RESEARCH PAPERS

On the Structure and Properties of the Layered Lanthanide (Ln) Barium Copper Oxyborates, LnBaCuO$_2$BO$_3$

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Abstract

An ordered structure model has been derived for the new series of layered lanthanide (Ln) cuprates, LnBaCuO$_2$BO$_3$, and some of its members have been synthesized. The cuprates were prepared under ambient pressure by reacting BaO$_2$, Ln$_2$O$_3$, CuO and B$_2$O$_3$ at 1190 K. The derived model, with the tetragonal space-group symmetry *P4bm* and $a = 5.5743\,(4)$, $c = 7.5053\,(6)$ Å for the La compound, has been successfully tested against X-ray powder diffraction data. The model has reasonable estimated bond-valence values. Measured magnetic susceptibilities of powder specimens of LaBaCuO$_2$BO$_3$ indicate a transition to a diamagnetic state at *ca* 29 K.

1. Introduction

Recently a new type of copper oxycarbonate, with the composition A_2CuO$_2$CO$_3$, where A is Sr^{2+} or a mixture of Sr^{2+} and Ba^{2+}, has been discovered (see *e.g.* Miyazaki, Yamane, Kajitani, Oku, Hiraga, Morii, Fuchizaki, Funahashi & Hirai, 1992; Armstrong & Edwards, 1992, and references therein). These carbonates, shown by powder diffraction techniques to contain infinite copper(II)–oxygen layers, can be made superconducting by hot isostatic pressing (Kinoshita & Yamada, 1992; Izumi, Kinoshita, Matsui, Yanagisawa, Ishigaki, Kamiyama, Yamada & Asano, 1992). Very recent results (Uehara, Nakata & Akimitsu, 1993) indicate that superconductivity can possibly be achieved by a partial substitution (15%) of the carbonate ion content with borate ions.

Inspired by these previous results (*cf.* above) and in line with our current research (Norrestam, Nygren & Bovin, 1992) on transition-metal oxyborates, we initiated high-temperature solid-state synthetic studies to prepare phases with the general composition LnACuO$_2$BO$_3$, where Ln is a trivalent lanthanide ion and A a divalent alkaline earth ion. With

A = Sr, a new type of strontium copper(II) borate (Norrestam, Carlson, Kritikos & Sjödin, 1994) with the composition SrCu$_2$(BO$_3$)$_2$, together with unreacted lanthanide oxide were the major phases. As shown by single-crystal diffraction studies, these new strontium copper(II) borates do not contain infinite copper(II) oxygen layers, but contain isolated copper–oxygen dimers with the composition Cu$_2$O$_6$. However, the syntheses containing trivalent lanthanide ions and A = Ba gave the anticipated result. Thus, a new series of compounds apparently related to the (Sr,Ba)$_2$CuO$_2$CO$_3$ phases were formed. Independent of the present study, Li, Kremer & Maier (1993) very recently published a study of the same types of new lanthanide barium copper(II) oxyborates. However, our synthetic procedure is slightly different and possibly more relevant as we completely avoid any carbonates as starting materials. The presence of carbonates might possibly lead to mixed borate–carbonate phases (Uehara *et al.*, 1993).

X-ray powder diffraction studies (see also Li *et al.*, 1993) indicate that the structures of these new copper borate phases are closely related to those of the previously known carbonate phases. Unfortunately, the lack of proper single crystals for an unambiguous structural characterization limits the relevance of the various models (Miyazaki *et al.*, 1992; Armstrong & Edwards, 1992; Izumi *et al.*, 1992) proposed for the copper carbonates and borates. The present paper describes a new structural model for the borate compounds. This model has apparent advantages over the models previously suggested for the carbonates by being simpler and by describing a completely ordered atomic arrangement, which agrees well with known features of related structures. Furthermore, the refinement of the present model from powder diffraction data converges smoothly, without the need to introduce any, possibly physically irrelevant, model constraints on *e.g.* thermal and/or occupation factors.

