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Polymorphs and Structures of Mercuric Iodide

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Abstract: Mercuric iodide, HgI_2, is a substance of technological interest because of its opto-electronic properties. It is of chemical and crystallographic interest because of the wealth of different crystal structures and structural motifs it assumes. At moderate temperatures and pressures, seven different phases have been reported. Three of them crystallize consecutively from organic solvents at room temperature: the stable red and two metastable orange and yellow phases. In this paper, we present the structures of the three phases at ambient conditions, where the orange one comprises three distinct structures, two structures at elevated temperature and pressure, and low-temperature studies of the red phase. The structures show a transition from semiconductor to molecular motifs: (1) HgI_4-tetrahedra corner-linked into layers in the red phase; (2) Hg_4I_{10}-supertetrahedra corner-linked into either polytypically disordered layers or into three-dimensional interpenetrating diamond-like frameworks in diverse orange structures; (3) linear I–Hg–I molecules in the metastable yellow phase at ambient conditions; (4) bent I–Hg–I molecules with relatively short intermolecular Hg-I contacts in different structures at moderately elevated temperature and pressure. Very complex, apparently cubic diffraction pictures of orange crystals are explained by multiple twins comprising domains of all structures with supertetrahedra. The yellow metastable structure is shown to be different from the yellow phase formed above 400 K. The thermal expansion and the atomic thermal displacements of the red phase have been studied between 6 K and room temperature. The thermal motion of Hg is always larger than that of I. The experimental methods used in this work comprise many of the tools available today for modern crystallographic research: single crystal diffractometers equipped with area detectors in the home laboratory, synchrotron high-resolution powder diffraction, synchrotron powder diffraction with diamond anvil cells and furnaces, and low-temperature neutron powder diffraction.

Keywords: High-pressure · Mercuric iodide · Phase transition · Polytype disorder · Twinning

1. Introduction

Mercuric iodide HgI_2 has been studied intensively for many years since the discovery in 1957 of its opto-electronic properties [1]. Single crystals of the red phase, stable at ambient conditions, are currently used as components in γ- and X-ray detectors [2]. Besides this red phase, additional metastable phases are known at ambient conditions, with colors ranging from yellow to various hues of orange. The pressure-temperature (P-T) phase diagram has been intensively studied and its general features appear to be well known [3]. At moderate temperatures and pressures, $T < 600$ K and $P < 1.5$ GPa, seven different phases have been reported [4–6]. However, several of these phases are incompletely characterized, and crystal structures have only been proposed for the three room-temperature phases [5][7][8].

Mercury(II) in its halides normally adopts the coordination numbers 4 or 2 (except in the fluorite-type HgF_2). This leads to very different crystal structures of HgI_2: tetrahedral framework structures on the one hand, and molecular structures on the other. For example, at ambient conditions iodine in the red and orange phases adopts a cubic closest sphere packing and mercury occupies corner-linked tetrahedral voids, whereas the metastable yellow phase shows linear HgI_2 molecules [5]. The red form sublimes at and above room-temperature, presumably giving off HgI_2 molecules.

The study of the wealth of structures adopted by HgI_2, of the numerous phase transitions and their mechanisms, and of the atomic thermal vibrations as functions of temperature is therefore of chemical and physical interest. Some of the structures pose very demanding crystallographic problems such as polytypic disorder, complicated multi-domain twinning and structure solution from powder diagrams of samples in diamond anvil pressure cells. Experimental techniques include single-crystal and powder diffraction with in-house and synchrotron X-rays and with neutrons at various temperatures and pressures, using various types of area detectors. The work presented here may thus serve as an example of research interests of crystallographers at the University of Lausanne, and the techniques available to them.

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2. Ambient Pressure and Temperature: Red, Yellow and Orange Phases

