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Structural transitions in Cu_2O at pressures up to 11 GPa

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Abstract

The structural states of Cu_2O at pressures between ambient and 11 GPa were re-investigated, using angle-dispersive diffraction, an area detector and synchrotron radiation. Thanks to the latter's naturally high collimation, a hitherto suspected transition from the parent cubic phase to a new tetragonal phase was experimentally confirmed at pressures between 0.7 and 2.2 GPa, depending on the hydrostaticity of the pressure medium used. The other transformation, into a pseudocubic phase, was detected at about 8.5 GPa. In the same pressure range, the application of pressure also resulted in a general and strong broadening of the diffraction peaks. This broadening is attributed to the presence of microscopic strains and a reduction in grain size down to the nanocrystalline scale.

1. Introduction

Copper oxide is one of the main chemical constituents of most high-temperature superconductors; it is precisely the electronic properties of the Cu–O chains that are believed to be responsible for their superconductivity [1, 2]. The study of the structural behaviour of various copper oxide forms, under different thermodynamic conditions, is therefore important for the understanding of the nature of high-temperature superconductivity.

In (divalent) cupric oxide, CuO , the initial monoclinic phase is stable up to a pressure of 70 GPa and temperatures up to 3000 K [3, 4] and within this p, T range its structural behaviour is fully understood. In (monovalent) cuprous oxide, however, the situation is a bit more complex. The semiconductor Cu_2O (cuprite in the mineral world) exhibits sundry structural and chemical transformations in the pressure range up to 20 GPa [5–9] and ambient

temperature. The equilibrium phase diagram of copper oxide contains the line of the chemical reaction $\text{Cu}_2\text{O} \rightarrow \text{CuO} + \text{Cu}$ with, at room temperature, an equilibrium pressure value of 4–5 GPa [5]. All phase transitions observed at higher pressure in this compound occur therefore between metastable phases.

Under ambient conditions, Cu_2O crystallizes in the cubic space group $Pn\bar{3}m$ ($Z = 2$), with $a_0 = 4.627 \text{ \AA}$. Its structure can be represented as the result of two interpenetrating face-centred (for the Cu atoms) and body-centred (for the O atoms) lattice complexes. In the course of a recent highly accurate electron-density study, its structure was re-determined and its salient features discussed thoroughly [6].

At high pressure (and ambient temperature) the structural behaviour of Cu_2O was studied first by Kalliomaki *et al* [7] and later by Werner and Hochheimer [8]; their results differ mostly in the observed sequence of phase transitions, and this difference can be attributed to different the sample environments and observational techniques used. Kalliomaki *et al* [7] observed the following sequence of phase transitions (with $P \leq 16 \text{ GPa}$ and RT):

phase I (cubic) $\xrightarrow{\sim 5.0 \text{ GPa}}$ phase Ia (structure unknown) $\xrightarrow{\sim 12.0 \text{ GPa}}$ phase II (hexagonal; structure unknown) $\xrightarrow{\sim 15.0 \text{ GPa}}$ chemical decomposition reaction $\text{Cu}_2\text{O} \rightarrow \text{CuO} + \text{Cu}$,

where the notation for the crystalline phases corresponds to [8]. This later work [8] was carried out under hydrostatic conditions at $P \leq 24 \text{ GPa}$, with x-ray diffraction patterns collected in the energy-dispersive mode, and the following transition sequence reported:

phase I $\xrightarrow{\approx 10.0 \text{ GPa}}$ phase II (hexagonal; structure unknown) $\xrightarrow{\sim 18.0 \text{ GPa}}$ phase III (hexagonal; CdCl_2 -type) $\rightarrow$ no decomposition up to 24 GPa.

It seems thus that hydrostatic conditions suppress the growth of phase Ia and lower the transition pressure from cubic phase I to the first hexagonal phase II. However, the largest volume effect, a contraction of about 11%, is connected with the $\text{II} \rightarrow \text{III}$ transition. Finally, Werner and Hochheimer [8] observed no chemical decomposition reaction, such as $\text{Cu}_2\text{O} \rightarrow \text{CuO} + \text{Cu}$, at pressures up to 24.0 GPa.