2. Experimental

Black coloured specimens of $LnBaCuO_2BO_3$ with Ln = La, Nd, Sm, Gd, Tb were prepared by heating stoichiometric mixtures of Ln_2O_3, BaO_2, CuO and a 10% excess of B_2O_3, pressed into pellets, in platinum tubes in air. The pellets were firstly heated $(400\ K\ h^{-1})$ to 1070 K, kept for *ca* 1 h at this temperature, then the temperature was raised $(100\ K\ h^{-1})$ to 1190 K. All specimens were annealed at 1190 K for *ca* 50 h, followed by cooling $(200\ K\ h^{-1})$ to 570 K and then rapidly cooled (2 h) to room temperature. As judged from X-ray powder photographs (*cf*. below), some partial decomposition of *i.a.* $LaBaCuO_2BO_3$ can be detected after a 50 h annealing at 1270 K. Annealing at 1320 K for 50 h led to complete decomposition. However, specimens of $LaBaCuO_2BO_3$ could be annealed at 1220 K for 35 days without any appreciable decomposition. With the synthesis procedure described above, no detectable amounts (X-ray powder diffraction) of $LnBaCuO_2BO_3$ phases were formed for the smaller lanthanide ions. Thus, these new phases seem to exist only for the largest lanthanide ions from La to Tb. Attempts to prepare such phases for cerium, when using CeO_2 as starting material, or for bismuth (using Bi_2O_3) failed.

The metal compositions of the prepared $LnBaCuO_2BO_3$ specimens were determined by energy-dispersive X-ray analysis (EDX), using a JEOL-820 scanning electron microscope (SEM) equipped with a Link AN10000 EDX system. The EDX analyses gave values close to the expected metal ratio (Ln:Ba:Cu) 1:1:1 and the SEM images showed that the crystal sizes in the specimens were less than 1 μm. Several, so far unsuccessful, attempts to grow crystals suitable for single-crystal X-ray diffraction studies have been performed. These attempts also include the use of various flux media, including obvious ones like larger excesses of BaO_2, CuO or B_2O_3 in the syntheses.

X-ray powder photographs (Cu $K\alpha_1$ radiation) were collected with a Guinier–Hägg camera using silicon ($a = 5.430880$ Å at 295 K) as an internal standard. The reflection positions on the photographs could be indexed with a unit cell of tetragonal metric symmetry. The cell parameters obtained by least-squares fitting to 20 indexed positions are listed in Table 1.* Preliminary high-resolution electron microscopy (HREM) studies supported the adopted tetragonal cell symmetry and indicated that reflections with $h + k$ odd were generally very weak.

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* Lists of powder diffraction data for the compounds listed in Table 1 and observed and calculated powder diffraction intensity data have been deposited with the IUCr (Reference: AB0325). Copies may be obtained from The Managing Editor, The International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Tetragonal unit-cell parameters* (Å) *and unit-cell volumes* (Å³) *with e.s.d.'s for the synthesized* $LnBaCuO_2BO_3$ *compounds*

Compound	a	c	V
$LaBaCuO_2BO_3$	5.5743 (4)	7.5053 (6)	233.21 (3)
$La_{0.9}Nd_{0.1}BaCuO_2BO_3$	5.5693 (3)	7.5050 (5)	232.78 (2)
$NdBaCuO_2BO_3$	5.5251 (4)	7.4381 (6)	227.06 (3)
$SmBaCuO_2BO_3$	5.4974 (3)	7.4079 (5)	223.88 (2)
$GdBaCuO_2BO_3$	5.4798 (3)	7.3957 (5)	222.08 (2)
$TbBaCuO_2BO_3$	5.4677 (3)	7.3805 (5)	220.65 (2)

Reflections $0kl$, with k odd, were either absent or very weak. No indications of doubled cell parameters, as found in one case for the related oxycarbonates (Miyazaki *et al.*, 1992), were observed.

Accurate X-ray powder diffraction intensity data (*cf*. Fig. 1) of the lanthanum compound [$Z = 2$, $V = 233.21$ (3) Å³, $M_r = 430.59$, $\mu = 1416\ cm^{-1}$, $D_x = 6.132\ g\ cm^{-3}$] were collected at 295 K for a flat rotating sample in a symmetric mode, with a Stoe Stadi/P powder diffractometer. A focusing germanium crystal monochromator (focal distance 440 mm) was used to obtain Cu $K\alpha_1$ radiation. The data were collected with a linear position-sensitive detector covering $6.4°$ in 2θ, that was moved in steps of $0.2°$, giving average intensities of 32 measurements for each 2θ value ($10 \le 2\theta \le 125°$).

