GROWTH OF A CRYSTAL OF HEXAGONAL SELENIUM FROM A SINGLE CRYSTAL OF MONOCLINIC SELENIUM DURING A POLYMORPHIC TRANSFORMATION

CRYSTALLOGRAPHY

1967

SovietRxiv

Abstract

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UDC 548.33+548.552
CRYSTALLOGRAPHY

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GROWTH OF A CRYSTAL OF HEXAGONAL SELENIUM FROM A SINGLE CRYSTAL OF MONOCLINIC SELENIUM DURING A POLYMORPHIC TRANSFORMATION

(Presented by Academician A. V. Shubnikov, 29 IV 1966)

As is known, selenium at room temperature and normal atmospheric pressure exists both in amorphous, glassy, metallic, and in α- and β-red monotropic forms. Of these modifications, gray metallic selenium is stable up to the melting temperature. The other modifications of selenium, depending on external conditions (temperature and pressure), irreversibly transform into metallic selenium. It has been established that metallic selenium has a hexagonal structure ([1]), while α- and β-red selenium have a monoclinic structure ([2,3]). Numerous works have been devoted to the mechanism of transformation of amorphous and glassy selenium into hexagonal selenium (for example, ([4–6])). Concerning the mechanism of transformation of red selenium into hexagonal selenium, there exists only a supposition ([2,3,7]).

The purpose of the present investigation is to elucidate the character and mechanism of the transformation of a transparent single crystal of red selenium into opaque metallic selenium.

Experimental Part

Single crystals of red selenium were grown from a solution of amorphous selenium of 99.99999% purity in carbon disulfide. For optical and X-ray studies, more than 30 single crystals of α-red selenium, identical in size, shape, and color, were selected.

Observations under an optical polarizing microscope equipped with a heating stage and a photographic attachment for microphotography showed that up to a temperature of 125° a single crystal of red selenium does not change its color or transparency. Only at 125° do crystallization nuclei of hexagonal selenium form in the single crystal of monoclinic selenium. Depending on the perfection of the matrix crystal, nuclei of crystallization of the new phase sometimes form at a temperature of 145°.

Fig. 2. Lauegrams of monoclinic selenium (a) and hexagonal selenium (after the transformation of monoclinic selenium into hexagonal) (b)

Figure 1: Fig. 2. Lauegrams of monoclinic selenium (a) and hexagonal selenium (after the transformation of monoclinic selenium into hexagonal) (b)

Fig. 1

Figure 2: Fig. 1

Crystals of hexagonal selenium grow from amorphous and glassy selenium in the form of spherulites, and from a single crystal of red monoclinic selenium in the form of dendrites (Fig. 1). Figure 2 gives a Laue pattern of a single crystal of red monoclinic selenium and a Laue pattern taken after the transformation of monoclinic selenium into hexagonal selenium. Series of Laue patterns obtained in this way show that, irrespective of the choice of heating regime, a single crystal of monoclinic selenium always transforms into a polycrystal of hexagonal selenium. As we indicated earlier ([8]), this is also due to the fact that the difference between the densities of the matrix and the growing crystal is very large ($\rho_{\text{grow}} - \rho_{\text{matrix}} = 0.436$ g/cm^3).

The growth of a dendrite in the case of the transformation of a single crystal of monoclinic selenium into hexagonal selenium differs in no way from the dendritic growth of crystals from solutions, melts, and during vapor condensation. Observations and microphotography of more than 20 crystals of monoclinic selenium during transformation

Fig. 2. Lauegrams of monoclinic selenium *(a)* and hexagonal selenium (after the transformation of monoclinic selenium into hexagonal) *(b)*

in a hexagonal one showed that the growth of the dendrite—the direction of its main trunk—does not depend on the crystallographic direction of the matrix crystal. The branches of the dendrite form an angle of $\sim 58^\circ$ with the main trunk and are strictly parallel to one another. As is seen from Fig. 1II, the main trunks of two

Fig. 1. Growth of a crystal of hexagonal selenium inside a single crystal of red monoclinic selenium. *I*—dendritic growth of hexagonal selenium inside a single crystal of red selenium, 60×; *II*—enlarged form of region I, bounded by dashed lines, 1350×

dendrites are parallel, and the branches of the second are as if a continuation of the first. The growth of the dendrite in the solid single-crystalline state depends strongly on the heating rate and on $\Delta T = T_{\text{trans}} - T_0$.

Discussion of the results

It is known that the molecule of monoclinic selenium is an 8-atom closed ring. The unit cell contains 4 molecules. In the ring, the Se–Se distance is 2.34 Å, and the shortest distance between atoms of neighboring molecules is 3.53 Å. The molecule of hexagonal selenium consists of atomic chains arranged in a screw-like fashion in the [0001] direction. The shortest interatomic distance in the chain of hexagonal selenium is 2.34 Å, and the shortest distance between chains is 3.53 Å. The unit cell contains 3 atoms. In both modifications, within the rings and chains, homopolar bonds act between the atoms, while the rings and chains themselves are connected with one another by significantly weaker nonpolar forces.

During the transformation of a single crystal of monoclinic selenium into hexagonal selenium, in contrast to our previous studies ([9]), the following occur simultaneously: a) destruction of the closed ring of the 8-atom molecule of the matrix crystal; b) formation of a short-chain molecule with free radical-like ends. After such preliminary preparation, crystallization nuclei of hexagonal selenium are formed. As a rule, a crystallization nucleus of the new phase always forms at a defective site (dislocation, vacancy, etc.), where the regular arrangement of molecules is disturbed.

Upon heating a single crystal of monoclinic selenium, the amplitude of the thermal vibration of the atoms in the molecule and the amplitude of the thermal vibration of the molecule itself increase. Since in a defective region of the crystal the freedom and energy of the molecule are greater, the molecule there is probably deformed. In the deformed molecule, the Se–Se bonds are broken at some point. These destroyed molecules probably form nuclei of crystallization of hexagonal selenium. Since the intermolecular distances along different crystallographic directions are different, the work that must be performed to move along these directions is also different; consequently, one may expect that crystal growth in the solid single-crystalline state is characterized by anisotropy, which is characteristic of the physical properties of a crystal. The anisotropy should be expressed the more sharply, the lower the symmetry of the crystal lattice of the matrix crystal. Indeed, if this were not so, the anisotropy of the matrix single crystal would always direct the nuclei of crystallization of the new phase in some crystallographic direction, i.e., there would be a rigid connection between the growing and the initial phases.

However, a study of polymorphism in a low-symmetry single crystal (ˆ9) has shown that the anisotropy of the matrix crystal does not affect the crystal of the new phase growing inside it: the initial phase serves, as it were, as an isotropic medium for the new growing crystal. Apparently, this is due to the fact that, during the formation of a nucleus and during the direct growth of the crystal of the new phase inside a nonequilibrium phase under the action of the released heat of crystallization, the anisotropy of the matrix crystal cannot play a dominant role.

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Received
27 IV 1966

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