These variously colored crystals crystallize consecutively by evaporation from organic solvents [9]. Depending on the solvent, red, orange and yellow crystals are obtained in various ratios. As in [5][8], we have obtained all samples by evaporation of a saturated solution of commercial HgI_2 powder (Fluka 83379) in 2-chloro-ethanol. The proportion of different crystals obtained depends on the temperature and the concentration of the solution. The higher the temperature, the more yellow crystals are formed. Above 323 K these are the only product. The yellow form crystallizes first within a few hours, after a day the orange crystals start to appear and finally the stable red crystals form after days or even weeks. Raman spectroscopy of the solution indicates that HgI_2 is present in molecular form. Both the yellow and the orange crystals are mechanically unstable. Touching them with an object such as a needle easily induces the transition to the red form. Most unstable and extremely difficult to handle are the yellow crystals: a red nucleation appears at the contact point and spreads through a crystal with dimensions of 0.1 to 0.5 mm within a few seconds. In the more stable orange crystals, irregularly shaped red domains may appear which grow through the crystal in the course of a few hours. It is possible to mount orange crystals on glass fibers without creating red domains. These may stay orange for weeks, and some have survived for months, with a maximum of twelve months for one exceptional individual. After the transformation from orange to red, the resulting crystal quality is poor as evidenced by broad Bragg reflections. Some orange crystals, after exposure to X-rays, do not convert into the red form but instead become colourless and transparent and lose their crystallinity. They appear to be amorphous and may be decomposition products. In one case, a three-month old orange sample had transformed into yet another orange phase with a different, more yellow, hue and a different diffraction picture that will be presented below. The orange crystals may be heated up to 400 K, where they transform into the high-temperature yellow phase. This latter phase is not identical with the metastable yellow phase and will be described below.

The orthorhombic structure of the metastable yellow form crystallized by sublimation has been determined by Jeffrey and Vlasse [5]. It is isomorphous to the $HgBr_2$ structure and shows nearly linear and symmetrical HgI_2 molecules with a mean Hg–I distance of 2.617(6) Å and an I–Hg–I angle of 178.3(3)° (Fig. 1). Alternatively, the structure may be described as a CdI_2-type with very distorted octahedra, the next-shortest Hg–I distance being 3.507(6) Å. We have found the same structure for the yellow crystals obtained from 2-chloro-ethanol.

The tetragonal structure of the red form [5][7] (Fig. 1) consists of layers of corner-linked HgI_4-tetrahedra (Hg–I = 2.783(3), I–I = 4.367(4) Å) that are densely stacked with van der Waals I–I = 4.142(4) Å contacts.

The orange crystals were first investigated by Gorskii [6] who reported two different crystal morphologies: tetragonal truncated pyramids or bipyramids (a = 8.73(3), c = 24.45(4) Å), and hexagonal plates (a = 17.4 Å, c not measured). Jeffrey and Vlasse [5] found an apparent cubic cell with a = 24.85(5) Å for a crystal believed to be a multiple growth twin as indicated by polarised light microscopy. Schwarzenbach [8] confirmed the tetragonal unit cell of Gorskii. His precession photographs showed rods of diffuse intensity and systematic absences in excess of space-group absences, suggesting a disordered layer structure. From this information, an idealized polytypic layer structure was proposed. Using modern fast area detectors (imaging plate and charge-coupled device) and Mo$K\alpha$ X-rays, we have now collected complete diffraction data sets on several orange single crystals at room temperature and at 200 K. These new observations provide a convincing explanation of the various previous results [5][6][8], and allowed for the first time complete structure refinements. There are three types of diffraction pictures:

(a) Fig. 2a shows the $h0l$ reciprocal plane of a tetragonal crystal exhibiting rods of diffuse intensity and peculiar non-space group systematic absences, a_1 = 8.7860(9), c_1 = 24.705(9) Å $\approx 2\sqrt{2}\, a_1$ at room temperature. The resulting polytypic structure is essentially the one proposed in [8]. A polytypic structure family comprising structures of varying degrees of order always includes end members with maximum degree of order (MDO's), as *e.g.* the *fcc* and *hcp* structures in the

