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Symmetry and Martensitic Transformations in ZnS Crystals

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Abstract

ZnS polytypes are formed by martensitic transformations from their common parent, the hexagonal $2H$ structure, and their crystallographic characteristics depend on the detailed transformation mechanism. The ratio of the number of rhombohedral to the number of non-rhombohedral polytypes in the population of the currently identified polytypes is 1·5. It was formerly argued that the expected ratio is 2 and that the discrepancy indicates that the population is biased. An analysis based on the established properties of martensitic transformations in ZnS shows that the ratio of rhombohedral to non-rhombohedral polytypes depends on the transformation probability by a dislocation dipole; it is further shown that the experimental ratio of 1·5 can be derived by assuming the plausible value of $0{\cdot}8\pm0{\cdot}1$ for this probability.

Introduction

Martensitic transformations in vapor-phase-grown ZnS crystals are responsible for the formation of a large number of stable close-packed structures, namely polytypes. Their crystallographic characteristics depend on the detailed mechanism of the transformation. It was demonstrated that a statistical analysis of such characteristics can lead to a better understanding of that mechanism (Mardix, 1986*a*). The population which the analysis was based on was the set of all identified polytypes; it is clearly essential that this population constitutes an unbiased sample.

One of the characteristics which can be studied is the ratio N_R/N_L of the number of rhombohedral to non-rhombohedral structures in a given population. A claim was made (Steinberger, 1983) that the expected value of this ratio in an unbiased population of ZnS polytypes should be $N_R/N_L=2$. The discrepancy between the value of 1·6 found for the population of all identified polytypes at the time of the above publication and the expected value of two led Steinberger to the conclusion that a bias exists in the procedure for selecting polytypes for identification. In a more recent list including a larger number of identified polytypes (Mardix, 1986*a*), the experimental value of the ratio N_R/N_L is 1·5, giving an even larger apparent discrepancy.

We shall show that the transformation mechanism of ZnS polytypes may lead to a wide range of values of N_R/N_L and that the experimental ratio of 1·5 is well within that range. Furthermore, we shall show that the experimental value of N_R/N_L can be used to find an approximation for the transformation probability of a polytype by a dipole of partial dislocation.

Polytype formation in ZnS crystals

A review of the crystallography of vapor-phase-grown ZnS (Mardix, 1986*b*) describes in detail the formation mechanism of its polytypes and brings a large volume of substantiative experimental evidence. We give here a summary of the mechansim.

ZnS crystals grow at a temperature of about 1340 K and have the hexagonal $2H$ close-packed structure. A region of a crystal in which polytypes are found includes a single screw dislocation with a Burgers vector parallel to the crystal c axis. The magnitude of the Burgers vector is given by $|\mathbf{B}|=2nc_0$ where n is an integer and c_0 is the basal plane interlayer distance. The average value of n for the polytypes identified so far is about 20 and the highest value is 64. The existence of the screw dislocation makes the topology of the basal planes of a polytype resemble that of an interleaved set of helicoidal surfaces all with the same pitch $|\mathbf{B}|$.

As the crystals cool down to room temperature, basal-plane Shockley partials start moving, leaving behind them a spreading stacking fault. Owing to the helicoidal nature of the basal planes, the partials will find themselves climbing in both directions of the c axis, creating stacking faults $2n$ layers apart. The resulting transformed structure will have the same basic periodicity as its parent, namely $|\mathbf{B}|/c_0$ or $2n$.

The driving force for the moving partials comes from the free-energy difference between the transformed and parent structures. As the stability of the hexagonal stacking goes down with temperature one finds that the net result of the transformation is to reduce the number of hexagonally stacked layers (h layers), converting them to cubically stacked ones (c layers). The transformation process can continue while there are still h layers left which can be converted with a decrease in free energy. The probability

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of the above transformation will strongly depend on the magnitude of the energy decrease.

