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Electron diffraction study of phase transformations in copper sulfides

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Abstract

The order–disorder transformation behavior of chalcocite and djurleite, and digenite and anilite has been studied by direct observations of the transformations in a transmission electron microscope. Chalcocite and djurleite represent low-temperature superstructures of the high-temperature disordered chalcocite subcell, and there need be no compositional difference between them. The djurleite superstructure is the more stable form at room temperature. The intermediate structure in digenite forms through modulated structures rather than through twinning. A metastable *6a* digenite type superstructure, isochemical with anilite, forms on heating. This *6a* superstructure is metastable relative to the formation of anilite.

Introduction

For compositions near Cu_2S a number of phases are known to exist at room temperature. These may be divided into two broad categories based on the nature of the sulfur close-packing in the structure: (1) chalcocite and djurleite with structures based on hexagonal close-packing of sulfur atoms: (2) digenite-like structures and anilite with sulfur atoms in approximately cubic close-packing. The low-temperature phase relations have been summarized by Morimoto and Gyobu (1971) and Barton (1973). The transformation behavior of some of these phases and the relationships between them have been studied by direct observation of the transformations in a transmission electron microscope.

Method

Naturally-occurring crystals of the phases were crushed, after chilling in liquid nitrogen to prevent deformation. The finest grains were collected from a suspension in absolute alcohol and mounted on a standard carbon-coated copper grid for observations in an AEI EM6G transmission electron microscope operating at 100kV. Observations were made firstly on untransformed grains by using a small condenser aperture and a defocussed beam to keep the illumination and the heating effect of the beam minimal. Transformations in the grains, both on heating and cooling, can be observed by focussing and defocussing the beam or by moving the beam laterally on and off the grain. Although the temperature in the grain cannot be directly measured in this way, the course of a transformation can be followed dynamically, and subtle changes which would be very difficult to observe by X-ray methods can clearly be seen.

I: The transformation behavior of chalcocite and djurleite

Chalcocite is generally considered to have a composition very close to Cu_2S, whereas djurleite, originally thought to be $Cu_{1.97}S$ (Roseboom, 1966; Takeda *et al.*, 1967a) is now considered to be a solid solution with a composition range from about $Cu_{1.93}S$ to $Cu_{1.97}S$ (Mathieu and Rickert, 1972; Potter, 1974).

The phases and cell dimensions of chalcocite and djurleite may be summarized as follows. Between 104° and 435°C chalcocite is hexagonal with $a_h = 3.95$, $c_h = 6.75$ Å and space group $P6_3/mmc$. Above 435°C it has the cubic close-packed digenite structure. Below 104°C a pseudo-orthorhombic cell with $a = 11.92$, $b = 27.34$, $c = 13.44$ Å, space group $Ab2m$ is formed (Buerger and Buerger, 1944). This can be described as a superstructure of the hexagonal form with $a = 3a_h$, $b = 4\sqrt{3}a_h$, $c = 2c_h$. More recently it has been shown that low-chalcocite is monoclinic (Evans, 1971), but the pseudo-orthorhombic cell will be used here for convenience.

Djurleite is orthorhombic, diffraction aspect $P{*}n{*}$ with cell dimensions $a = 26.90$, $b = 15.72$, $c = 13.57$ Å. The diffraction aspect is also compatible with the monoclinic space group $P2_1/n$. Takeda *et al.* (1967a) point out that these cell dimensions are closely re-