AC magnetic susceptibility data were collected on polycrystalline samples in the temperature range 14–325 K, using a Lake Shore Inc. AC Susceptometer, model 7130, equipped with a helium cryostat. The experimental susceptibilities were corrected for sample holder diamagnetism. A frequency of 125 Hz and a magnetic field strength of 500 A m⁻¹ were used in the case of $LaBaCuO_2BO_3$ and $La_{0.9}Nd_{0.1}BaCuO_2BO_3$. For $NdBaCuO_2BO_3$, a fre-
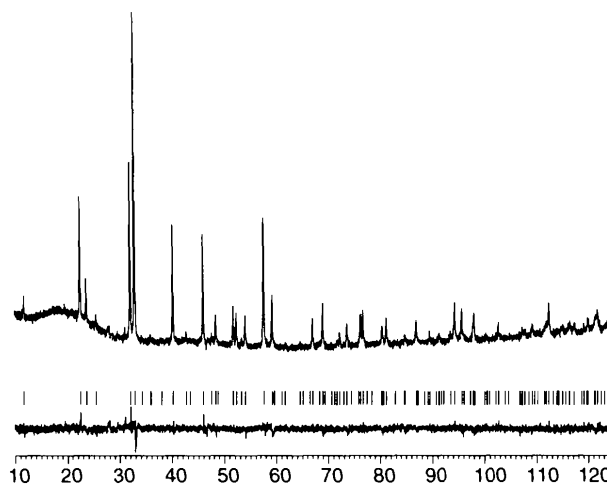

Fig. 1. The X-ray powder diffraction pattern of $LaBaCuO_2BO_3$. A difference (obs. − calc.) profile is shown beneath. The tic marks represent reflection positions.

quency of 500 Hz and a magnetic field strength of 125 A m^{-1} was used.

3. Structure determination and refinement

Full-profile refinements (Rietveld, 1969) of the collected powder diffraction data for $LaBaCuO_2BO_3$ were performed with a local version of the program DBW3.2S (Wiles, Sakthivel & Young, 1987). Initial refinements included correction factors for absorption effects, yielding a μr value of 1.68. Three different models proposed for the related oxycarbonate phases (Miyazaki *et al.*, 1992; Armstrong & Edwards, 1992; Izumi *et al.*, 1992) were used as starting models. As regards the major features of the structures (metal-atom positions, presence of copper–oxygen layers), the models are closely related. However, two of the models (Armstrong & Edwards, 1992; Izumi *et al.*, 1992) include pronounced disorder of the triangular carbonate groups (analogous to the borate group in the present compound). One of the models (Izumi *et al.*, 1992) also includes a disorder of a fraction of the Cu atoms. Although all three suggested models are tetragonal, they assume different unit-cell sizes and different space-group symmetries, *viz.* $\bar{I}4$, $P4/mmm$ and $P42_12$, respectively. Despite this variety of structure models tested, none refined properly for our borate diffraction data as they yielded physically unreasonable bond-distance distributions, thermal displacement parameters and/or occupation factors for some of the atoms.

At this stage it was considered necessary to derive a new and different structure model for $LaBaCuO_2-BO_3$. As no information (*e.g.* splitting of reflections at high 2θ values) is contained in the diffraction data, the tetragonal symmetry was retained. To avoid introducing disorder of the borate groups and to avoid mixing the barium and lanthanum positions, a reasonably low, possibly polar, tetragonal space-group symmetry could be anticipated. With these assumptions, a very reasonable model with the symmetry $P4bm$ could be derived. The few very weak $0kl$ reflections with k odd observed by the HREM studies might probably be ascribed to *e.g.* dynamical scattering and/or intergrowth effects, but might also indicate a very small real deviation from the assumed symmetry. The outcome of the final refinements (Fig. 1) does not indicate that the diffraction data collected contain information on such a deviation. The final full-profile refinement of the derived non-disordered model of $LaBaCuO_2BO_3$ refined smoothly and yielded reasonable distributions of thermal parameters, interatomic distances and contact distances (Tables 2–4).* The structure factor R_F and the

* See deposition footnote.

