

A high-pressure X-ray powder diffraction and infrared study of copper germanate, a high- T_c model

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 5183

(<http://iopscience.iop.org/0953-8984/3/27/011>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 23:31

Please note that [terms and conditions apply](#).

A high-pressure x-ray powder diffraction and infrared study of copper germanate, a high- T_c model

David M Adams, Julian Haines and Simon Leonard

Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

Received 15 November 1990, in final form 5 April 1991

Abstract. Copper germanate has been examined by synchrotron x-ray powder diffraction at high pressure in a diamond anvil cell at pressures up to 220 kbar, and by infrared spectroscopy to 162 kbar. These concur in showing a phase transition at 66–73 kbar: the x-ray powder diffraction data have been indexed successfully on the basis of a $P2_1/a$ cell, deduced from a model of the phase change in which germanate chains slip relative to each other along their axes.

Slow changes in diffraction pattern from 110–220 kbar suggest existence of a further, very sluggish, phase change. CuGeO_3 turns black near 5 kbar due to a band shift.

Contraction of the orthorhombic cell constants of the initial phase is markedly anisotropic, the principal changes being in the plane which contains the long Cu–O bonds. These are twice as easily compressed as the short Cu–O bonds.

1. Introduction

The current interest in high- T_c superconductors has generated a need for better understanding of copper–oxygen structures in general. Recently reported compression data on $\text{La}_2\text{BaCuO}_4$ indicated almost no change in the ratios of the lattice parameters with pressure [1]. This is contrary to intuitive expectations based upon the known Jahn–Teller distorted geometry at Cu(II), with its four short plus two long Cu–O bonds, although this particular result can be understood on the basis of La–O repulsions. We have studied CuGeO_3 because of its particularly simple structure in which the effect of pressure upon the Jahn–Teller geometry at Cu(II) can be seen in isolation from such complications. CuGeO_3 contains chains of vertex-sharing (GeO_4) tetrahedra aligned along the b axis of an orthorhombic cell ($Pmma$, $Z = 2$) with two chains per cell [2]. These are linked by copper atoms in classical Jahn–Teller tetragonal geometry, with two Cu–O bonds of 2.766 Å and four of 1.942 Å. There are no reports of x-ray diffraction from CuGeO_3 at high pressures but it has been shown to decompose into GeO_2 and Cu_2GeO_4 under high-temperature, high-pressure conditions, although the rate of decomposition is very slow below 700 °C and 35 kbar [3].

2. Experimental

CuGeO_3 was prepared by mixing equimolar proportions of Aldrich ‘Gold Label’ (> 99.99% purity) CuO and GeO_2 , which were then fused at 1000 °C for three hours in

a platinum crucible. The product was allowed to cool to room temperature in the furnace, and appeared as a turquoise-blue powder. It was then ground and heated to 1000 °C for a further forty hours. These conditions are known to yield a pure, monophasic product [3].

High-pressure data were obtained with samples in a diamond anvil cell, mounted in the synchrotron x-ray beam at the SERC Daresbury Laboratory. Samples were in stainless steel AISI 316 gaskets with an initial hole diameter of 0.30 mm. The incident x-ray beam was 0.10 mm in diameter.

Variable pressure infrared (IR) spectra (4 cm^{-1} resolution) were acquired with a Digilab FTS-40 FTIR spectrometer. The sample was diluted with KBr and placed in the 0.40 mm diameter hole of the pre-indented gasket, together with a layer of 0.21% w/w NaNO_3 in NaBr. The pressure was estimated with respect to the frequency shift of the antisymmetric stretch of the nitrate ion [4]. All IR measurements were at 30 °C.

3. Results

3.1. The EDXRPD evidence

The initial orthorhombic phase was stable to 66 kbar. At this pressure three new peaks appeared in the diffraction pattern ($d = 2.906, 2.751$ and 2.269 \AA). Concurrently, there was a significant decrease in intensity of the (021) peak. By 73 kbar no sign remained of the orthorhombic phase (Figure 1). The new phase, CuGeO_3 II, remained stable to 110 kbar, when a peak with $d = 2.456\text{ \AA}$ began to decrease in intensity, and completely disappeared by 180 kbar (figure 2). At this pressure a new feature was seen ($d = 2.644\text{ \AA}$) which became more prominent by 220 kbar, the limit of our observations. The final EDXRPD pattern is a simple one, indicative of high symmetry.