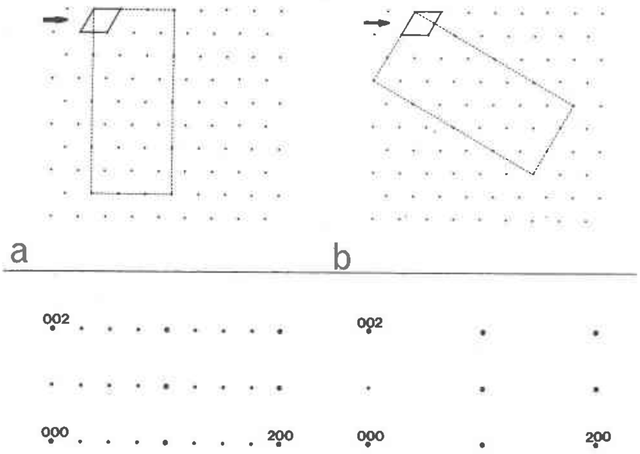

Fig. 1 a,b. The top direct lattice illustrations show two of the three possible orientations of the chalcocite superstructure (dashed line) relative to the high-chalcocite subcell (full line). The arrow on the left is the direction of the electron beam which leads to the formation of the a^*c^* diffraction pattern below each diagram. In these diffraction patterns the large spots are the subcell reflections while the smaller spots are due to the superlattice orientation above.

lated to the hexagonal chalcocite subcell with $a = 4c_h$, $b = 4a_h$, $c = 2\sqrt{3}a_h$. Roseboom (1966) and Potter (1974) reported that djurleite decomposes to hexagonal chalcocite and high-temperature digenite above 93°C, whereas Cook (1972) found that djurleite transformed to a tetragonal form above 93°C. This tetragonal form, first described by Djurle (1958) has been encountered for compositions $Cu_{1.96}S$ (Janosi, 1964) and Cu_2S (Skinner *et al.*, 1964; Serebryanaya, 1966) and has sulfur atoms in approximately cubic close-packing.

As chalcocite and djurleite are often finely intergrown (Evans, 1971), and transformations from chalcocite to djurleite have been reported (Cook *et al.*, 1970), the relationship between these two phases needs further investigation. Transmission electron microscopy provides a method of studying such intergrowths and observing transformations in these materials.

Results

Crystals of chalcocite from Carn Brae, St. Just, Penzance, and St. Ives in Cornwall, and Bristol Mine, Connecticut, were examined in the electron microscope. In all samples observations made on a large number of untransformed grains indicated that both chalcocite and djurleite were present and that djurleite was often the more abundant phase. Bulk compositional analysis of the starting material was not made.

Electron diffraction patterns showed that twinning was common in both phases, and to illustrate this and to identify the phase present, grains were sought in an orientation such that the diffraction patterns contained the a^* and c^* axes of the hexagonal subcell, *i.e.*, the beam was parallel to the [010] direction in the grain. Such reciprocal lattice sections are used throughout this investigation.

Interpretation of electron diffraction patterns. Both low-chalcocite and djurleite are simple superstructures of the high-chalcocite hexagonal subcell, and this relationship gives rise to three possible orientations of the low-temperature orthorhombic forms relative to the subcell. These three orientations are related by 60° rotations about the hexagonal c axis. Figures 1a and b show two of these orientations for the chalcocite superstructure together with a^*c^* reciprocal lattice sections obtained in each case. The third orientation of the superstructure produces a diffraction pattern as for Figure 1b. Figures 2a and b show the similar situation for the djurleite superstructure with the two different a^*c^* reciprocal lattice sections.

The diffraction patterns from untransformed grains in various orientations are consistent with the above interpretation of different twin orientations in both chalcocite and djurleite. The twinning in djurleite is the same as that described by Takeda *et al.* (1967b).

Transformation behavior. Crystal grains which showed only a single phase were selected for the heating experiments. Increasing the temperature by beam heating causes the spontaneous disappearance of the superstructure spots in both chalcocite and djurleite, leaving the high-chalcocite subcell reflections (Fig. 3a). On slow cooling, spots appear at the reciprocal lattice points $\langle \frac{1}{2}\,\frac{1}{2}\,0 \rangle$, indicating the for-