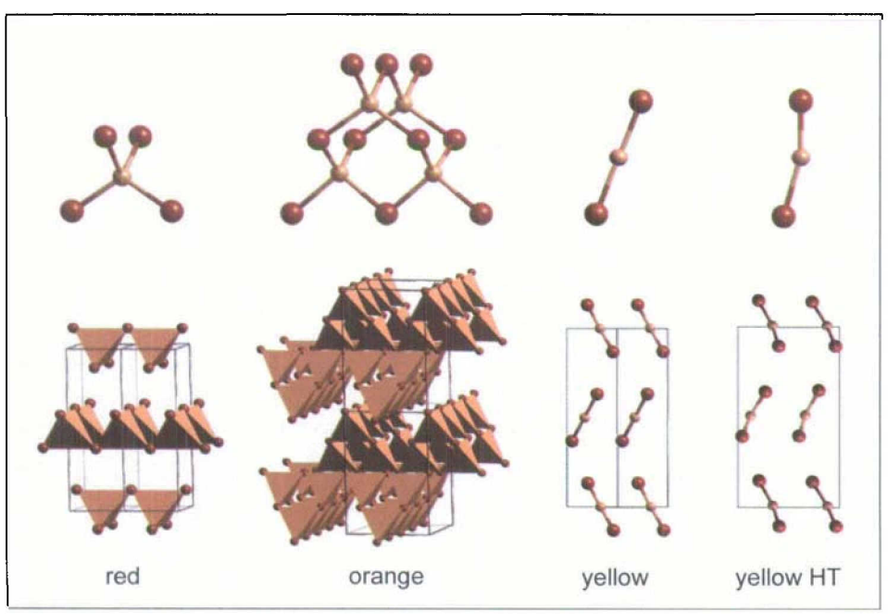

Fig. 1. Structural motifs and crystal structures of the red, orange polytypic, yellow metastable and yellow high-temperature polymorphs of HgI_2. Successive molecular layers in the yellow structures are stacked perpendicular to the plane of the plots.

family of densest sphere packings. The diffraction pictures of polytypic orange HgI_2 are well explained by the superposition of two MDO's with space group symmetries $I4_1/amd$ and $P4_2/nmc$ and lattice constants a_1, c_1 and a_1, $c_1/2$, respectively. The structure was refined with software developed for the purpose.

(b) The diffraction picture of a three-month-old X-ray irradiated crystal is shown in Fig. 2b. The symmetry is again tetragonal, $I4_1/acd$, and lattice constants $a_2 \approx \sqrt{2}a_1$ and $c_2 \approx c_1$. No rods of diffuse intensities are observed.

(c) Fig. 2c shows the $hk2$ plane of a cubic diffraction picture with lattice constant $a_3 \approx c_1 \approx c_2$, and diffuse rods as in (1). These observations are quantitatively explained by the presence of 3-fold twin domains of both structure (a) including the diffuse rods, and structure (b). Since the relations between the lattice constants are only approximate, the reflections from different domains do not fall exactly on the cubic grid.

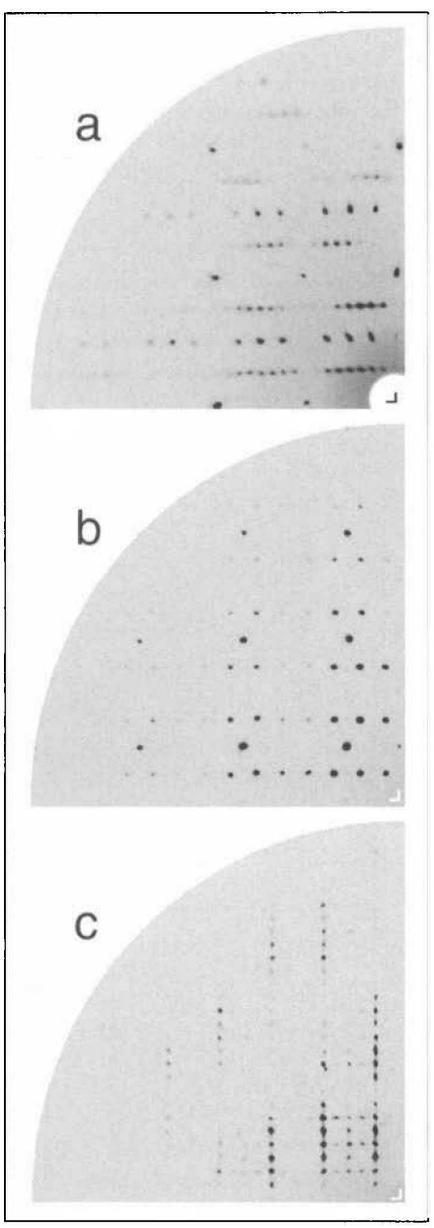

Fig. 2. Diffraction diagrams of the orange phase, reconstituted from area detector data recorded at room temperature. (a) Polytypic structure, layer $0kl$ referred to the tetragonal cell a_1, $c_1 \approx 2\sqrt{2}a_1$. (b) Diamond-type framework structure, layer $2kl$ referred to the tetragonal cell $a_2 \approx \sqrt{2}a_1$, $c_2 \approx c_1$. (c) Twinned crystal, layer $hk2$ referred to the cubic cell $a_3 \approx c_1$.