Transformations by moving partials

Both the Pauling (1945) and the Zhdanov (1945) notations will be used here to describe the stacking sequence of a close-packed structure. The Pauling notation gives the sequence of *h* and *c* layers in the structure while the Zhdanov notation specifies the consecutive distances between *h* layers. For example, the periodic sequence ... *hch*, *hccchcchch*, *hcc*..., where the commas delimit one period, will be presented as 4 3 2 1 in the Zhdanov notation. The Zhdanov symbol of a periodic structure must have an even number of elements. The property of a close-packed structure with the Zhdanov symbol $a_1, a_2, \ldots, a_n$ to be rhombohedral ($R3m$) or non-rhombohedral ($P3m1$ or $P6_3mc$) can be derived from the difference

$$D = \sum_{k=1}^{n/2} (a_{2k} - a_{2k-1}).$$

If $D = 0 \pmod 3$, the structure is non-rhombohedral (L structure); it is rhombohedral (R) for $D \neq 0 \pmod 3$.

It should be noted that in the special case of polytypes with an even number of layers in their basic period, which is the case for all known ZnS polytypes, D is an even number; particularly $D = 0$ for the parent hexagonal $2H$ structure. A transformation event taking place by the motion of a single Shockley partial affects a pair of neighboring layers, an *h* layer of the pair transforms into a *c* layer and *vice versa.* There are, therefore, four possible pair transformations associated with such an event, *hh* to *cc*, *hc* to *ch*, *ch* to *hc* and *cc* to *hh*, each of which changes the value of D by $\Delta D = \pm 2$. A structure with $D = 0 \pmod 3$ (an L structure) can therefore transform to an R structure only, while an R structure [$D \neq 0 \pmod 3$] can transform either to an L or to another type of R structure: a structure with $D = 1 \pmod 3$ may transform to one with $D = 2 \pmod 3$ and *vice versa.*

In addition to transformations by a single Shockley partial, dipoles of partials can be involved in a transformation event (Steinberger, 1973). A dipole consists of two partials with Burgers vectors in opposite directions residing on neighboring planes with a short distance between them.

While the crystallographic effect of a transformation taking place by a single partial dislocation is to sheer the crystal in the direction perpendicular to its *c* axis, the motion of a dipole results in the sliding of a single layer, or a group of them, between the two parts of the crystal on both sides. The strain energy associated with a dipole is lower than that of two single partials far away from each other, favoring its formation.

The transformation by a dipole can be considered as a single event composed of two transformations by single partials. Such a transformation, in contrast to that created by a single partial, does not change the structural symmetry, L and R structures transform respectively into other L and R structures of the same type.

The martensitic transformation from the parent $2H$ structure (... *hhhhh*...) to the final room-temperature stable polytype can be broken into a chain of transformation events. Each event can be caused either by the motion of a single partial or by a dipole. The condition for an event to happen with a high probability is that it will lead to a reduction of the free energy of the crystal, which implies that the number of *h* layers must go down after each transformation event. Both possible types of transformation, by a single partial or by a dipole, can change the number of *h* layers by zero, two or four, depending on the geometry and location of the transformation dislocations. We shall assume that only transformations resulting in a reduction in the number of *h* layers happen. Thus the number of *h* layers in the basic period has to go down by either two or four after each transformation event.

An important point to notice is that the chain of transformation events will consist of a small number of events. For a complete transformation from the hexagonal $2H$ to a cubic structure there should be about $N/3$ such events, where N is the number of layers in the basic period. If multipoles take part in the transformation mechanism the number of events will be even smaller. As the average number of *h* layers in the population of identified ZnS polytypes is about four and most of their basic periods fall between eight and 40, one can estimate the number of transformation events forming the known ZnS polytypes to be somewhere between two and 12 with an average of about seven.

Symmetry of the identified polytypes

We shall consider the system S of polytypes formed during the martensitic transformations of the parent $2H$ to the room-temperature stable structure. The two states in which the system can be found are the rhombohedral (R) and non-rhombohedral (L). After each of the transformation events $t = 0, 1, 2, \ldots, n$, S can be either in an R state or in an L state. We shall denote by p_{ij} the probability that the system which at $t = k$ is in the state i will transform at $t = k+1$ to the state j. The matrix $P = (p_{ij})$ has four elements:

$$P = \begin{pmatrix} p_{LL} & p_{LR} \\ p_{RL} & p_{RR} \end{pmatrix}.$$

Following the discussion in the former sections we shall now list the assumed properties of the system S.