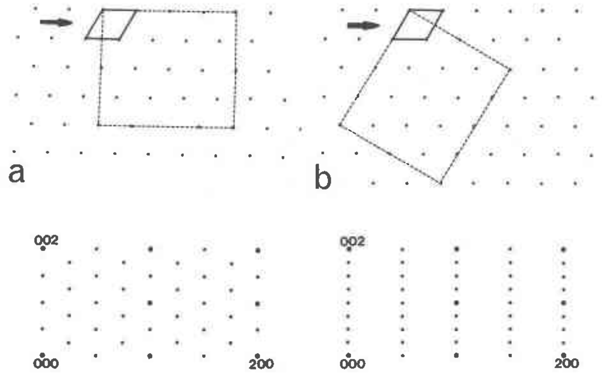

Fig. 2 a,b. The equivalent situation to Fig. 1 for the djurleite superstructure.

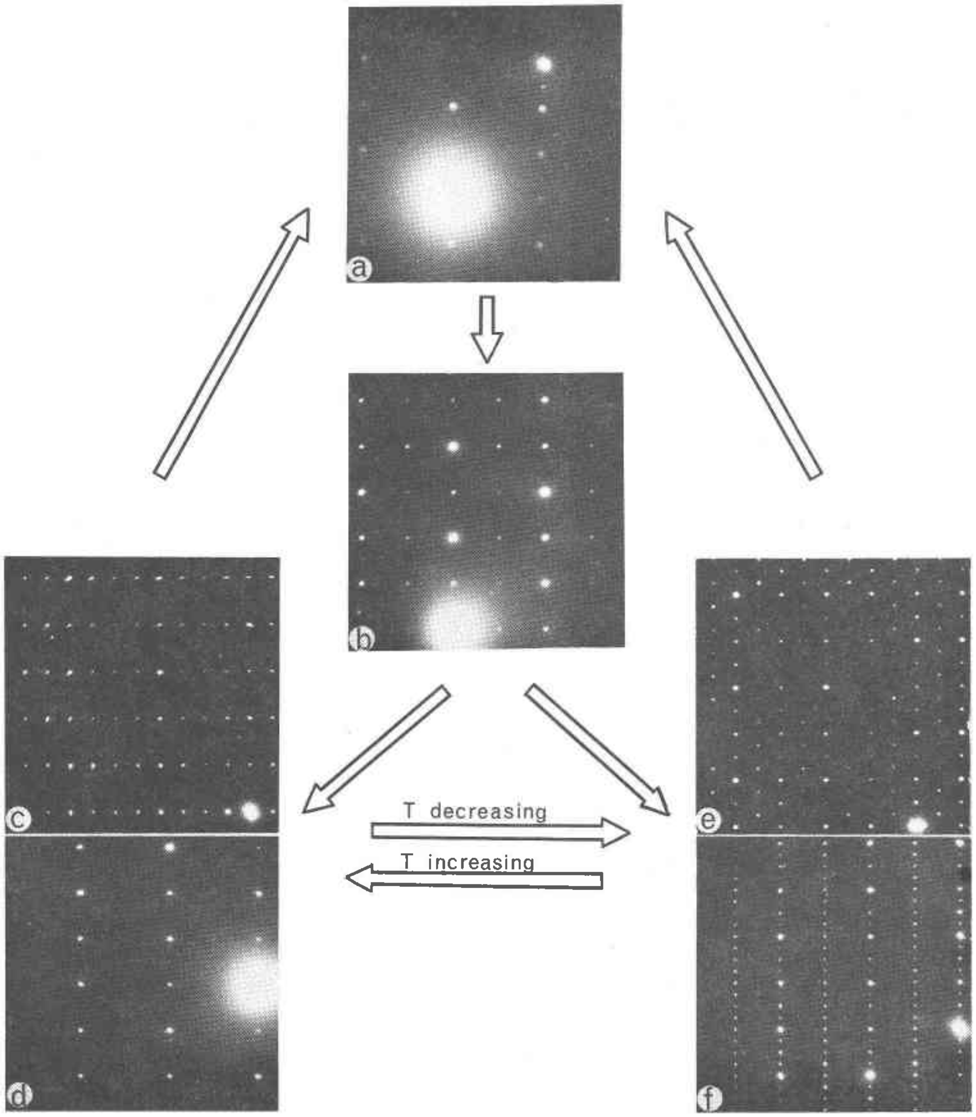

Fig. 3. The sequence of transformations observed in an a^*c^* diffraction pattern. (a) The high-temperature chalcocite subcell. (b) The intermediate $2a_h \times 1c_h$ superstructure. (c,d) Twinned orientations of the chalcocite superstructure. (e,f) Twinned orientations of the djurleite superstructure. The key to these diffraction patterns is in Figs. 1,2. The arrows show a cooling and reheating cycle, with equal possibility of forming the chalcocite or djurleite superstructure and the reversible chalcocite to djurleite transformation.

mation of a $2a \times 1c$ hexagonal superlattice (Fig. 3b). This diffracted intensity appears continuously and changes as a function of temperature, characteristic of a second-order transformation. On further cooling the superstructure reflections corresponding to either chalcocite or djurleite appear, irrespective of the superstructure of the original untransformed grain. This transformation occurs as a distinct discontinuity. Repeating the heating and cooling cycle shows that the end product of the transformation sequence has an approximately equal likelihood of being the chalcocite or the djurleite superstructure, although the region from which diffracted beams are collected is the same in each case. (The selected area aperture used collects diffracted intensity from a circular area approximately 1000 Å in diameter.) Commonly the djurleite superstructure forms from the chalcocite superstructure as the grain cools and transforms back to the chalcocite superstructure with slight heating. This transformation behavior is illustrated in Figure 3, which shows the sequence of a^*c^* diffraction patterns seen in a single grain cycled through the transformations.