The orange phase of HgI_2 comprises three distinct structures. The characteristic motifs are corner-linked $[Hg_4I_{10}]$ supertetrahedra, which are fractal enlargements of the $[HgI_4]$ tetrahedra of the red phase (Fig. 1). In structure (a), these form layers analogous to the layers of the red phase (Fig. 1). Nearest neighbor layers can be stacked in two different positions with the same interlayer contact and this ambiguity results in the stacking disorder and two distinct MDO structures. The somewhat distorted supertetrahedra in the third structure (b) are linked into two interlocking diamond-like frameworks (Fig. 3). In all structures, including the red form, iodine is close to cubic densest packed and the Hg–I–Hg angles are close to 109.5°. The structures differ only in the distribution of mercury atoms, but not in nearest-neighbor coordinations. It can be shown that under these conditions, structures (a) and (b) are the simplest, highest-symmetric and most homogeneous extended frameworks of supertetrahedra. Small domains of one structure inside the other can easily be imagined to result in twinned orientations.

3. The Yellow Phase at 414 K

On heating at ambient pressure, red HgI_2 transforms into a yellow phase at 400 K. Yellow nuclei appear on the surfaces of the red crystals [10]. The resulting yellow powder is much coarser grained than the original red one. It thus appears that the yellow phase grows by vapour transport from sublimated material. On cooling, the transition begins between 350 and 380 K and shows a huge hysteresis. Some powder grains remain yellow down to room temperature. The nucleation now occurs in the volume [10]. The structure of this phase has long been supposed to be identical with the metastable orthorhombic yellow phase [5] composed of linear HgI_2 molecules (Fig. 1). However, high-resolution synchrotron powder diffraction at 414 K shows the structure to be monoclinic, rather than orthorhombic (Fig. 1). It shows bent and somewhat asymmetric molecules. The average Hg–I distances of 2.426(3) and 2.557(4) Å are shorter than in the metastable form, the I–Hg–I angle is 162.8(1)°. Similar to the metastable phase, the structure may also be described as a variant of the CdI_2 structure. The arrangement of I is closer to a densest sphere packing than in the former, but Hg does not occupy the centers of the octahedral voids.

4. High-pressure Phases

HgI_2 forms numerous high-pressure phases, none of whose structures has previously been determined. We therefore decided to undertake high-pressure powder diffraction studies with diamond-anvil cells, synchrotron radiation and a MAR345 imaging plate area detector. Surprisingly, two new phases were discovered in addition to the ones already reported in [4–6]. We now believe that nine different phases exist in the pressure–temperature range $P < 10$ GPa and $T < 600$ K. The phase diagram is very complicated. Some transitions are reconstructive and produce dramatic changes in the coordination of the mercury atoms. This is the case at 1.3 GPa when the red tetrahedral layer structure transforms into the molecular structure of phase VI. When the pressure is again decreased, phase VI reverts to the red phase with a large hysteresis of up to 0.6 GPa. The HgI_2 molecules in this high-pressure monoclinic structure (Fig. 4) are bent as in the yellow high-temperature phase of Fig. 1. Preliminary results indicate a

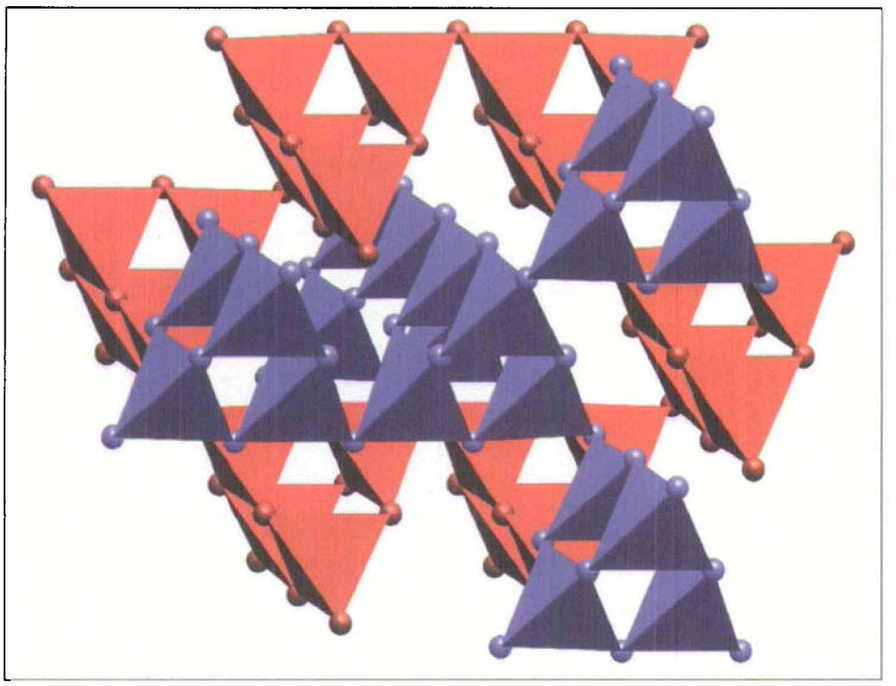

Fig. 3. Structure (b) of the orange crystals showing diamond-like interpenetrating frameworks of supertetrahedra. The red part shows a six-membered ring, the blue part the coordination of a supertetrahedron with symmetry $\bar{4}$ (S_4).

