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# Crystal chemistry of $HgBa_2CaCu_2O_{8+\delta}$ and $HgBa_2Ca_2Cu_3O_{8+\delta}$ Single-crystal X-ray diffraction results

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## Abstract

Crystal structures of $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212) and $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) have been determined on single crystals at room temperature conditions by X-ray diffraction techniques. Both tetragonal specimens are isomorphous with compounds in the Tl–Ba–Ca–Cu–O system. We observe excess oxygen in both samples on two sites near the $z=0$ plane: at ($\frac{1}{2}00$) and close to ($\frac{1}{2}$, 0.4, 0) – but no oxygen at ($\frac{1}{2}\frac{1}{2}0$) as reported in earlier studies. Refined Hg occupancies for both samples indicate a substitution of Cu for Hg of more than ten percent. If the substitution of Cu for Hg and excess O at ($\frac{1}{2}00$) are coupled, then the effect is to insert a perovskite-like six-coordinated copper site at (000). No evidence was found for a split atom at the barium sites in these compounds.

## 1. Introduction

The series of mercury-based superconductors, $HgBa_2Ca_{n-1}Cu_nO_{2n+3}$, are notable both for their relatively high critical temperatures [1–3] and the unique pressure dependence of the superconducting transition temperature [4–6]. Detailed structural information is essential to model the properties of these phases, to compare them with other copper-oxide superconductors, and to predict possible compositional variants with enhanced properties.

The mercury compounds are isomorphous with the well-known thallium compounds, $TlBa_2R_{n-1}Cu_nO_{2n+3}$. The Tl and Hg series differ primarily in oxygen occupancy of the (001) plane containing Tl or Hg, which is greater than 0.75 in the thallium compounds [7–10], but significantly less than 0.5 in the mercury superconductors [1,4,11–13].

Several X-ray and neutron powder diffraction studies have revealed the basic structural characteristics of $HgBa_2CuO_{4+\delta}$ (Hg-1201) [2,14–17] and $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) [13,17,18]. Structural questions remain, however, particularly regarding the locations of excess oxygen atoms, the possible substitution of copper for mercury as observed by Wagner et al. in Hg-1201 [11], and the split-atom model for barium in the latter structure proposed by Chmaissem et al. [13]. Furthermore, anisotropic thermal parameters, which may be important in modeling superconductivity at the relatively high temperatures of these samples, have not been reported previously.

The present study presents the first single-crystal X-ray data for $HgBa_2CaCu_2O_{8+\delta}$ (Hg-1212) and Hg-1223 – measurements that provide insight on the crystal chemistry of these compounds.

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## 2. Experimental

### 2.1. Sample description

The Hg-1212 and Hg-1223 samples investigated here were synthesized by the controlled vapor/solid reaction technique [19] by heating a precursor pellet of $Ba_2CaCu_2O_x$ or $Ba_2Ca_2Cu_3O_x$ (not compounds) and a composite Hg-source in an evacuated quartz tube. The precursor pellet was prepared by first dissolving appropriate amounts of $Ba(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, and $Cu(NO_3)_2 \cdot 2H_2O$ in deionized water inside a beaker. The solution was slowly stirred, heated, and finally dried into a blue powder, which was removed from the beaker, ground, and placed in an alumina crucible. It was then slowly heated to between 500 and 550°C and kept at this temperature for 0.5 h, before being further heated to between 600 and 620°C, which temperature was maintained for 1 h. The resulting black mixture was then ground, compacted, and sintered in flowing oxygen at 900°C for 24 h.

These precursor pellets were either used immediately, or else they were stored in a desiccator for later use to minimize their exposure to humid air. Some of the pellets were placed in a glove box where they were pulverized, thoroughly mixed with HgO, and compacted to form the composite Hg-source. A small precursor pellet and a large composite Hg-source in a mass ratio of ~0.3 were subsequently sealed in an evacuated quartz tube, which was in turn placed inside a welded stainless steel tube as a safety measure, heated to 800 to 850°C at a rate of 160°C/h, and kept at this temperature for 5–6 h before cooling to room temperature. The pellet was maintained at 300°C in flowing oxygen for 10 h for oxygenation. Critical temperatures for these two samples at room pressure are 127 and 134 K for Hg-1212 and Hg-1223, respectively.