The transformation cycle could be repeated many times, and has been observed in many grains with various orientations. In each case the result has been the same, with the chalcocite and djurleite superstructures forming with approximately equal probability as high-chalcocite is cooled. The transformation from the chalcocite to the djurleite superstructure often observed on cooling suggests that the latter is the more stable form at room temperature. The tetragonal form (Janosi, 1964; Skinner *et al.*, 1964) was not encountered in this study, evidently because the transformation to the tetragonal form is sluggish (Cook, 1972).

At these temperatures there is no evidence for any bulk compositional changes in the grains due to sulfur loss, and the reversibility of the transformations indicates an isochemical process.

Discussion

The transformation sequence clearly implies that the chalcocite and djurleite superstructures can exist at the same chemical composition. This conclusion requires a reexamination of the relationship between these two phases, and the compositional variation possible in both the disordered high-chalcocite structure and the ordered structures formed on cooling. At low temperatures the maximum copper deficiency of an ordered structure based on the high-chalcocite structure is about $Cu_{1.93}S$ (Potter, 1974) and the compositional range extends to stoichiometric Cu_2S. Within this field a number of phases, all superstructures of a high-chalcocite subcell, are known to exist. The two most common phases are djurleite, with a composition range from about $Cu_{1.93}S$ to $Cu_{1.97}S$, and chalcocite, which is apparently restricted to compositions very close to Cu_2S. Cook *et al.* (1970) report a $4a_h \times 2c_h$ hexagonal phase with composition Cu_xS ($1.96 \geq x \geq 1.8$), and Eliseev *et al.* (1964) have described a hexagonal phase with a $3a_h \times 2c_h$ superstructure and a composition around $Cu_{1.91}S$. A djurleite-like phase with a Cu-rich composition (protodjurleite) has also been reported (Mulder, 1973), but is metastable with respect to chalcocite and djurleite.

Clearly, in a system where there are so many possible ordering arrangements of disordered high-chalcocite, low-temperature phase relationships are complicated by the narrow free-energy range over which they must exist and therefore by the kinetics of the transformations between such ordered phases.