much smaller I–Hg–I angle of 130(5)° with a shortest Hg–I distance of 2.3(1) Å. Neighboring molecules form dimers as judged by the shortest intermolecular Hg–I contact of 2.6(1) Å. The resulting coordination of Hg is best described as approximately trigonal-pyramidal, rather than approximately octahedral. This structure is still in the process of being refined.

At room temperature, phase VI is stable up to 8.3 GPa where it transforms into phase VII. The powder diagram of phase VII has been successfully indexed with an orthorhombic unit cell. The structure is presently being determined.

5. Red HgI_2 as a Function of Temperature

HgI_2 adopts the structure of the red form stable at ambient conditions down to lowest temperatures, but the colour gradually changes from red to light-yellow. At 100 K, the sample is shiny 'canary' yellow. We have collected high-resolution powder diffraction data as a function of temperature between 6 K and 300 K with both synchrotron and neutron radiations. Fig. 5 shows the thermal expansion of the unit cell derived from neutron data. The expansion of the layer separation along the tetragonal c-axis is larger than the expansion within the layer perpendicular to c. With increasing tem-

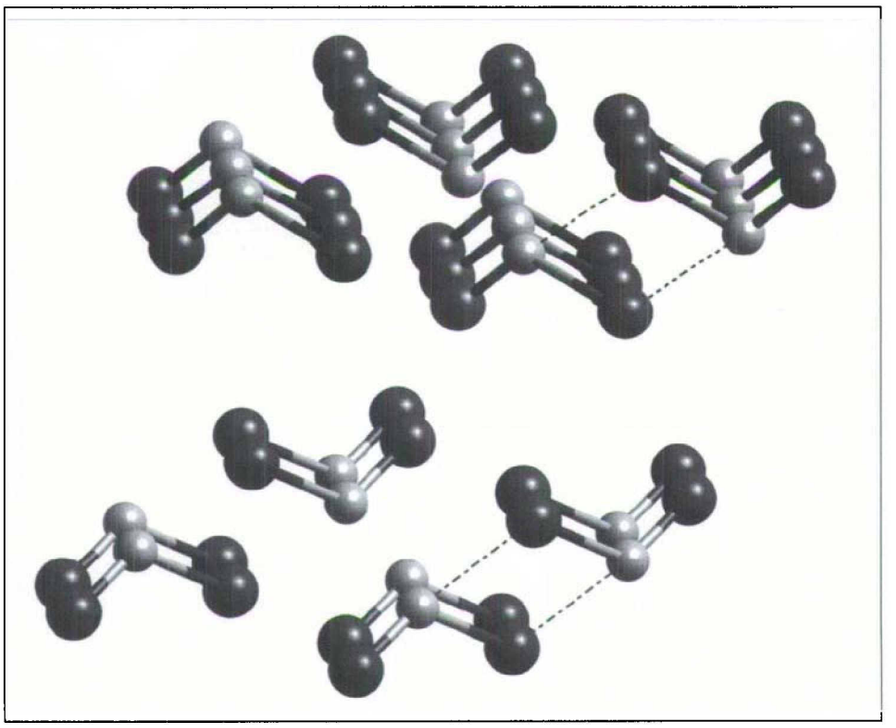

Fig. 4. Structure of the high-pressure phase VI above 1.3 GPa showing dimers of molecules.

