main peak in their Boron-K-edge NEXAFS for the samples of MgB<sub>2</sub> and ascribed those to B<sub>2</sub>O<sub>3</sub> and other contaminants of B. Similarly, Zhu *et al* (2002) and McGuinness *et al* (2001) reported the presence of extra peaks at 191.7 and 193.6 eV. Other workers (Foo *et al* 1991; Vasquez *et al* 2001) also observed the extra peaks in B-1*s* spectrum and ascribed those to B<sub>2</sub>O<sub>3</sub>, sub-oxides and hydroxides of boron.

It can be seen that at 790°C, MgB<sub>2</sub> phase is formed predominantly along with reduced fraction of MgO, which is

in reasonable agreement with the observed XRD results. The observation of the Mg-2*p* peak corresponding to pure Mg in all the three investigated samples is in contrast with the XRD observations (see figure 3). This could well be due to the slight degradation of the sample surface leading to Mg-enrichment, as is also reported previously (Aswal *et al* 2002). The absence of peak at 187 eV in the B-1*s* spectra (figure 4b) for the samples synthesized at 550°C shows complete consumption of B (which is expected as the Mg was in excess in these samples from MB4 batch). At 790°C, however, unreacted B appears whose concentration decreases with increase in *T<sub>h</sub>* to 850°C, due to the formation of B<sub>2</sub>O<sub>3</sub>. Thus, for samples of MB4 batch, the processing temperature, ~790°C, is most suitable for the synthesis of MgB<sub>2</sub> samples with improved superconducting properties. This clearly demonstrates the essential requirement of excess Mg in the starting mixture in this simple and economic synthesis technique.

#### 4. Conclusions

Starting with 100% excess magnesium in the mixture of Mg and B and without requiring the sealing of the starting powder mixture either in quartz ampoules or Ta/Nb liners it has been possible to form magnesium diboride phase having optimal superconducting characteristics. The best samples having maximum fraction of MgB<sub>2</sub> and exhibiting superconducting transition at 40.5 K with  $\Delta T = 0.6$  K were prepared by heat treating the Mg rich pellets (Mg : B :: 2 : 2) in flowing Ar at 790°C for 1 h. The maximum critical current density, estimated from the a.c. susceptibility data, is found to be  $1.5 \times 10^7$  A/m<sup>2</sup> at 39.6 K. From both XPS and XRD results, it is found that the processing temperature of 790°C is optimum for the formation of MgB<sub>2</sub> phase from a starting mixture having 100% excess of Mg.

#### Acknowledgement

The authors thank A Lohani, Department of Physics, Indian Institute of Technology Bombay, Mumbai, for X-ray photoelectron spectroscopic measurements.

#### References

- Aswal D K, Muthe K P, Tawde S, Chodhury S, Bagkar N, Singh A, Gupta S K and Yakhmi J V 2002 *J. Cryst. Growth* **236** 661
- Beans C P 1962 *Phys. Rev. Lett.* **8** 250
- Botta D *et al* 2002 *Physica* **C369** 232
- Bud'ko S L, Canfield P C and Kogan V G 2002 *Physica* **C382** 85
- Buzae C and Yamashita T 2001 *Supercond. Sci. Technol.* **14** R115
- Canfield P C, Finnemore D K, Bud'ko S L, Ostenson J E, Lapertot G, Cunningham C E and Petrovic C 2001 *Phys. Rev. Lett.* **86** 2423

- Cardwell D A, Hari Babu N, Kambara M and Campbell A M 2002 *Physica* **C312** 1262
- Cava R J, Zandbergen H W and Inumaru K 2003 *Physica* **C385** 8
- Chen D-X, Nogues J and Rao K V 1989 *Cryogenics* **29** 800
- Clem J R 1994 *Phys. Rev.* **B50** 9355
- Crist B V 1999 *Handbook of elements and native oxides* (XPS International, Inc.) Vol. 1
- Drozd V A, Gabovich A M, Gierlowski P, Pekala M and Szymezak H 2004 *Physica* **C402** 325
- Feng Q R *et al* 2004 *cond-mat/0408597*
- Foo W C, Ozcomert J S and Ternary M 1991 *Surf. Sci.* **255** 245
- Garg K B, Chatterji T, Dalela S, Heinonnen M, Leiro J, Dalela B and Singhal R K 2004 *Solid State Commun.* **131** 343
- Jariwala C *et al* 2003 *Phys. Rev.* **B68** 174506
- Jin S, Mavoori H, Bower C and Dover R B 2001 *Nature* **411** 563
- King R B 2002 *Polyhedron* **21** 2347
- Kumakura H, Takano Y, Fujii H, Togano K, Kito H and Ihara H 2001 *Physica* **C363** 179
- Liu Z-K, Schlom D G, Li Q and Xi X X 2001 *Appl. Phys. Lett.* **78** 3678
- Massalski T 1990 *Binary alloy phase diagrams* (Materials Park, OH: ASM International) 2nd ed.
- McGuinness C *et al* 2001 *Europhys. Lett.* **56** 112
- Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Aki-mitsu J 2001 *Nature* **410** 63
- Ribeiro R A, Bud'ko S L, Petrovic C and Canfield P C 2003 *Physica* **C385** 16
- Shen J-Q, Fang M-H, Zheng Y, Wang H T, Lu Y and Xu Z-A 2003 *Physica* **C386** 663
- Vasquez R P 2001 *Phys. Rev.* **B64** 052510
- Wagner C D, Riggs W M, Davis L E and Moduler J F 1979 *Handbook of X-ray photoelectron spectroscopy* (ed.) G E Muilenberg (Minnesota: Perkin-Elmer Corporation)
- Welp U *et al* 2003 *Physica* **C385** 154
- Zhu Y *et al* 2002 *Phys. Rev. Lett.* **88** 247002