In contrast, disordered high-chalcocite is generally considered to have a very narrow compositional field near Cu_2S (Roseboom, 1966). The stability field widens with decreasing temperature, although different investigators disagree on the estimated deviations from stoichiometry. Roseboom (1966) detected no compositional deviation at 180°C, but Wagner and Wagner (1957) found that at 400°C chalcocite coexisting with digenite of composition $Cu_{1.8}S$ can have a Cu:S ratio of less than 1.93.

Although the present study does not contribute to the question of the compositional variations which may be possible in the ordered forms, nor to the likelihood that djurleite may be more stable at a slightly copper-deficient composition, it does conclude that the chalcocite and djurleite superstructures are different ordering schemes of high-chalcocite and that they need not be associated with a difference in composition.

This conclusion implies a free-energy difference between the two superstructures, and hence one form has the lower free energy at room temperature. The electron diffraction evidence suggests that the djurleite superstructure may be the more stable. This is supported by the fact that, in a sequence of polymorphic transformations involving superlattice formation with a decrease in temperature, the largest superlattice would have the lowest symmetry and would generally be the most stable form. On this basis, as the true symmetry of chalcocite is monoclinic, djurleite should be monoclinic as well. Electron diffraction patterns of twinned crystals do in fact show a relative displacement of superstructure spots from each twin member, indicating a symmetry less than orthorhombic. This is compatible with the results of Takeda *et al.* (1967a) and the monoclinic space group $P2_1/n$. Cook *et al.* (1970) have reported that over a two-year period a chalcocite needle was converted to djurleite, but assumed a compositional change due to oxidation; my results suggest that this may occur isochemically.

The free-energy difference between chalcocite and djurleite at room temperatures would be small, and hence transformations from chalcocite to djurleite in bulk samples would be very slow. This could well account for the difficulty in synthesising djurleite in short-term experiments (Roseboom, 1966). The observation of the chalcocite to djurleite transformation in the electron microscope may be possible because of the slightly elevated temperature in the grain and enhanced nucleation in the very thin specimens used.

Ordering experiments in high-chalcocite have been carried out by Mulder (1973) who found that on cooling, a metastable djurleite-like phase, termed protodjurleite, formed before transformation to a mixture of low-chalcocite and djurleite. Protodjurleite may be related to the $2a \times 1c$ intermediate phase reported here.

The problem of describing the behavior of a system in which a number of possible ordered phases exists can only be resolved in terms of an analysis of the mechanism and kinetics of the transformations involved. A detailed analysis along these lines must await the determination of the structures and hence the nature of the ordering processes in the djurleite solid solution.

II: The transformation behaviour of digenite and anilite

Both digenite and anilite have structures based on a cubic close-packed network of sulfur atoms, with the cations ordered in the tetrahedral sites. Above about 75°C the cations are disordered and a solid solution field of high-digenite exists, with a broad compositional range increasing with temperature (Roseboom, 1966; Rau, 1966). The structure is face-centered cubic with $a_c = 5.56$ Å.

Morimoto and Gyobu (1971) distinguish natural digenite (sensu stricto) which has a stability field in the Cu–Fe–S system with Fe between 0.4 and 1.6 atomic percent, and the digenite-type solid solution in the system Cu–S which is metastable relative to anilite at room temperatures (Morimoto and Koto, 1970). Digenite (sensu stricto) quenched from above 75°C has a cubic superstructure of period $5a_c$ with the characteristic that only reflections with indices $(10m \pm l, 10n \pm l, l)$ are present where m and n are integers. This has been interpreted (Donnay *et al.*, 1958; Morimoto and Kullerud, 1966) in terms of four-component multiple twins of a rhombohedral cell with the four triad axes parallel to the triads of the cube. Over a period of time the missing reflections appear, although the relationship between this modified $5a$ type structure and the twinning hypothesis has not been made clear.