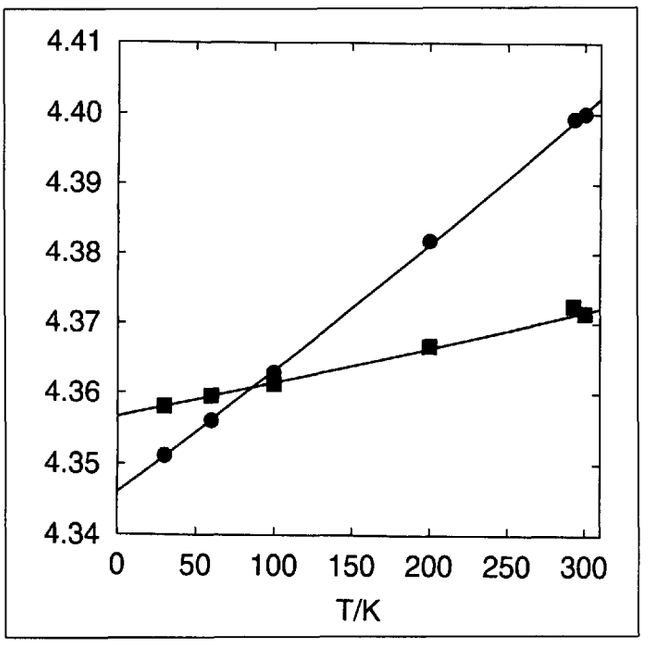

Fig. 5. Thermal expansion of the red form. Squares for the *a*-axis, circles for $c/2\sqrt{2}$ in Å.

perature, the background at large scattering angles of the neutron powder diffraction spectra strongly increases and is surprisingly large at ambient temperature. This is probably due to thermal diffuse scattering. Refinements of structural parameters against neutron and X-ray powder data show that the temperature motions of mercury are larger than those of iodine at all temperatures, and increasingly so at higher temperatures. A similar effect has been observed in rutile, TiO_2 [11]. It appears that iodine is quite rigidly packed whereas mercury shows a mobility it certainly exploits in the transitions between the orange phases and from the orange to the red phase. The increase of the thermal displacement parameters at the higher temperatures is steeper than linear indicating the presence of anharmonic terms.

6. Conclusions

The number of different polymorphs and structures HgI_2 adopts is impressive. This is all the more remarkable as the complicated phase diagram is realized in the very modest temperature–pressure domain of $T < 600$ K, $P < 10$ GPa. The crystal structures known today belong to radically different structure types. Some are molecular showing linear or bent HgI_2 molecules and various next-nearest neighbor Hg–I distances. Others are extended semiconductor structures with iodine adopting a densest sphere packing, tetrahedral metal coordination and Hg–I–Hg angles close to 109°. The red and orange forms realize four of the simplest arrangements of corner-linked tetrahedra with these properties: there are only five such structures where all tetrahedra are symmetry-equivalent. The point symmetries of the tetrahedra are $\bar{4}\,2m$ (D_{2d}) in the red form, m (C_s) in the polytypic orange forms and 1 (C_1) in the diamond-like orange framework, the symmetries of the corresponding fractal-type supertetrahedra being $\bar{4}\,2m$ and $\bar{4}$ (S_4). The structures of the orange form finally solve a long-standing problem and explain the results of experiments published during the past 70 years.

The physical properties of the different phases are as diverse as their structures. Some molecular phases show nonlinear optical effects, whereas the semiconductor phases have important optoelectronic properties. The other mercury halides are molecular at ambient conditions with the exception of the fluorite-type HgF_2.

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[1] R.H. Bube, *Phys. Rev.* **1957**, *106*, 703.
[2] S.L. Sharma, T. Pal, H.N. Acharya, *J. Appl. Phys.* **1994**, *75*, 7884; B. Steiner, L. Van den Berg, U. Laor, *J. Appl. Phys.* **1999**, *86*, 4677.
[3] C. Guminski, *J. Phase Equil.* **1997**, *18*, 206.
[4] E.D. Tonkov, N.A. Tichomirova, *Sov. Phys. Cryst.* **1971**, *15*, 945.
[5] G.A. Jeffrey, M. Vlasse, *Inorg. Chem.* **1967**, *6*, 396.
[6] V.S. Gorskii, *Physik. Z. Sowjetunion* **1934**, *6*, 515; V.S. Gorskii, *J. Explt. Theoret. Phys. USSR* **1935**, *5*, 155.
[7] J.M. Bijvoet, A. Claassen, A. Karssen, *Proc. Acad. Sci. Amsterdam* **1926**, 29, 529.
[8] D. Schwarzenbach, *Z. Kristallogr.* **1969**, *128*, 97.
[9] W. Kleber, H. Raidt, K.O. Leupold, *Kristall und Technik* **1968**, *3*, 65.
[10] J.B. Newkirk, *Acta Metal.* **1956**, *4*, 316.
[11] R. Restori, D. Schwarzenbach, *Acta Crystallogr.* **1987**, *B43*, 251.