Very recently, Ponyatovsky *et al* [10] subjected Cu_2O to pressures lower than 10 GPa and to temperatures up to 430 K, and observed under the electron microscope that the grain size after thermobaric treatment decreased to 5–20 nm, down substantially from the initial 5–10 μm . This drastic grain size decrease was observed under both hydrostatic and nonhydrostatic conditions. X-ray diffraction spectra measured for the same specimens with a laboratory x-ray source and a powder diffractometer revealed again no intermediate phase Ia, but solely an intense broadening of the diffraction lines, as expected from the observed drastic reduction in grain size. However, peak broadening could not only stem from the particle size reduction, but also be associated with microstrains appearing in the crystallites, and mask the structural transition $\text{I} \rightarrow \text{Ia}$ observed by Kalliomaki *et al* [7].

To resolve the contradictions, detailed *in situ* study of the Cu_2O structure at pressures up to 11 GPa seemed called for, using more powerful tools (synchrotron radiation and area detector) than in the past.

2. Experimental details

Powder samples of Cu_2O were prepared by multiple melting of 1:1 $\text{CuO} + \text{Cu}$ mixtures. The samples obtained were characterized by XRD and the subsequent high-pressure study carried out only on crushed single crystals. Diffraction measurements at high pressure and with synchrotron radiation were performed at the European Synchrotron Radiation Facility

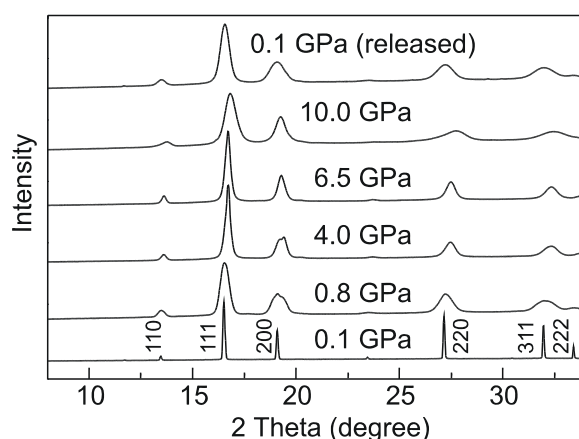


Figure 1. Representative diffraction patterns of Cu_2O ; the dependence on nonhydrostatic pressure to 10 GPa.

(Grenoble, France) on beam line BM1A. A diamond anvil cell with diamond culets of diameter $600\ \mu\text{m}$ was used. The samples were loaded into a hole $150\ \mu\text{m}$ in diameter drilled in stainless steel gaskets pre-indented to $60\ \mu\text{m}$. Pressure was determined using the ruby fluorescence technique [11]. Diffraction patterns were collected in angle-dispersive geometry with an image plate detector (MAR345) and a monochromatic beam ($\lambda = 0.7109\ \text{\AA}$) slit-collimated down to $80 \times 80\ \mu\text{m}^2$. Sample-to-detector distances and image plate inclination angles were accurately calibrated using silicon as standard. The two-dimensional diffraction images were processed with Fit2D, yielding intensity versus 2θ histograms [12].

The measurements were carried out at room temperature in the pressure range ambient to 11 GPa. In the nonhydrostatic experiments, the Cu_2O powder was loaded into the gasket hole without any pressure-transmitting medium; in the other cases, silicon oil was used to maintain quasihydrostatic conditions. Silicon oil is known to stiffen into a rigid solid around 2.5 GPa at room temperature so quasihydrostatic conditions are provided up to about 8 GPa.

3. Results and discussion

3.1. Phase transitions

Whether cuprite was compressed under quasihydrostatic or under nonhydrostatic conditions did not greatly affect the evolution of the diffraction spectra with pressure (figures 1 and 2). The visually most obvious difference was observed in the width of the diffraction profiles. In the quasihydrostatic regime diffraction lines remain quite narrow up to ~ 3.0 GPa, whereas in the nonhydrostatic regime the same lines were already dramatically increased in width, Δ , at moderate pressures (below 1.0 GPa), as shown in figure 3. It is important to note that remarkable deviation from the hydrostatic regime, monitored with the width of the R_1 – R_2 fluorescence lines of ruby, under quasihydrostatic loading starts only above 5 GPa. Upon decompression, the reflections remained broad, i.e. this effect is irreversible, while the peak positions recovered their initial values (figures 1 and 2).