Table 2. *Fractional coordinates* ($\times 10^3$) *and isotropic thermal parameters* (Å^2) *for the structural model of* $LaBaCuO_2BO_3$ *with space group symmetry P4bm*

Estimated standard deviations (e.s.d.'s) are given in parentheses. The z coordinate of La is fixed to 0, to define the origin along the polar z axis.

	x	y	z	B
La	0	0	0	1.8 (1)
Ba	0	0	502 (1)	0.3 (1)
Cu	500	0	731 (2)	0.8 (1)
O(1)	245 (9)	745 (9)	770 (5)	1.5 (5)
O(2)	500	0	460 (3)	1.1 (6)
O(3)	150 (3)	650 (9)	166 (3)	2.6 (7)
B	500	0	270	2.0

Table 3. *Metal–oxygen distances* (Å) *less than* 3.9 Å, *with e.s.d.'s in* $LaBaCuO_2BO_3$

	Multiplicity	Distance
La—O(1)	4	2.62 (5)
La—O(3)	4	2.46 (2)
Ba—O(1)	4	2.82 (5)
Ba—O(2)	4	2.81 (1)
Ba—O(3)	4	3.30 (2)
Cu—O(1)	2	2.03 (5)
Cu—O(1)	2	1.96 (5)
Cu—O(2)	1	2.04 (2)
Cu—O(3)	2	3.48 (2)
B—O(2)	1	1.43 (1)
B—O(3)	2	1.42 (2)

Table 4. *The shorter metal–metal and oxygen–oxygen contact distances* (Å) *with e.s.d.'s in* $LaBaCuO_2BO_3$

	Multiplicity	Distance
La⋯La	4	3.94
La⋯Ba	1	3.74 (1)
La⋯Ba	1	3.77 (1)
La⋯Cu	4	3.44 (1)
Ba⋯Ba	4	3.94 (1)
Ba⋯Cu	4	3.28 (1)
Cu⋯Cu	4	3.94 (1)
O(3)⋯O(3)	1	2.37 (3)
O(2)⋯O(3)	2	2.51 (2)
O(1)⋯O(1)	4	2.79 (7)

profile R_{wp} values decrease from 0.079 to 0.053 and from 0.053 to 0.041, respectively, when the O atoms are included in the model. Due to the relatively weak X-ray scattering power of boron, the refinement of the B atom position yielded very uneven B—O bond distances in the triangular borate groups and also a rather high temperature factor (8 Å^2). Although the e.s.d.'s for the boron parameters were so large that proper values were within a few e.s.d.'s from the refined ones, it was decided to keep the B atom at the centroid position of the borate group. Furthermore, its temperature factor was kept fixed to a value of the same magnitude (2 Å^2) as those of the borate O atoms. The final R values became: $R_p = 0.033$, $R_{wp} = 0.041$, $R_F = 0.053$ and $R_B = 0.063$. The atomic labelling used is shown in Fig. 2.
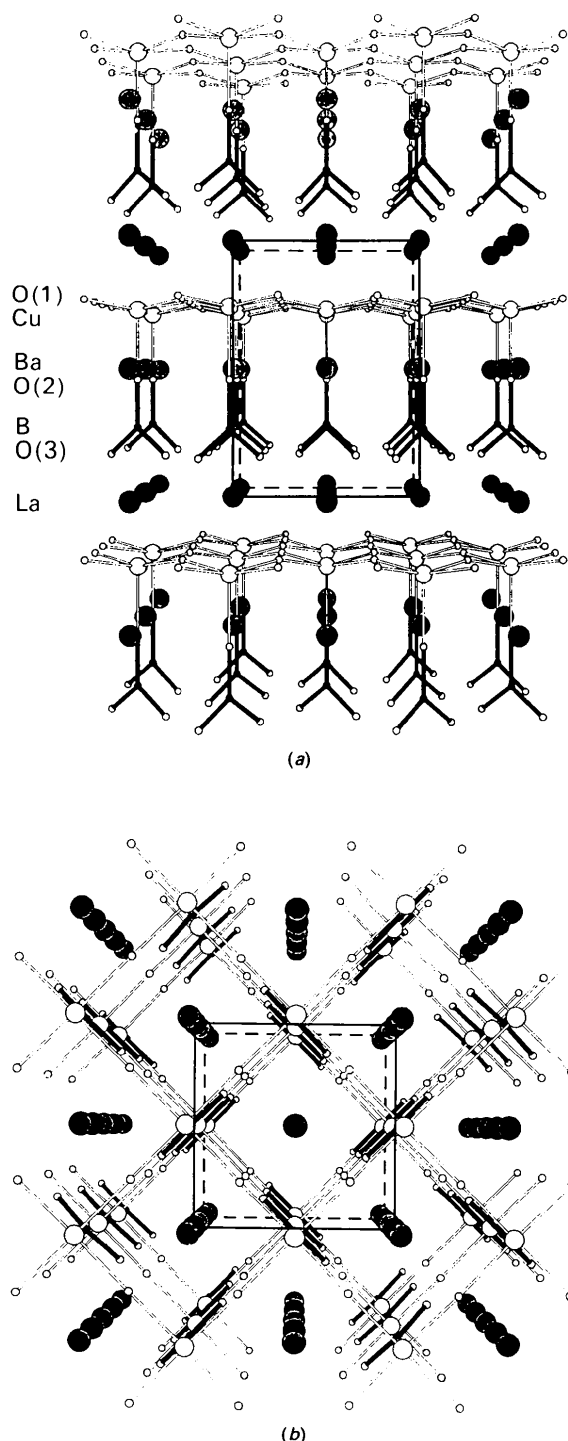
O(1)
Cu