Digenite compositions synthesized in the Cu–S system form similar superstructural phases on cooling below 75°C with periodicities varying from $5a_c$ to $6a_c$ depending on composition (Morimoto and Koto, 1970). At room temperature these break down to anilite and djurleite.

Anilite is orthorhombic, space group *Pnma* with $a = 7.89$, $b = 7.84$, $c = 11.01$ Å. As the high-temperature digenite subcell is only slightly distorted (Koto and Morimoto, 1970) anilite can be considered as a superstructure of high-digenite with $a \approx b = \sqrt{2}a_c$, $c = 2a_c$, and will be referred to in this way.

Results

Digenite from Butte, Montana, has been used in this investigation. Untransformed grains showed the $5a$ type superstructure consistent with that reported for natural digenite. On heating, the superstructure spots disappear, leaving the high-digenite subcell (Fig. 4a). The ordering behavior observed on recooling takes place in stages, as demonstrated by the evolution of the diffraction patterns. Figure 4a–d shows the series of diffraction patterns obtained with decreasing temperature.

The onset of ordering is marked by the appearance of satellite reflections about the main subcell reflections (Fig. 4b). In reciprocal space the position of these satellites can be described by the reciprocal lattice vectors $\langle \frac{1}{5}\,\frac{1}{5}\,\frac{1}{5} \rangle$, and indicates the formation of a structure modulated along the [111] directions of the high-temperature cell. These satellites are at first

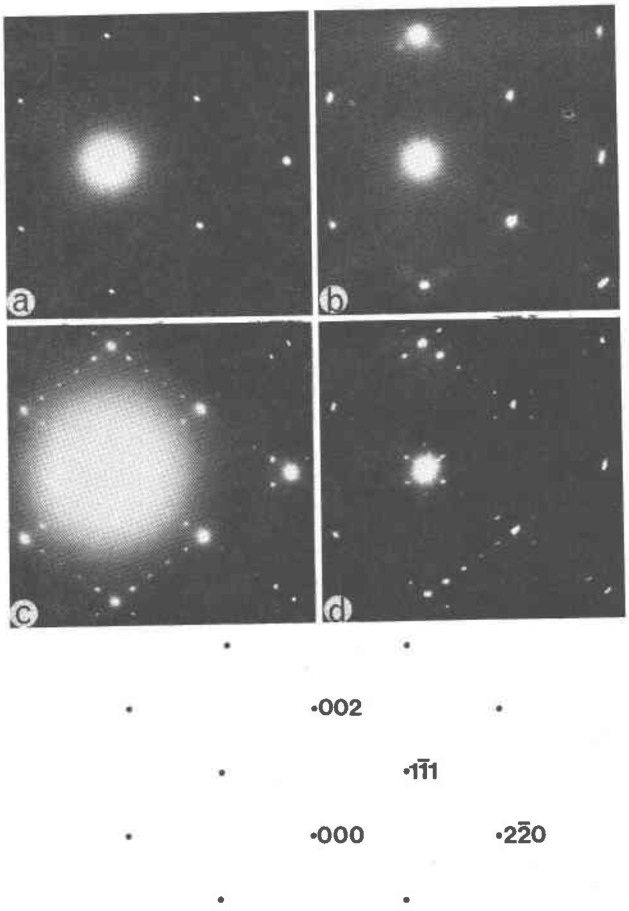

Fig. 4. A series of [110] diffraction patterns showing the transformation sequence in natural digenite. (a) The high-temperature digenite structure. (b) The satellites at $\langle \frac{1}{5}\,\frac{1}{5}\,\frac{1}{5} \rangle$. (c) Development of $5a$ superstructure spots along [111]. (d) The full $5a$ superstructure.