Furthermore, in the quasihydrostatic regime, the diffraction peaks 200, 220 and 311 of cubic phase I started to split at pressures upward of 0.7 GPa, indicating a transition to another

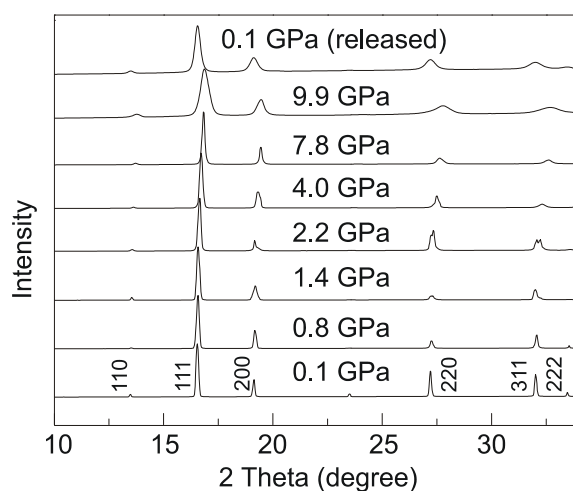


Figure 2. Evolution of the Cu_2O diffraction pattern; the dependence on the quasihydrostatic pressure of silicon oil to 10 GPa.

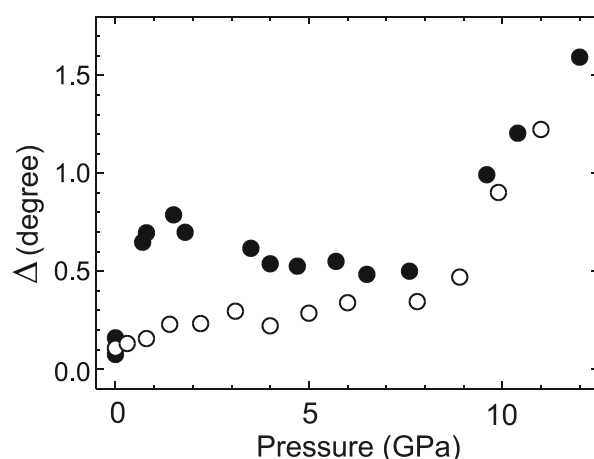


Figure 3. The pressure dependence of the full width at half-maximum, Δ , of the (002) reflection under nonhydrostatic (solid symbols) and quasihydrostatic conditions (open symbols).

phase⁶. In the nonhydrostatic regime, it is not unlikely that a similar peak splitting took place, but was masked by the much larger line broadening already occurring at lower pressure.

The peak splitting observed particularly well under quasihydrostatic conditions (see figure 2) can be interpreted as a slight tetragonal distortion of the cubic parent lattice. All the diffraction lines of the distorted structure can be indexed in space group $P4_2/nnm$ ($Z = 2$), an equitranslational subgroup of $Pn\bar{3}m$. Rietveld refinement of the new structure, Ia, was performed using the program FULLPROF [13] and the results are summarized in table 1. The calculated and the experimental diffraction profiles at $P = 5.7$ GPa together with the difference curve obtained after refinement are shown in figure 4. The volume jump due to the $\text{I} \rightarrow \text{Ia}$ phase transition is about 1%. In such a *proper ferroelastic* transition, *spontaneous* physical quantities,

⁶ It should be emphasized that silicon oil is liquid in this pressure range and that therefore the sample environment is hydrostatic at these pressures.

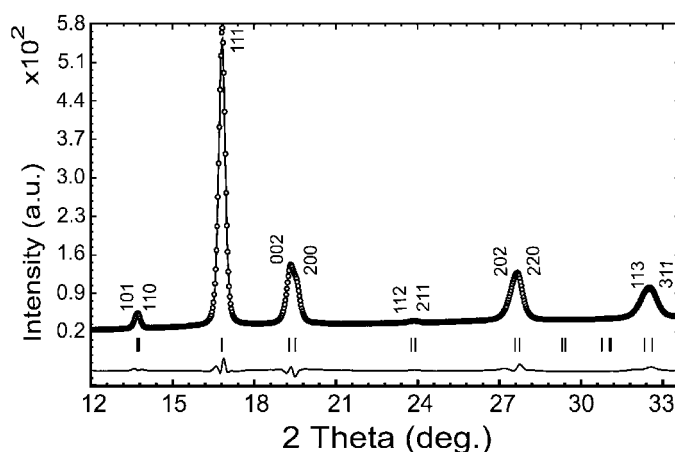


Figure 4. An example of profile-refined x-ray diffraction data collected at 5.7 GPa under quasihydrostatic conditions. The open symbols represent experimental data; the solid curve running through the data relates to the calculated pattern. The corresponding difference curve is plotted below the diagram. The tick marks indicate the positions of calculated Bragg reflections.