Ba
O(2)

B
O(3)

La

(a)

(b)

Fig. 2. (a) Perspective view along (Ī00) of the crystal structure of LaBaCuO₂BO₃, together with the atomic labels adopted. For clarity, the B—O bonds of the triangular borate groups are drawn as dark grey. The indicated unit cell has its origin at the lower left corner, with y horizontal, z vertical and x pointing out from the paper plane. (b) View along (00Ī) of LaBaCuO₂-BO₃, with the unit-cell origin at the upper left corner, y horizontal, x vertical and z pointing out from the paper plane.

4. Results and discussion

The structure of LaBaCuO₂BO₃, shown in Fig. 2, can be described as consisting of infinite layers of corner-sharing square pyramids of CuO₅, stacked along (001) and separated by a unit-cell translation (7.50 Å). The apex O atoms [O(2)] of the pyramids belong to adjacent borate groups. The Ba atoms are located between the borate groups to form slabs ($0.166 \leq z \leq 0.77$ in Fig. 2) with the composition BaCuO₂BO₃, which are separated by the La atoms.

The La atoms are coordinated by eight O atoms that form a cube, slightly twisted towards an anti-prism. The Ba atoms are coordinated by eight O atoms that form an archimedean antiprism, with Ba—O distances of ca 2.8 Å (Table 3). Further away (3.3 Å) there are four more O atoms and the Ba atoms can thus be considered as 8 + 4 coordinated. The Cu—O distances are equal (ranging from 1.96 to 2.04 Å) to within a few e.s.d.'s and the Cu atoms are, as can be expected, located above [0.29 (5) Å] the square plane of the coordination pyramid. However, the magnitudes of the e.s.d.'s (up to 0.05 Å) limit the relevance of any more detailed analysis of the coordination.

The adopted space-group symmetry implies that the La and Ba positions both will have a crystallographic C_4 point symmetry, while the Cu and B positions have C_{2v} symmetry. It also follows that the B—O(2)—Cu bond angle is symmetry restricted to become 180°. The C_{2v} symmetry of the borate group means that the O atoms of the borate groups [O(2) and O(3)] have to form an isosceles triangle. The two equivalent edges (2.51 Å) of the triangle are slightly longer than the third edge (2.37 Å). This indicates that the borate group is probably significantly distorted from its ideal D_{3h} symmetry.

Although the observed bond distances seem to agree well with expected values (Shannon, 1976), a more revealing test of the chemical relevance of the bond distance distributions in the structure is obtained by calculating empirical bond-valence sums (b.v.s. values) for all atoms. With the parameter values for the bond valence–bond distance correlation functions given by Brown & Altermatt (1985), the b.v.s. values for the metal atoms La, Ba and Cu are 3.0, 2.0 and 2.1, respectively. The b.v.s. values for the three types of O atoms O(1), O(2) and O(3) are 1.9, 2.0 and 1.9, respectively. The agreement with the formal valences is remarkably good and assures that the bond-distance distributions in the present structure model are normal and agree well with the distributions in all the oxides from which Brown and Altermatt derived their parameter values. It could be noted that by calculating b.v.s. values with the parameters for Ba at the La position and with the La parameters for the Ba positions gave the unrealistic

values of 4.1 for the La position and 1.4 for the Ba position. Thus, despite the difficulty to differentiate between La and Ba due to their very similar X-ray scattering powers, the metal distribution suggested from the bond valence analysis is the only one that is realistic.