3.2. Infrared evidence

There are five bands in the mid IR spectrum of CuGeO_3 [5]: we have measured them under pressures up to 162 kbar (see figures 3 and 4 and table 1) and find that they behave similarly, indicating that all the Ge-O bonds suffer equivalent shortening.

Major changes were observed in the IR spectrum near 70 kbar, in agreement with the x-ray evidence. Thus, the band at 738 cm^{-1} (69 kbar) decreased considerably and another at 642 cm^{-1} increased in intensity. In addition, following a region of intergrowth, two new bands appeared.

3.3. Visual observations

CuGeO_3 turns from pale blue to black, reversibly, at very low pressure (about 5 kbar). This band shift precluded Raman studies but indicates that electrical conductivity study should be rewarding. This is presumably an insulator-metal transition, although the conduction band is likely to be narrow.

3.4. Conclusions from the x-ray and IR results

CuGeO_3 exhibits a phase change which sets in at 66 kbar and is complete at 73 kbar. The insulator-metal transition near 5 kbar has no observable influence upon the EDXRPD

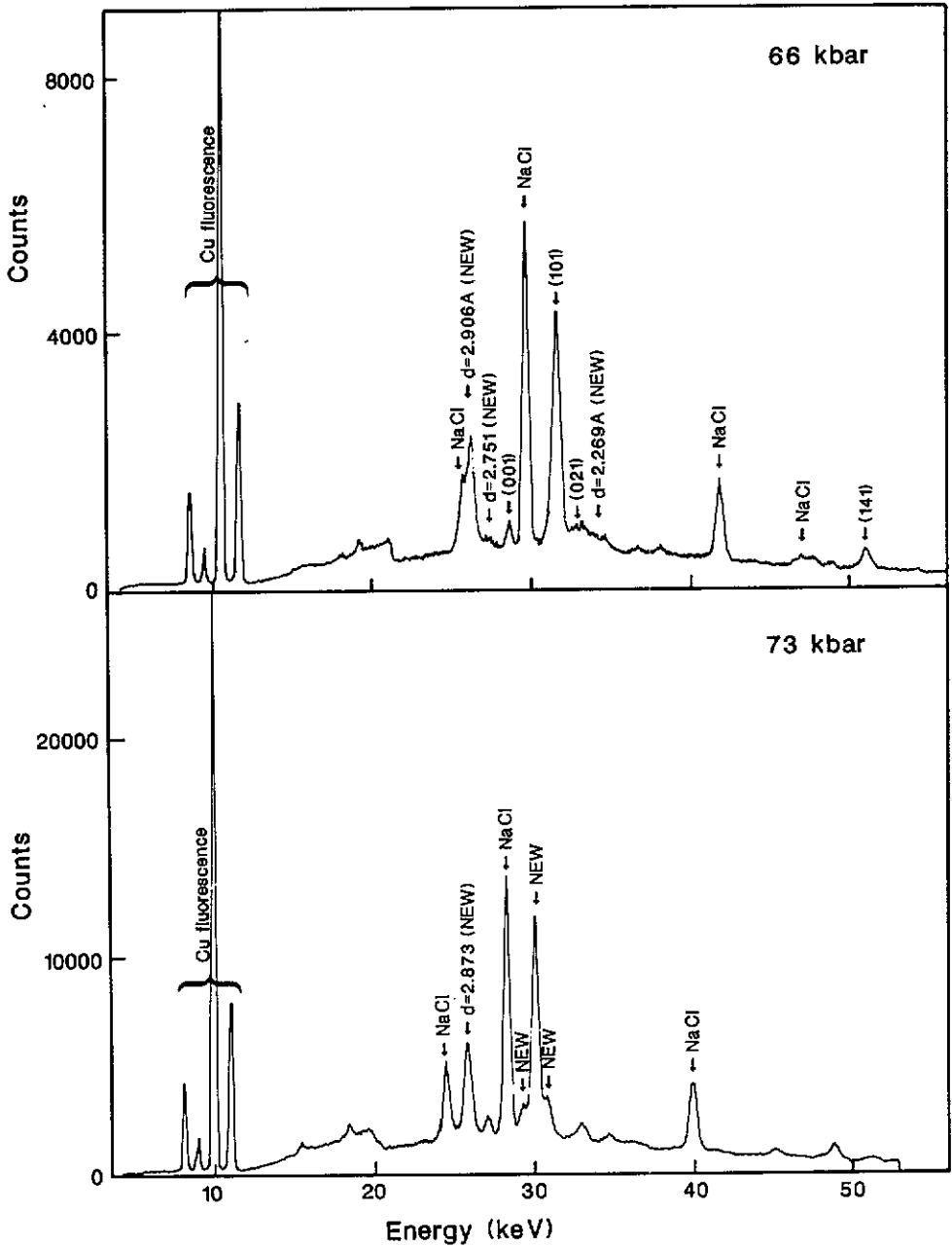


Figure 1. EDXRPD spectra of CuGeO_3 at 66 and 73 kbar.

pattern. Slow changes in diffraction pattern as the pressure varies from 110–220 kbar suggest a second, very sluggish, phase transition, probably to a phase of higher symmetry.

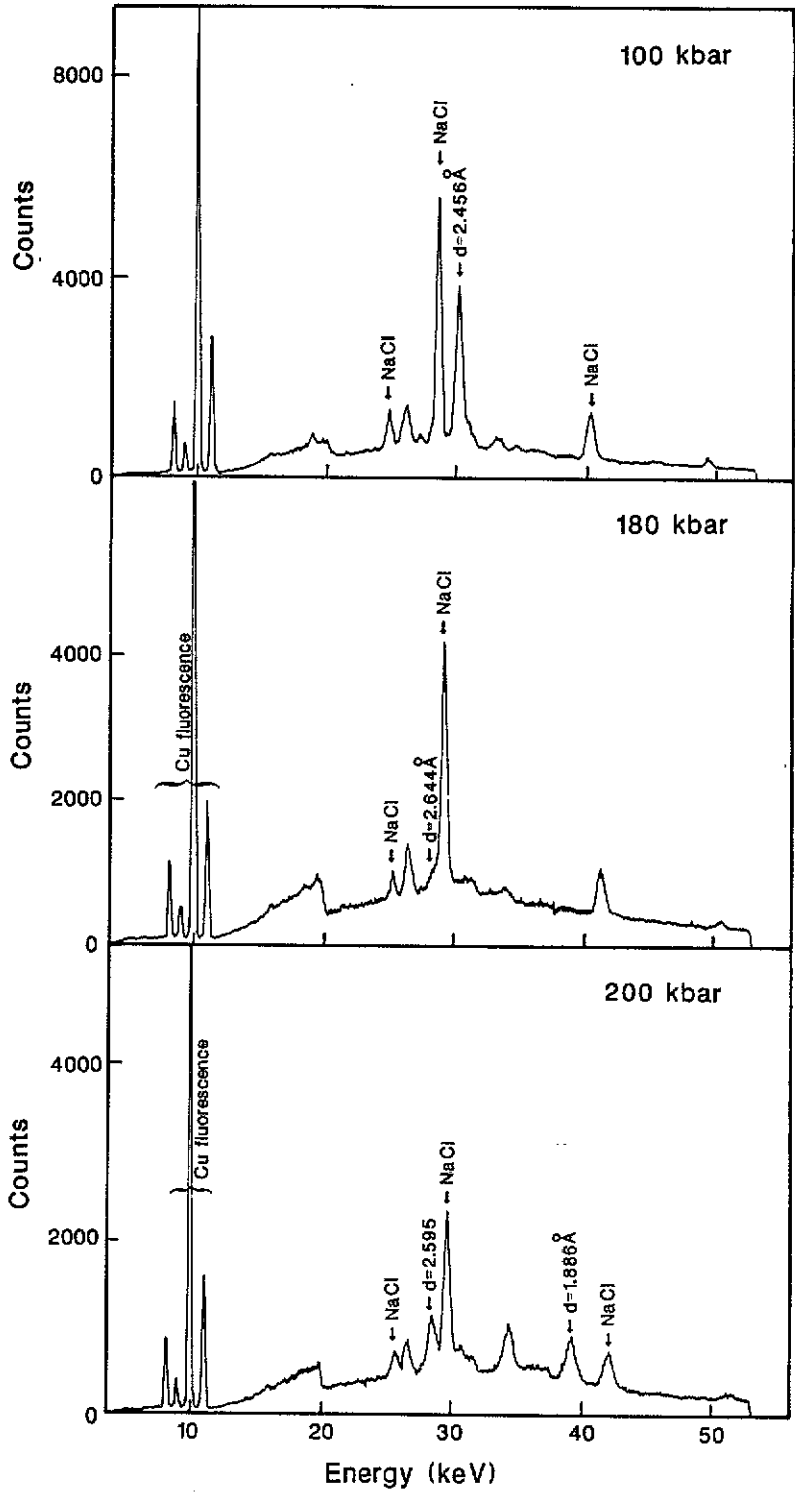


Figure 2. EDXRPD spectra of CuGeO_3 at 100, 180 and 200 kbar.