1. At $t = 0$, S is in state L.

2. The number of events n is finite.
3. n depends on M, the number of layers in the basic unit, and is approximately equal to $M/3$.
4. The value of n for most structures in the population of identified ZnS polytypes is between two and 12 with an average of seven.
5. $p_{LL} = p$, where p is the probability that the transformation event was due to a dipole. Note that $\Delta D = 0$ for a transformation by a dipole.
6. $p_{LR} = 1 - p$ is the probability that a single partial is responsible for the transformation event ($D \neq 0$ for a transformation by a single dislocation).
7. $p_{RL} = (1-p)/2$. The value of ΔD for a transformation by a single partial was given as $\Delta D = \pm 2$. We shall assume that a transformation with $\Delta D = +2$ has the same probability as one with $\Delta D = -2$. One of the above will transform an R structure to an L structure while the other will transform one type of R structure [$D = 1$ (mod 3) or $D = 2$ (mod 3)] to the other type of R structure.
8. $p_{RR} = (1+p)/2$.

Let $p_L(k)$ and $p_R(k)$ denote the probabilities that, for $t = k$, S is in states L and R, respectively. From 1 it follows that:

9. $p_L(0) = 1$; $p_R(0) = 0$;

from 5 and 7:

10. $p_L(k) = p_L(k-1)p + p_R(k-1)(1-p)/2$;

and from 6 and 8:

11. $p_R(k) = p_L(k-1)(1-p) + p_R(k-1)(1+p)/2$.

We are interested in the series Q which has as its elements the ratios $Q_k = p_R(k)/p_L(k)$. Q_k is the expected ratio of rhombohedral to non-rhombohedral structures in a randomly selected population of polytypes formed by k transformation events. Considering p (the transformation probability by a dipole) as a parameter, we notice that $Q_k = Q_k(p)$. It should be noted that the ratio N_R/N_L for a given population is expected to be equal to $Q_k(p)$ where k is the average value of the number of transformation events which took place during the creation of the population and p is the probability of a structure of this population to be transformed by a dipole. N_R/N_L is presented in Fig. 1 for the range of p values 0·5 to 0·9. Values of N_R/N_L with the same p value are sequentially connected by straight segments. From the experimental value of 1·5 for N_R/N_L and the average value of seven for t, we see from Fig. 1 that p is approximately 0·8. It should be noted that for $N_R/N_L = 1{\cdot}5$ the selected value of p is not very sensitive to the number of transformation events, a value of $p = 0{\cdot}8 \pm 0{\cdot}1$ can account for the experimental ratio of N_R/N_L for a wide range of t values, $4 \leq t \leq 14$, which is the expected range of the number of transformation events in the experimental population.

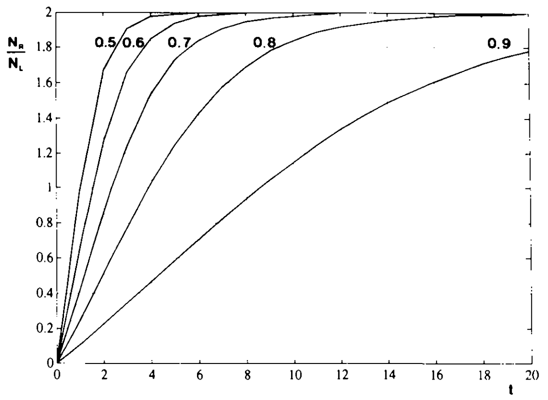

Fig. 1. The calculated ratios N_R/N_L of the number of rhombohedral to non-rhombohedral polytypes *versus* the number of transformation events t necessary to form the polytypes, for the range of transformation probability by a dislocation dipole, p, of 0·5 to 0·9. The values of p are denoted in the figure.

From Fig. 1 we can also see that N_R/N_L converges to two for all values of p, more rapidly for smaller values.