Crushing of this material revealed an average grain size less than 10 μm for both Hg-1212 and Hg-1223 specimens, though a few crystals up to 30 μm maximum dimension was recovered. We examined a number of flat, rectangular crystals and selected euhedral specimens of Hg-1212 (approximately $30 \times 30 \times 10$ μm) and of Hg-1223 (approximately $25 \times 30 \times 8$ μm) for further study.

### 2.2. Data collection and refinement

Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer equipped with a rotating-anode generator operated at 45 kV and 180 mA. We used graphite-monochromatized Mo Kα radiation ($\lambda = 0.7093$ Å) to measure a hemisphere of data to $(\sin \Theta)/\lambda = 0.71$. Three reflections were monitored as orientation and intensity standards every 150 reflections, and they showed no significant variation during the data collection.

Most diffraction maxima for both Hg-1212 and Hg-1223 were broad, and many of the observed peaks were doublets, perhaps due to the stacking of multiple crystals in close alignment. One member of each split diffraction peak (presumably the component from the main crystal) was always well centered. These centered peaks were integrated using a new program that fit step-scan data to multiple constrained Gaussian doublets, corresponding to the $K\alpha_1$–$K\alpha_2$ wavelengths of the Mo source. When more than one doublet was present, only the central peak was retained. Peaks that appeared to be single but significantly exceeded the expected peak width (implying an unresolved doublet) were rejected by this procedure. These reflections were corrected for Lorentz polarization and absorption ($\mu_l = 367.7$ and 325.0 $cm^{-1}$ for Hg-1212 and Hg-1223, respectively) effects and reduced to structure factors [20]. For Hg-1223, the crystal description was not sufficient and an empirical correction was also included. Reflections were averaged according to Laue group 4/mmm, which yielded 167 symmetrically distinct observations ($I \geqslant 3\sigma$) for Hg-1212 ($R_{int} = 0.032$), and 169 reflections for Hg-1223 ($R_{int} = 0.048$); however, all 1693 observations were used in the refinement of the empirical absorption correction.

We initiated the structure refinements with parameters reported for thallium isomorphs [10]. Our refinements included a scale factor, variable atomic coordinates, and anisotropic thermal parameters for all fully-occupied sites. In addition, for both crystals we refined Cu occupancy of the Hg sites at (000), oxygen occupancy parameters for atoms at $(\frac{1}{2}\frac{1}{2}0)$ designated O3 in Hg-1212 and O4 in Hg-1223, and oxygen occupancies for atoms at $(\frac{1}{2}0 \approx 0)$ designated O4 and O5 in Hg-1212 and Hg-1223, respectively.

Refinements were performed with RFINE90, a version of RFINE4 [21]. A weight of $w=\sigma^{-2}(F_0)$ was assigned to each reflection, where $\sigma F_0$ is the error derived from counting statistics, and the function, $\sum w(|F_0|-|F_c|)^2$, was minimized.

Initial refinement of Hg-1212 incorporated six atoms (Hg/Cu, Ba, Ca, Cu, O1, and O2) with isotropic temperature factors and an occupancy factor for the Hg/Cu site. We used this refinement to generate a difference Fourier map of the (001) plane at $z=0$ (Fig. 1), in an effort to locate extra oxygen positions. Several previous studies have documented an O3 oxygen at $(\frac{1}{2}\frac{1}{2}0)$ [13–16], while Wagner et al. observe a coupled substitution of copper for Hg plus extra oxygen at $(\frac{1}{2}00)$ in Hg-1201 [11]. Our difference map reveals two prominent positive features. A maximum at $(\frac{1}{2}00)$, hereafter designated O4, corresponds to the oxygen position observed by Wagner et al.; we, too, observe significant Cu substitution on the Hg site. A second maximum at approximately $(\frac{1}{2}, 0.40, 0)$ is close to, but distinct from, the previously reported partially filled "O3" at $(\frac{1}{2}\frac{1}{2}0)$. We propose that O3 is, in fact, a split atom. The Hg–O3 and Ba–O3 distances resulting from this off-centering of O3 are 2.46 and 2.83 Å, respectively.