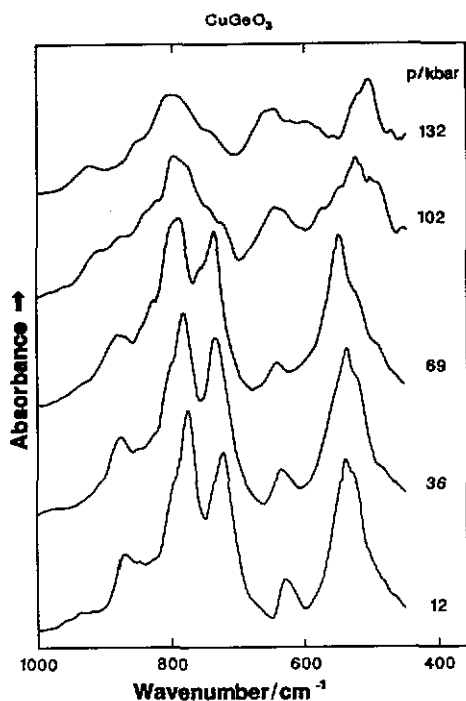


Figure 3. Infrared spectra of CuGeO_3 at various pressures (kbar).

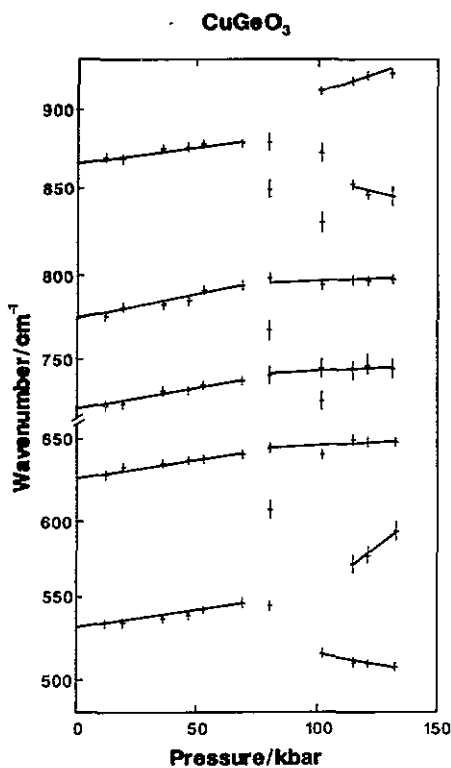


Figure 4. Variation with pressure of the mid IR vibrational modes of CuGeO_3 .

Table 1. Infrared bands (cm^{-1}) and mode shifts ($\text{cm}^{-1} \text{kbar}^{-1}$) for CuGeO_3 at high pressures.

Phase I			
Assignment	ν (0 kbar) ^a	ν (12 kbar)	$d\nu/dP$
ν (Ge—O—Ge) _{as}	864	871 m	0.27
ν (Ge—O)	774	776 s	0.29
		723 s	0.27
ν (Ge—O—Ge) _s	625	629 m	0.27
ν (Cu—O)	532	535 s	0.22
Phase II			
	ν (0 kbar) ^a	ν (132 kbar)	$d\nu/dP$
	871	923 w	0.40
	900	847 sh	-0.40
	797.5	798 s	0
	734.9	746 sh	0.09
	635	651 m	0.10
	424	594 sh	1.3
	543	508 s	-0.30

^a = intercept of line.