Discussion

The model used to derive the dipole transformation probability p was based on some simplifying assumptions. The most significant is the implied assumption that the probability p stays constant throughout the transformation process. As a matter of fact, one can expect this probability to be high at the initial stages and to go down at the final stages as the number of h chains containing more than two h layers becomes smaller. Use of a more sophisticated model may change somewhat the average value of p but with the available population of identified structures the change is not expected to be statistically significant.

The reasoning which led to the conclusion that the ratio N_R/N_L should be two was stated as follows (Steinberger, 1983):

'According to the model discussed the polytype resulting from the transformation will be trigonal or hexogonal, if after the introduction of the stacking faults within a block of height mc_0 a layer sequence is formed with the $m+1$-th layer in the same position (A, B or C) as the first one, otherwise it will be rhombohedral. With a random distribution of stacking faults the probability for this is obviously 1/3. It follows that rhombohedral polytypes ought to occur twice as frequently as trigonal (including hexagonal) ones.' (m in this statement denotes the number of layers in the basic period, denoted in this paper by M.)

The main fault in the above reasoning is the implied assumption that the presented model of polytype formation leads to a random distribution of stacking faults. This would have been correct if at each stage of the transformation the stacking fault had been introduced independently of the parent structure and in such a way that the stacking fault would have the same *a priori* probability to be introduced and spread between any two layers in the basic period. The experimental evidence against this mode of transformation and against a random distribution of stacking faults in the polytypes is overwhelming.

The observation (see Fig. 1) that the asymptotic value of N_R/N_L is two indicates that the transformation mechanism does contribute to the randomization of layer positions so that for structures created by a large number of transformations the type of the layer in the $M+1$ position does indeed become randomly related to the first one. This however does not imply that the stacking faults are randomly distributed.

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Anisotropy of Anomalous Dispersion in X-ray Diffraction

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Abstract

Polarization-dependent resonant Bragg diffraction in crystals is investigated both theoretically and experimentally. In order to describe the effects of anisotropic anomalous dispersion on intensity and polarization of kinematically diffracted X-radiation, a general scattering model is developed on the basis of site-symmetry-compatible second-rank scattering-factor tensors for the absorbing atoms. For conventional four-circle single-crystal diffractometry it is shown that intensity and polarization of the diffracted beam can be predicted as functions of both crystal orientation and polarization of the incident radiation. In principle, anisotropy of anomalous dispersion may affect any reflection. In particular, it can give rise to the observation of intensities for reflections being systematically extinct by space-group symmetry. Both effects are discussed. Experimental proof of the model's validity was obtained by synchrotron-radiation X-ray diffraction measurements of mainly 'forbidden' reflections in cubic cuprite, Cu_2O and tetragonal rutile type TiO_2 and MnF_2. The experiments were carried out at the respective K-absorption edges of the cations using different instruments at HASYLAB/DESY during dedicated mode of DORIS II (3·78 GeV). Significant anisotropy of anomalous dispersion due to excitation of K electrons into p states was observed in each case, allowing studies of the dependence of 'forbidden' reflection intensities on both radiation energy and rotation (Ψ) around the scattering vector **h**. Comparison of the observations with the analytical intensity functions derived from the scattering model shows full agreement on a relative scale. For cuprite, estimates of the anisotropies of the real and imaginary components of the anomalous dispersion of Cu were obtained from the allowed reflection 330. The values derived from two different experiments (energies) are $f' = -0{\cdot}56$, $-0{\cdot}35$ and $f'' = -0{\cdot}23$, $0{\cdot}0$ electrons, respectively.

Introduction

The anisotropy of the anomalous dispersion (AAD) of X-rays is an energy-dependent resonance effect which is likely to occur in the vicinity of an absorption edge of a bonded atom. As a pure consequence of chemical bonding it reflects two phenomena in the XANES and EXAFS regions, respectively:

(i) dipole and (to a much smaller extent) quadrupole transitions from the initial 'core' state to excited states which are vacant, allowed and related to the local symmetry and the chemical environment of the absorbing 'edge' atom,

(ii) interference of the outgoing wave of 'true' photoelectrons, *i.e.* with positive energy, with the wave backscattered from surrounding neighbor atoms.

In crystalline material of lower than cubic symmetry both effects can manifest themselves in an anisotropic refractive index and consequently in

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