Final refinement of Hg-1212 with twenty variable parameters (one scale factor, one extinction parameter, five fractional coordinates, eight anisotropic thermal parameters for metal atoms, two isotropic temperature factors for oxygen, and occupancies for Hg, O3, and O4), based on 167 observed reflections, converged to a weighted $R(R_w=\sigma^{-2}(F_0-F_c)^2/\sigma^{-2}F_0^2)$ of 0.035, and unweighted $R(R=\sum||F_0|-|F_c||/\sum|F_0|)$ of 0.046. The goodness of fit for the converged refinement is 1.1. Refined positional, thermal parameters, and occupancies for Hg-1212 appear in Table 1.

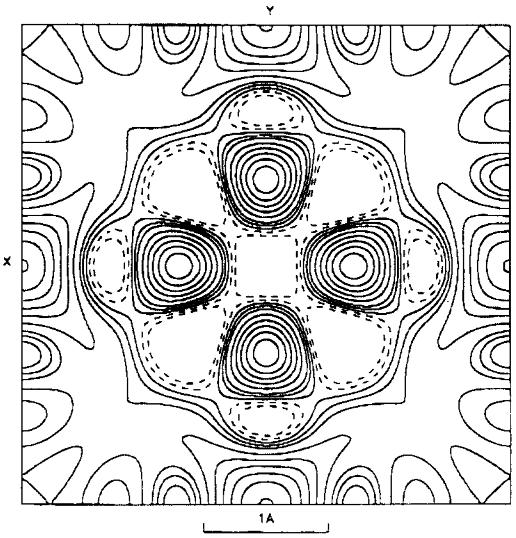

Fig. 1. Difference electron density map for the *xy*0 section of Hg-1212. No defect oxygen sites are included in the calculated structure factors. Contour interval is approximately 0.4 e/Å$^3$. The positive features at $(\frac{1}{2}00)$ and $(\frac{1}{2}, 0.4, 0)$, the negative feature at $(\frac{1}{2}\frac{1}{2}0)$ and the substitution of Cu for Hg are the basis for the defect model proposed.

Initial refinement of Hg-1223 without extra O4 and O5 oxygens at $(\frac{1}{2}\frac{1}{2}0)$ and $(\frac{1}{2}00)$, respectively, was used to generate a difference Fourier as described above for Hg-1212. Positive features at $(\frac{1}{2}, 0.40, 0)$ an $(\frac{1}{2}00)$ were observed and included in subsequent refinements. The Hg-1223 refinement of 25 parameters, based on 1693 observations, converged to weighted $R=0.069$ and unweighted $R=0.092$, with a goodness of fit = 2.0. Positional and thermal parameters are listed in Table 2. Refined occupancies of the Hg, O4, and O5 are strongly correlated to temperature factors and the O4 occupancy, furthermore, is inversely correlated to that of Hg. Refined values of these occupancies, therefore, are not quantitatively reliable. All refined models contain at least 10% Cu on the Hg site and at least 10% occupancy of O5. The refined O4 occupancy, however, varies from less than 1% for a model with 18% Cu on Hg, to 25% for a model with 10% Cu on Hg. Further constraints on Hg-1223 occupancies must await synthesis of im-

Table 1
Refined structural parameters for Hg-1212 at room temperature

| Atom | $x$ | $y$ | $z$ | $B$ (eq) | $\mu_\parallel/\mu_\perp$ [a] |
|---|---|---|---|---|---|
| Hg/Cu [b] | 0 | 0 | 0 | 1.15(6) | 0.77 |
| Ba | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.2205(2) | 0.65(5) | 1.05 |
| Ca | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.49(7) | 0.67 |
| Cu | 0 | 0 | 0.3765(3) | 0.46(6) | 1.12 |
| O1 | 0 | $\frac{1}{2}$ | 0.3758(11) | 0.4(2) | |
| O2 | 0 | 0 | 0.1553(18) | 1.0(4) | |
| O3 [c] | $\frac{1}{2}$ | 0.40(4) | 0 | 0.8 [d] | |
| O4 [e] | $\frac{1}{2}$ | 0 | 0 | 0.8 | |

[a] $\mu_\parallel/\mu_\perp$ is the ratio of the rms amplitudes of vibration parallel and perpendicular to the *c* axis.

[b] Refined Cu occupancy = 0.13(2).

[c] Refined O3 occupancy = 0.10(3).

[d] Isotropic temperature factors for O3 and O4 are fixed.