Table 1. Refined structural parameters of Cu₂O for $P = 5.7$ GPa.

Rietveld refinement		
$P4_2/nmm$ (No 134)		
$a = 4.1937(3) \text{ \AA}$, $c = 4.2435(7) \text{ \AA}$	Cu(x, y, z): 0, 0, 0	
$V = 74.633 \text{ \AA}^3$	O(x, y, z): 0.25, 0.75, 0.25	
$D_{\text{cal}} = 6.142 \text{ g cm}^{-3}$		
$\lambda = 0.7019 \text{ \AA}$	$\eta = 0.43$ (6)	
$2\theta = 10.0^\circ - 34.03^\circ$	$U = 0.184$ (1)	
Data points: 883	$V = 1.532$ (4)	
Bragg positions: 16	$W = -0.152$ (8)	
Parameters: 10		
$R_{\text{p(conv)}} = 8.3\%$		
$R_{\text{wp(conv)}} = 6.9\%$		
$R_{\text{exp(conv)}} = 9.47\%$		
$R_{\text{Bragg}} = 1.75\%$		
$R_{\text{F}} = 0.98\%$		
GoF = 0.73		

namely the second-rank *strain tensor components*, play the role of a primary order parameter. According to Landau theory the primary order parameter for the $m3m-4/mmm$ phase transition is proportional the spontaneous strain $e_t = (2e_{zz} - e_{xx} - e_{yy}) = (a_t - c_t)/(a_t + c_t)$. Figure 5(a) shows the pressure dependence of the lattice parameters in the pressure range from ambient to 10 GPa, and figure 5(b) displays the evolution of the corresponding order parameter e_t . One can see a considerable discontinuity at about 1.0 GPa in the order parameter behaviour. Such an anomaly is not surprising as the order parameter of the $m3m-4/mmm$ proper ferroelastic transition does not satisfy the Landau condition, i.e. the corresponding nonequilibrium energy expansion contains the third-degree term and a continuous phase transition is possible only at an isolated point of the phase diagram [14].

In contrast with expectations, the tetragonal distortion decreases when pressure increases. It vanishes completely at $P = 8.5$ GPa (figure 5) which indicates a transformation into

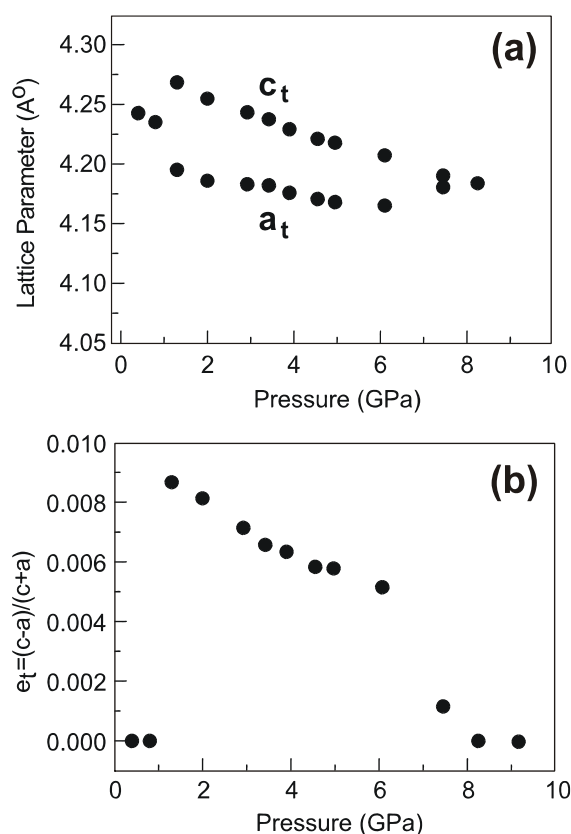


Figure 5. (a) Evolution with pressure of the cell parameters in tetragonal Cu_2O obtained from least-squares refinement of the (200)–(002) doublet. (b) Spontaneous strain e_t as a function of pressure.

new phase Ib. Diffraction patterns collected at pressures above 8.5 GPa resemble the ones from the low-pressure cubic parent structure (see figure 2, for example). However, despite such similarity of the whole patterns, the broadened character of the Bragg peaks makes identification of phase Ib ambiguous. The large line broadening can mask characteristic splitting of the strong peaks or the appearance of weak superstructure satellites. For example, Rietveld refinement performed with a model of the parent cubic structure proper and with a model of its rhombohedrally distorted version ($a_c = a_R$, $\gamma_R = 90.28^\circ$, which means $e_{xy} = e_{yz} = e_{xz} = 0.0024$) yields equal R -factors.