The disordered structure proposed by Izumi et al. (1992) for the superconducting alkaline earth copper oxycarbonate has unit-cell dimensions similar to those of the present model, but with a different space group symmetry ($P42_12$). It is tempting to consider an alternative hypothetical model of this oxycarbonate that is more closely related to the present borate structure. Such a model could be derived by having $(Ba,Sr)CuO_2CO_3$ slabs separated by Sr atoms. To achieve reasonable b.v.s. values for these Sr atoms, the distance between the slabs (viz. the c translation) has to be increased compared with that of LaBaCuO$_2$BO$_3$. Such an increase is also observed, as the c axis increases from ca 7.50 Å in the present case to ca 7.85 Å for the oxycarbonate (Izumi et al., 1992).

The measurements of magnetic susceptibilities showed [Fig. 3(a)] that the prepared LaBaCuO$_2$BO$_3$ specimen has a weak temperature-independent paramagnetic susceptibility between 29 and 300 K. At temperatures below 29 K a translation to a diamagnetic state occurs with a linear decrease of the susceptibility down to 14 K, which is the lowest temperature experimentally attainable with our instrument. The volume susceptibility at 14 K is too small ($< 1\%$) to be interpreted as a Meissner effect. A possible source for the diamagnetic transition might be due to minor impurities of the known superconducting $(La,Ba)_2CuO_4$ phases (Bednorz & Müller, 1986). However, powder diffraction patterns do not indicate the presence of any such phases in the LaBaCuO$_2$BO$_3$ specimens. Detailed studies of the low-temperature magnetic behaviour (e.g. below 30 K) is needed for further characterization of this interesting new phase. The pure Nd phase, NdBaCuO$_2$BO$_3$, showed a similar susceptibility curve [Fig. 3(b)] as that recently reported by Li et al. (1993). The linear high-temperature region ($110 < T < 300$ K) of the susceptibility were extrapolated to give a Weiss temperature of about -107 K. At low temperatures a negative deviation from the Curie–Weiss law was observed. This could possibly be interpreted as an antiferromagnetic ordering at low temperatures. The paramagnetic behaviour of La$_{0.9}$Nd$_{0.1}$BaCuO$_2$BO$_3$ [Fig. 3(c)] clearly shows the effect of the incorporation of trivalent Nd ions into the LaBaCuO$_2$BO$_3$ structure. As for the pure Nd compound, the (La,Nd) phase follows a Curie–Weiss law at high temperatures ($110 < T < 300$ K) with $\theta = -165$ K. The negative deviation of the susceptibility at low temperature suggests that crystal field effects become important.
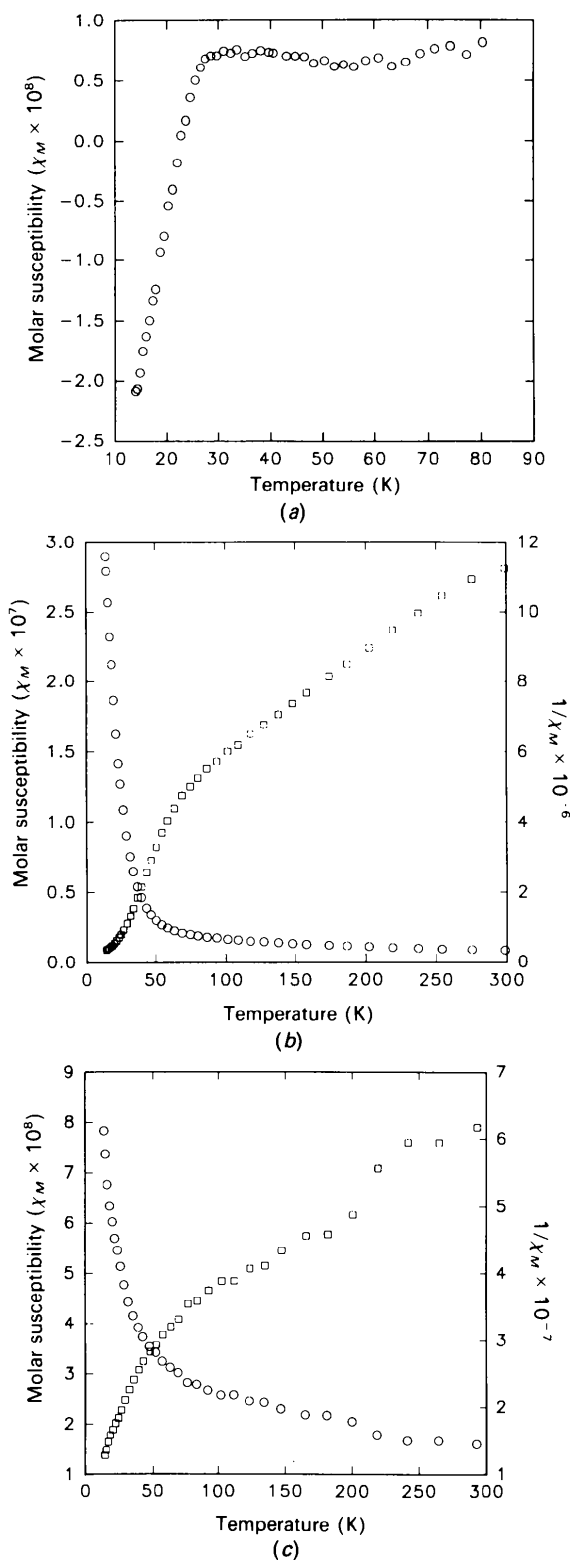