[e] Refined O4 occupancy = 0.12(5).

Table 2
Refined structural parameters for Hg-1223 at room temperature

| Atom | $x$ | $y$ | $z$ | $B$ (eq) | $\mu_\parallel/\mu_\perp$ [a] |
|---|---|---|---|---|---|
| Hg/Cu [b] | 0 | 0 | 0 | 1.29(4) | 1.12 |
| Ba | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.17491(8) | 0.68(2) | 1.11 |
| Ca | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.39758(28) | 0.50(6) | 1.43 |
| Cu1 | 0 | 0 | $\frac{1}{2}$ | 0.43(5) | 1.67 |
| Cu2 | 0 | 0 | 0.30068(17) | 0.41(4) | 1.95 |
| O1 | 0 | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.3(2) | |
| O2 | $\frac{1}{2}$ | 0 | 0.3060(7) | 0.9(5) | |
| O3 | 0 | 0 | 0.1228(12) | 1.7(7) | |
| O4 [c] | $\frac{1}{2}$ | 0.36 [d] | 0 | 0.8 [e] | |
| O5 [f] | $\frac{1}{2}$ | 0 | 0 | 0.8 | |

[a] $\mu_\parallel/\mu_\perp$ is the ratio of the rms amplitudes of vibration parallel and perpendicular to the $c$ axis.
[b] Refined Cu occupancy = 0.18(1).
[c] Refined O4 occupancy = 0.00(2).
[d] $y$ coordinate of O4 fixed at value determined from difference electron density map.
[e] Isotropic temperature factors for O4 and O5 are fixed.
[f] Refined O5 occupancy = 0.13(5).

Table 3
Selected interatomic distances (Å) and Cu–O–Cu angles for Hg-1212 and Hg-1223 at room temperature

| Bond | Hg-1212 | Bond | Hg-1223 |
|---|---|---|---|
| Hg–O2[2] | 1.97(2) | Hg–O3[2] | 1.975(19) |
| Hg–O3[4] | 2.46(8) | Hg–O4[4] | 2.4(1) |
| Ba–O1[4] | 2.757(10) | Ba–O2[4] | 2.824(8) |
| Ba–O2[4] | 2.848(7) | Ba–O3[4] | 2.837(5) |
| Ba–O3[1] | 2.83(2) | Ba–O4[1] | 2.81(2) |
| Ca–O1[8] | 2.490(9) | Ca–O1[4] | 2.516(3) |
| | | Ca–O2[4] | 2.413(7) |
| Cu–O1[4] | 1.928(1) | Cu1–O1[4] | 1.927(1) |
| Cu–O2[1] | 2.81(2) | Cu2–O2[4] | 1.929(1) |
| | | Cu2–O3[1] | 2.78(2) |
| Cu–O1–Cu | 179.5(9) | Cu2–O2–Cu2 | 175.4(7) |

proved crystals or higher-resolution powder diffraction data.

Calculated and observed structure factors are available from the authors.

## 3. Results and discussion

### 3.1. Structure of $HgBa_2CaCu_2O_{6+\delta}$

All known members of the mercury superconductor series have tetragonal unit cells. We measured unit cells for two Hg-1212 crystals (one crystal with $a=3.8554(10)$ Å, $c=12.693(7)$ Å, $V=188.66(13)$ Å$^3$; and the crystal used in intensity measurements with $a=3.8564(9)$ Å, $c=12.682(4)$ Å, $V=188.60(9)$ Å$^3$), giving a calculated density of 6.36 g/cm$^3$.

Copper–oxygen, calcium–oxygen, and barium–oxygen bond distances in $HgBa_2CaCu_2O_{6+\delta}$ are similar to those observed in the isostructural compound $TlBa_2CaCu_2O_7$ [10,22]. The principal differences occur in the substitution of Hg (and Cu) for Tl at (000), and partial occupancy of O3 at ($\frac{1}{2}$, 0.40, 0). In the thallium compound the oxygen site at ($\frac{1}{2}\frac{1}{2}0$) is fully occupied, but in the mercury analogs the site is significantly less than half occupied – 0.10(3) in our sample. Thus thallium is six-coordinated, while mercury is effectively two-coordinated. One consequence of this coordination difference is that the Hg–O2 distance (parallel to $c$) is shorter than the Tl–O distance (1.97(2) Å for Hg–O2 compared to more than 2.00 Å for Tl–O2). The mercury compound thus displays a slightly shorter $c$ axis than the thallium isomorph [22].