3.2. Microstrains and nanomerization

The irreversible broadening of the x-ray diffraction peaks was observed both under quasihydrostatic and under nonhydrostatic pressure conditions above 10 GPa at room temperature. According to Werner and Hochheimer [8], Cu_2O transforms to hexagonal phase II around this pressure. Our data confirm this observation and show that the Ib-to-II phase transformation starts at 11 GPa and is completed at 14 GPa, so crossing the phase coexistence region. This latter indicates a strongly first-order regime of the Ib-to-II transformation. One can assume therefore that the observed peak broadening is connected with the microscopic

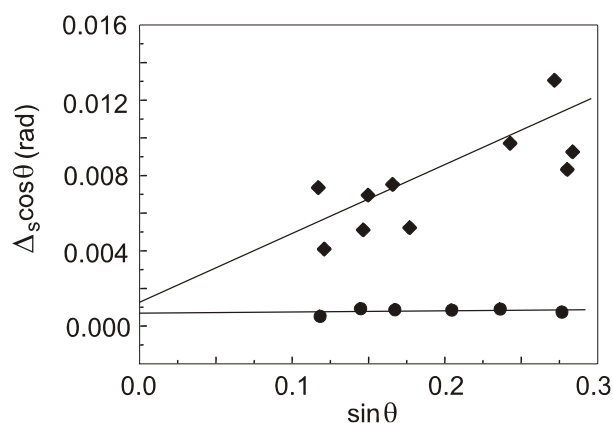


Figure 6. Williamson–Hall plots for reflections of Cu₂O for different pressures. Circles correspond to the sample at $P = 0.3$ GPa, diamonds to $P = 13.8$ GPa. Straight lines are the best least-squares fits.

internal strain arising in the sample near the phase transition. On the other hand, Ponyatovsky *et al* [10] also reported a strong broadening of the Cu₂O reflections, but in consequence of thermal treatment in the pressure range of 5–7 GPa where the phase transition does not occur. It was found using transmitting electron microscopy that peak broadening in this case is induced by the formation of the nanocrystalline mesoscopic structure in the major part of the sample. So, there are two mechanisms that can be responsible for the peak broadening observed here; these are the deformational mechanism connected with the microscopic strain due to nonhydrostatic conditions and the mechanism connected with formation of the nanosized grains. In order to distinguish between these two mechanisms, we also analysed the diffraction patterns of the samples recovered to normal conditions after compression runs under different conditions (the top curve in figures 1 and 2).

A clear demonstration of the existence of two contributions and their different impacts is provided by the Williamson–Hall plots shown in figure 6 for the quasi-hydrostatic loading. The method [15] proposed for analysis of the size broadening, Δ_L , and strain broadening, Δ_ε , relies on the hypothesis that they vary quite differently with respect to the Bragg angle, θ : one contribution, Δ_L , varies as

$$\Delta_L = \frac{K\lambda}{L \cos \theta},$$

where L is the ‘x-ray crystallite size’, λ is the radiation wavelength, K is a constant which depends on the assumptions regarding the peak shape and crystallite habit (typically $K = 0.9$). Microstrain broadens the specimen profile according to

$$\Delta_\varepsilon = C\varepsilon \tan \theta,$$

where ε represents the microstrain and C is a constant whose value depends on the assumption made concerning the nature of inhomogeneous strain ($2 \leq D \leq 4$). It was assumed [15] that the sample contribution to the peak broadening, Δ_s , is a simple sum of two components:

$$\Delta_s = \Delta_L + \Delta_\varepsilon.$$

Then, by plotting $\Delta_s \cos \theta$ versus $\sin \theta$ for observed diffraction peaks, one obtains the strain component from the slope and the size component from the intercept of the straight line approximating this dependence. Despite the well-known fact that the Williamson–Hall method

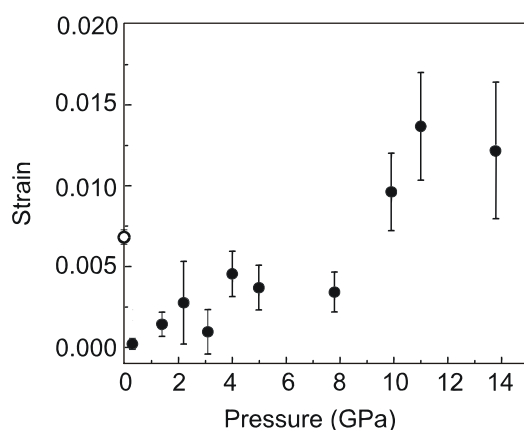


Figure 7. Microstrain induced in Cu_2O under high pressure. Open circle corresponds to the recovered sample.