Fig. 3. Molar ($\square$, m^3 mol^{-1}) and inverse molar ($\bigcirc$, mol m^{-3}) susceptibilities as a function of temperature for (a) LaBaCuO$_2$-BO$_3$, $14 < T < 80$ K; (b) NdBaCuO$_2$BO$_3$, $14 < T < 300$ K; (c) La$_{0.9}$Nd$_{0.1}$BaCuO$_2$BO$_3$, $14 < T < 300$ K.

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The Superstructure of Domain-Twinned η'-Cu$_6$Sn$_5$

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Abstract

The cell of the low-temperature modification of Cu$_6$Sn$_5$, the η -phase, has been determined by means of electron diffraction of single domains. The basic hexagonal NiAs (B8) type cell is pentupled, reflected in the reciprocal lattice by a fivefold superstructure running along [11$\bar{2}$1]*. The extensive domain-twinning macroscopically gives rise to perfect hexagonal symmetry, which explains the previously proposed hexagonal cell [$a = 5a_{NiAs}$, $c = 5c_{NiAs}$; Bernal (1928), *Nature*, **122**, 54]. The structure was solved by occupying every fifth trigonal bipyramidal site of the NiAs-type structure and shifting the atoms surrounding these additional Cu atoms to form Edshammar$_{11}$ polyhedra with Cu—Sn and Cu—Cu distances in the range 2.60–2.74 Å. The supercell reflections from the different domains of the twinned crystals are not superimposed, which facilitated the crystal structure refinement [space group $C2/c$; $a = 11.022$ (5), $b = 7.282$ (4), $c = 9.827$ (2) Å, $\beta = 98.84$ (4)° and $Z = 4$], by means of single-crystal X-ray diffraction on a domain-twinned specimen. The Edshammar$_{11}$ polyhedra form corner-connected zigzag chains along [001]. The structure of η'-Cu$_6$Sn$_5$ is hence a new superstructure-type belonging to the NiAs–Ni$_2$In structure group. The projections of this structure along the axes of the NiAs-type base cell are void of superstructure.

Introduction

This work is part of a series of investigations on structures of and structural relations between M—Sn intermetallic phases, where M are first-row transition metals. Apart from the theoretical importance, there is a vast technical interest in these systems. This investigation concerns the Cu–Sn phase diagram, which is also important in more complex systems since when Cu is present in a Sn melt, crystals of Cu$_6$Sn$_5$ easily grow. This phase (together with Cu$_3$Sn) is the phase growing in Sn/Pb solders of copper leads. Cu$_6$Sn$_5$ grows in certain amalgams; it forms in the processing of wires of the superconducting phase Nb$_3$Sn and in brass.

In this report, the domain crystal structure of one modification of Cu$_6$Sn$_5$, the low-temperature modification η', is studied. The high-temperature modification η-Cu$_6$Sn$_5$ was first reported to be of the NiAs structure type ($P6_3/mmc$, $a = 4.190$ Å and $c = 5.086$ Å) by Westgren & Phragmen (1928). Bernal (1928) found a superstructure of the low-temperature ordered modification η'. He suggested a fivefold superstructure along all axes yielding a hexagonal cell of the approximate dimensions $a = 20.8$, $c = 25.4$ Å. The same supercell of η' was also reported by Carlsson & Hägg (1932) and Gangulee, Das & Bever (1973). In the present investigation the cell is found to be monoclinic, but the domain-twinned