The Hg site in our sample incorporates 0.13(2) Cu – an amount balanced by the 0.12(5) oxygen atoms in the O4 site at ($\frac{1}{2}00$). The $z$ coordinate of O4 may deviate slightly from 0.00, but not by more than 0.4 Å, based on electron density maps.

### 3.2. Structure of $HgBa_2Ca_2Cu_3O_{8+\delta}$

The Hg-1223 unit cell is $a=3.842(5)$ Å, $c=15.832(8)$ Å, $V=233.58(44)$ Å$^3$, giving a calculated density of 6.21 g/cm$^3$.

Copper–oxygen and calcium–oxygen bond distances are typical of other 1223-type superconductors [10], while these distances and those of Hg–O agree closely with room-temperature values reported by Chmaissem et al. [13] based on neutron powder diffraction. In particular, we observe in-plane Cu1–O1 and Cu2–O2 distances of 1.927(1) and 1.929(1) Å, respectively, compared to 1.925 for both distances reported by Chmaissem et al. We observe mean Ca–O, Hg–O3, and Hg–O4 of 2.452(5), 1.97(2), and 2.4(1) Å, compared to 2.493(6), 1.95(1), and 2.7225(1) for the neutron study. The Hg–O3 bond, which is parallel to the $c$ axis, is significantly shorter than the Tl–O3 distance (greater than 2.0 Å) observed in the thallium isomorph [10]. The relatively short Hg–O distances in both mercury compounds of this study point to stronger interlayer coupling, which may contribute to the unusually high $T_c$.

Observed barium–oxygen distances conform to those of $TlBa_2Ca_2Cu_3O_9$: approximately 2.83 Å in both samples [8]. These Ba–O distances, however, are significantly different from values reported by Chmaissem et al. [13], who suggest that Ba may be modeled as a split atom with approximately half Ba displaced by 0.25 Å above and below the centric position, $(\frac{1}{2}\frac{1}{2}z)$. We observe no evidence for this splitting in refinements of single-crystal X-ray data. In fact, anisotropic temperature parameters are well behaved and reveal near-isotropic barium vibration with relatively small rms displacements, typical of nine-coordinated Ba in other oxides. These discrepancies between X-ray single crystal and neutron powder data may reflect differences in sample order.

Refined anisotropic thermal parameters reveal that the motions of mercury, calcium, barium, and oxygen atoms are close to isotropic, probably reflecting the uniform coordination of these atoms. Ratios of maximum to minimum vibration amplitudes for these atoms are less than 1.5. The two symmetrically distinct copper atoms, on the other hand, display elongated thermal motion parallel to [001] with atom displacements approaching two times greater parallel to *c* than parallel to *a* – an anisotropy typical of that observed in other structures with square-planar cation coordination.

### 3.3. Revised structural formulae for Hg superconductors

The observation by Wagner et al. and us of coupled substitution of approximately equal amounts of Cu for Hg at (000) and O on a new site at $(\frac{1}{2}00)$, requires a structural formula that acknowledges the presence of excess oxygen on two distinct sites. Our sample of Hg-1212, for example, may be described as: $(Hg_{0.87}Cu_{0.13})Ba_2CaCu_2O_{6.22}$. But, in more general terms, two oxygen $\delta$ terms are required: $(Hg_{1-\delta 1}Cu_{\delta 1})Ba_2CaCu_2O_{6+\delta 1+\delta 2}$, where $\delta 1$ and $\delta 2$ represent the fractional occupancies of oxygen at $(\frac{1}{2}00)$ and $(\frac{1}{2}, 0.40, 0)$, respectively. Further structural investigations, coupled with synthesis and analytical studies, will be required to resolve the details of this complex system.

Although the diffraction data for these experiments do not have the quality required to answer all questions regarding defect structures, the equality between the amount of Cu substitution in the Hg position and the amount of O at $(\frac{1}{2}00)$ is suggestive of partial substitution of a perovskite-like, octahedrally coordinated, Cu layer in both Hg-1212 and Hg-1223 samples. Because the substitution of Cu for Hg is not found in some studies [14,15], this effect may be due to some aspect of the synthesis. Alternatively, the distinctive characteristics of our sample may reflect the selection of the largest, most regular – and therefore possibly atypical – single crystals in otherwise fine-grained samples.