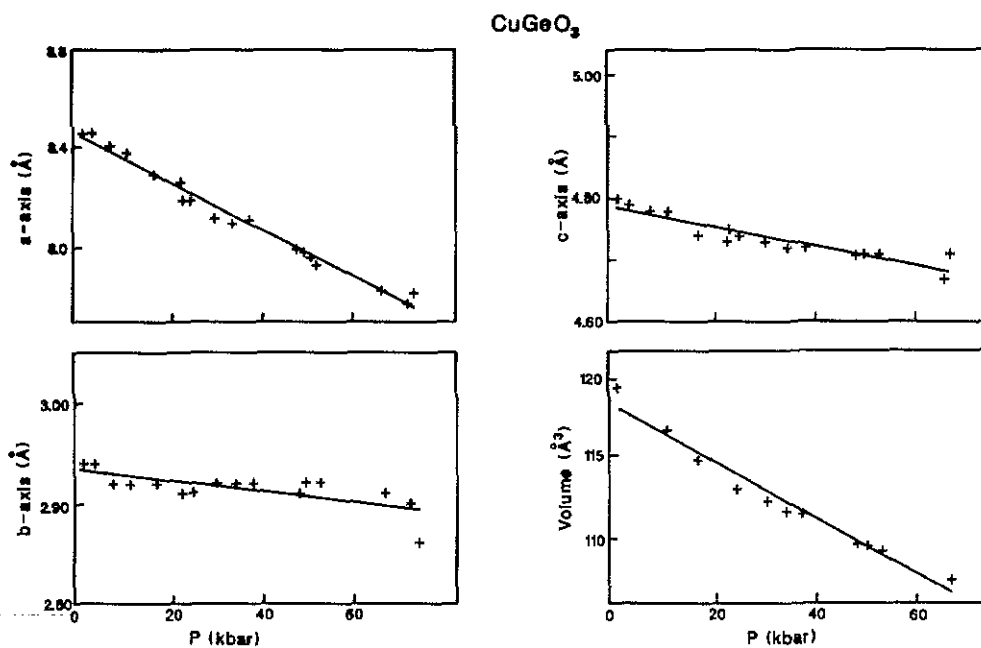


Figure 5. Variation with pressure of the lattice constants of CuGeO_3 .

3.5. Behaviour of the lattice parameters

Data obtained at ambient pressure ($2\theta = 9.56$ and 10.24°) refined to yield cell constants in close agreement with those from the single-crystal study. The same cell was used to refine data obtained up to 73 kbar (figure 5). These yielded uniaxial compressibilities:

$$\kappa_a = 17.9 \times 10^{-4}, \kappa_b = 3.2 \times 10^{-4}, \kappa_c = 11.0 \times 10^{-4} \text{ kbar}^{-1}$$

with a volume compressibility of $14.75 \times 10^{-4} \text{ kbar}^{-1}$. Hence, the three lattice vectors compress anisotropically in the ratio 1:3.4:5.6 for $b:c:a$.

4. Discussion

4.1. The lattice parameters

The most important result from this work is that the lattice response to pressure is highly anisotropic. It is least compressible in the b (the chain) direction, as expected from the highly covalent bonding within the (GeO_4) units. The long Cu–O bonds lie in the ac plane at about 45° to the axes and account readily for the high compressibilities in these directions.

Using the lattice parameters refined for the unit cell at 73 kbar (table 2) new bond lengths and angles were calculated (table 3). The atomic positions taken were those of the ambient cell as EDXRPD intensity data are unreliable. However, the Cu atoms on Wyckoff sites 2d are constrained by symmetry; the Ge(2e) and O1(2f) atoms may move along z ; whilst O2(4i) atoms are free to move in the xz -plane. Despite these limitations, the model shows that the long Cu–O bonds suffer twice the compression of the short

Table 2. Data for the orthorhombic unit cell of CuGeO_3 refined at 73 kbar. $a = 7.78$, $b = 2.90$, $c = 4.74 \text{ \AA}$, $V = 107.0 \text{ \AA}^3$.

D (obs)	D (calc)	(hkl)
2.9911	3.0072	(120)
2.4748	2.4740	(101)
2.3221	2.3256	(021)
1.6599	1.6597	(221)
1.5297	1.5293	(141)

Table 3. Bond lengths (\AA) in CuGeO_3 at atmospheric pressure and at 73 kbar.

	0.001 kbar [2]	73 kbar	% change
Cu-01	2.766	2.70	6
Cu-02	1.942	1.87	2.9
Ge-01	1.769	1.73	2
Ge-02	1.724	1.61	6.4

ones. This establishes an important point and confirms that the isotropic response to pressure of $\text{La}_2\text{BaCuO}_4$ is due to factors other than the local geometry of copper.