should not be used for absolute value determinations, it is a useful method if used in the relative sense. The upward shift of the intercept point of the peak-width angular dependence fitted to the high-pressure data, in figure 6, allows us to estimate a decrease of the average diameter of the coherently diffracting domains by a factor of two. However, one can see that such a shift is within an ‘error corridor’ and the main contribution to the peak broadening is provided by the strains appearing in the compressed sample. Figure 7 demonstrates a considerable increase in microstrain induced in the sample, resulting in the diffraction peak broadening. Moreover, the material remains essentially stressed even when pressure is released (figure 7). This latter effect indicates indirectly the onset, in the course of pressure treatment near 10 GPa, of a considerable degree of structural defect enhancement of the microstrains, keeping the sample in a stressed state. As the transition into the hexagonal phase, inducing an essential rearrangement of the Cu sublattice, takes place in this pressure range, the appearance of defects and the corresponding microstrains can be considered as a precursor for the phase transition. In particular, the Ib–II phase transition changes the packing sequence of the Cu-containing hexagonal layers from a cubic ABCABC... to a hexagonal ABAB... one. This rearrangement of the stacking sequence is known to generate a considerable number of low-energy stacking faults [16] and these faults can be retained after the pressure release.

4. Conclusions

The present study confirms the existence of a transition to the tetragonal (pseudocubic) Cu_2O phase at pressures in the range 0.7–2.2 GPa reported earlier by Kalliomaki *et al* [7] and later questioned by Werner *et al* [8]. However, both the transition pressure and the value of the tetragonal distortion are very sensitive to the state of stress of the samples. The other phase transition, into an unidentified pseudocubic phase, takes place at 8.5 GPa. Increase in pressure to 10 GPa results in strong broadening of the diffraction peaks that remains irreversible upon decompression to ambient pressure. The full peak profile analysis concludes that although the formation of nanosized grains contributes to the peak broadening under pressure treatment of Cu_2O , the main reason for the effect is the onset of microstrains.

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References

- [1] Anderson P W 1997 *The Theory of Superconductivity in the High- T_c Cuprates* (Princeton, NJ: Princeton University Press)
- [2] Maksimov E G 2000 *Phys.—Usp.* **43** 965
- [3] Bourne L C, Yu P Y, Zettl A and Cohen M L 1989 *Phys. Rev. B* **40** 10973
- [4] Wang Z, Pischedda V, Saxena S K and Lazor P 2002 *Solid State Commun.* **121** 275
- [5] Belash I T, Peresada G I and Ponyatovsky E G 1997 *Inorg. Mater. (USSR)* **13** 544
- [6] Restori R and Schwarzenbach D 1986 *Acta Crystallogr. B* **42** 201
- [7] Kalliomaki M, Meisalo V and Laisaar A 1979 *Phys. Status Solidi a* **56** K127
- [8] Werner A and Hochheimer H D 1982 *Phys. Rev. B* **25** 5929
- [9] Webb A, Carpenter E R, Towle L C Jr, Skelton E F and Liu C-Y 1990 *High Pressure Res.* **6** 107
- [10] Ponyatovskii E G, Abrosimova G E, Aronin A S, Kulakov V I, Kuleshov I V and Sinitsyn V V 2002 *Phys. Solid State* **44** 852
- [11] Piermarini G J, Block S, Barnett J D and Forman R A 1975 *J. Appl. Phys.* **46** 2774
- [12] Hammersley A P, Svensson S O, Hanfland M, Fitch A N and Hausermann D 1996 *High Pressure Res.* **14** 235
- [13] Rodriguez-Carvajal J 1993 *Physica B* **192** 55
- [14] Salje E K H 1990 *Phase Transitions in Ferroelastic and Co-Elastic Crystals* (Cambridge: Cambridge University Press)
- [15] Williamson G K and Hall W H 1953 *Acta Metall.* **1** 22
- [16] Sebastian M T and Krishna P 1994 *Random, Non-Random and Periodic Faulting in Crystals* (London: Gordon and Breach)