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## References

[1] S.N. Putilin, E.V. Antipov, O. Chmaissen and M. Marezio, Nature 362 (1993) 226.

[2] A. Schilling, M. Cantoni, J.D. Gao and H.R. Ott, Nature 363 (1993) 56.

[3] Z.J. Huang, R.L. Meng, X.D. Qui, Y.Y. Sun, J. Kulik, Y.Y. Xue and C.W. Chu, Physica C 217 (1993) 1.

[4] C.W. Chu, L. Gao, F. Chen, Z.J. Huang, R.L. Meng and Y.Y. Xue, Nature 365 (1993) 323.

[5] M. Nunez-Regueiro, J.L. Tholence, E.V. Antipov, J.J. Capponi and M. Marezio, Science 262 (1993) 97.

[6] L. Gao, Y.Y. Xue, F. Chen, Q. Xiong, R.L. Meng, D. Ramirez, C.W. Chu, J.H. Eggert and H.K. Mao, Phys. Rev. Lett. (1994), in press.

[7] S.S.P. Parkin, V.Y. Lee, A.I. Nazzal, R. Savoy, R. Beyers and S. LaPlaca, Phys. Rev. Lett. 61 (1988) 750.

[8] B. Moroson, D.S. Ginley, J.E. Schirber and E.L. Venturini, Physica C 156 (1988) 587.

[9] M.A. Subramanian, J.C. Calabrese, C.C. Torardi, J. Gopalakrishnan, T.R. Askew, R.B. Flippen, K.J. Morrissey, U. Chowdhry and A.W. Sleight, Nature 332 (1988) 420.

[10] R.M. Hazen, in: Physical Properties of High Temperature Superconductors, Vol. 2, ed. D.M. Ginsberg (1990) p. 121.

[11] J.L. Wagner, P.G. Radaelli, D.G. Hinks, J.D. Jorgensen, J.F. Mitchell, B. Dabrowski, G.S. Knapp and M.A. Beno, Physica C 210 (1993) 447.

[12] O. Chmaissem, Q. Huang, S.N. Putilin, M. Marezio and A. Santoro, Physica C 212 (1993) 259.

[13] O. Chmaissem, Q. Huang, E.V. Antipov, S.N. Putilin, M. Marezio, S.M. Loureiro, J.J. Capponi, J.L. Tholence and A. Santoro, Physica C 217 (1994) 265.

[14] P.G. Radaelli, J.L. Wagner, B.A. Hunter, M.A. Beno, G.S. Knapp, J.D. Jorgensen and D.G. Hinks, Physica C 216 (1993) 29.

[15] E.V. Antipov, J. Capponi, C. Chaillout, O. Chmaissem, S.M. Loureiro, M. Marezio, S.N. Putilin, A. Santoro and J.L. Tholence, Physica C 218 (1993) 348.

[16] Q. Huang, J.W. Lynn, R.L. Meng and C.W. Chu, Physica C 218 (1993) 356.

[17] B.A. Hunter, J.D. Jorgensen, J.L. Wagner, P.G. Raedelli, D.G. Hinks, H. Shaked, R.L. Hitterman and R.B. VonDreele, Physica C 221 (1994) 1.

[18] E.V. Antipov, S.M. Loureiro, C. Chaillout, J.J. Capponi, P. Bordet, J.L. Tholence, S.N. Putilin and M. Marezio, Physica C 215 (1993) 1.

[19] R.L. Meng, L. Beauvais, Z.N. Zhang, Z.J. Huang, Y.Y. Sun, Y.Y. Xue and C.W. Chu, Physica C 216 (1993) 21.

[20] C.W. Burnham, Am. Mineral. 51 (1966) 159.

[21] L.W. Finger and E. Prince, Natl. Bur. Standards Tech. Note 854 (1975) p. 128.

[22] B. Morosin, D.S. Ginley, P.F. Hlava, M.J. Carr, R.J. Baughman, J.E. Schirber, E.L. Venturini and J.F. Kwak, Physica C 152 (1988) 413.