As the ac plane of the unit cell is reduced in size, compression of the stronger short bonds can be minimized by swinging the plane defined by the four oxygen atoms closest to Cu about the b -axis to align it more closely with the a -axis. Since the chains themselves are constrained on planes at $\frac{1}{4}$ and $\frac{3}{4}$ along a , they move together symmetrically about Cu, preferentially shortening the long Cu–O bond. Concurrently, the O1–Cu–O2 angle is reduced from 86° . The geometry about the Cu atom, which was not accurately tetragonal in the first instance, is now even less so. Eventually, at 66 kbar, a structural transition is precipitated which must result in a less strained environment for Cu.

4.2. The 70 kbar phase transition

The structure of CuGeO_3 is unique among tetrahedral chain materials in having all the (MO_4) tetrahedra oriented on the same side of the chain. In all other germanates MGeO_3 they pack alternately with a two-tetrahedron repeat [6]. Nevertheless, it is instructive to note that orthorhombic MnGeO_3 exhibits a phase transition with pressure (at 15–25 kbar) in which the germanate chains slip relative to each other along their lengths [7], resulting in a monoclinic cell ($P2_1/m$). We have used the same process in modelling the 70 kbar transition in CuGeO_3 .

We note first that the IR evidence is also consistent with this model. Factor group analysis predicts the presence of fifteen IR-active bands in the spectrum of this phase. This is four more than were observed for phase I [5], for which two of the expected thirteen bands escaped detection. In transforming from the parent $Pmma = D_{2h}^5$ to the phase II $P2_1/a = C_{2h}^5$ structure, two A_u modes of D_{2h} become IR-active: as these modes arise from motions of the Cu and O2 atoms, it is entirely reasonable that they might generate bands where we have found new ones, although it is equally possible that the

Table 4. Experimental and calculated peak positions (keV) and d spacings (Å) using a monoclinic cell for CuGeO_3 at 73 kbar ($\theta = 10.24^\circ$). $a = 2.90$, $b = 4.74$, $c = 7.78$ Å, $\gamma = 99.0^\circ$, $V = 105.6$ Å³.

E (obs)	E (calc)	D (obs)	D (calc)	(hkl)
23.26	23.22	2.9915	2.9915	(012)
28.01	27.85	2.4942	2.4942	(111)
29.75	29.67	2.3412	2.3408	(020)
30.23	30.35	2.2887	2.2887	(110)
30.98	30.99	2.2415	2.2415	(021)
45.37	45.40	1.5300	1.5300	(031)
47.83	47.96	1.4483	1.4483	(032)

new bands correspond to the phase I bands which escaped detection. The IR evidence is therefore consistent with the change to the monoclinic structure proposed.

The initial lattice parameters chosen were those of the 73 kbar orthorhombic cell, with $\gamma = 99^\circ$. On this basis the seven observed lines could be indexed (table 4). The energy match is not exact but it is based upon a reasoned guess. These indices and energies were then used to refine a cell on d spacings, giving an excellent fit (table 4). We conclude that this model adequately describes this phase transition.

4.3. The 110 kbar phase transition

We note only that MnGeO_3 exhibits a second phase transition with pressure, forming MnGeO_3 III which has the ilmenite structure [7]. An analogous reconstruction may account for our 110 kbar phase change.

Acknowledgments

We thank the NSERC, Canada for award of a fellowship to JH, and the SERC for a maintenance grant to SL, and for other support.

References

- [1] Akhtar M J, Catlow C R A, Clark S M and Temmerman W M 1988 *J. Phys. C: Solid State Phys.* **21** L917
- [2] Völlenkne H, Wittmann A and Nowotny H 1967 *Monat. Chem.* **98** 1352
- [3] Hegenbart W, Rau F and Range K-J 1981 *Mater. Res. Bull.* **16** 413
- [4] Klug D D and Whalley E 1983 *Rev. Sci. Instrum.* **54** 1205
- [5] Adams D M and Fletcher P A 1988 *Spectrochim. Acta A* **44** 233
- [6] Wells A F 1975 *Structural Inorganic Chemistry* 4th edn (Oxford: Oxford University Press)
- [7] Liu L and Bassett W 1986 *Elements, Oxides and Silicates* (Oxford: Oxford University Press)