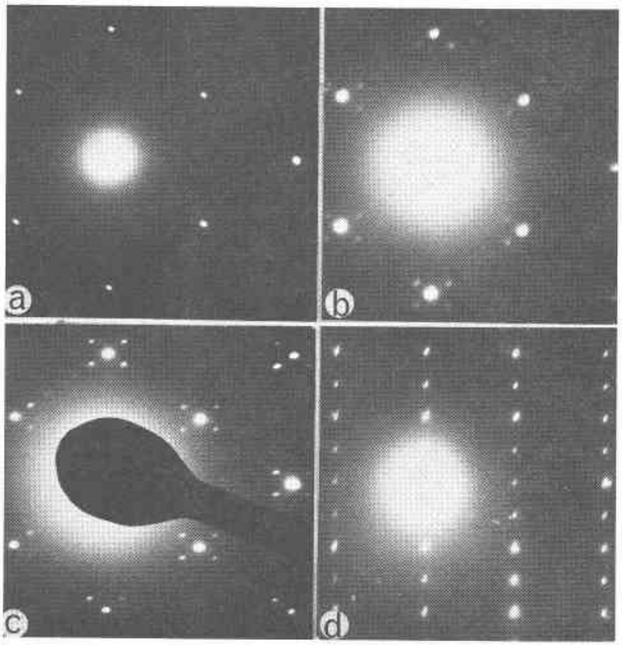

Fig. 5. A series of [110] diffraction patterns showing the transformation sequence in heat-treated digenite. (a) The high-temperature digenite structure. (b) The satellites at $\langle \tfrac{1}{6}\,\tfrac{1}{6}\,\tfrac{1}{6} \rangle$. (c) Development of 6*a* superstructure spots along [111]. (d) The anilite superstructure.

weak but become quite strong prior to the appearance of the additional 5*a* superlattice reflections along the [111] directions (Fig. 4c). The twinning hypothesis requires that the superlattice reflections along the four [111] directions originate from different regions of the crystal, the individual regions having rhombohedral symmetry. Dark-field observations using the different superlattice spots did not show the presence of any twinning, and if individual domains of rhombohedral symmetry exist they would have to be on a scale of less than about 15 Å. In all cases the intensity at point $\langle \tfrac{1}{5}\,\tfrac{1}{5}\,\tfrac{1}{5} \rangle$ develops simultaneously along the four [111] directions, inconsistent with an interpretation based on twinning. Further cooling produces the full suite of 5*a* superstructure reflections which appear after several minutes (Fig. 4d).

This ordering process is continuous in the sense that the appearance of the reflections is gradual and their intensity is a smooth function of time and temperature. The process of disordering and ordering could be repeated indefinitely with the same results.

If the disordered state is maintained for a period of time and the edge of the grain under observation is kept above the ordering temperature, an irreversible process takes place in the hottest part of the grain. In most cases there is no change in the appearance of the grain and only rarely is there any evidence (such as corroded grain boundaries) of any sulfur loss. On slowly recooling such a heat-treated grain, satellite reflections again appear about the subcell spots, but their position is now described by reciprocal-lattice vectors $\langle \tfrac{1}{6}\,\tfrac{1}{6}\,\tfrac{1}{6} \rangle$ (Fig. 5b). Further cooling produces the additional 6*a* superlattice reflections along [111] (Fig. 5c), but this process is often interrupted by the abrupt appearance of a superstructure consistent with that of anilite (Fig. 5d). On reheating, the anilite supercell disorders without the appearance of the 6*a* reflections, demonstrating that the behavior leading to the formation of the 6*a* modulation along [111] is metastable. Rapid cooling from the disordered form also results in the formation of the anilite superstructure by a discontinuous mechanism. This is also consistent with the interpretation that the formation of the 6*a* modulation is metastable behavior.

This sequence of transformations has been observed in many different grains, and shows that the ordering behavior in untreated natural digenite involves a series of continuous events leading to the formation of a 5*a* superlattice. Heat treatment of the grain above the ordering temperature results in a change of behavior such that, on recooling, the continuous ordering process leads to a 6*a* modulation along [111] which gives way to the formation, by a discontinuous event, of the more stable anilite structure.

Discussion

My observations on the ordering process in digenite indicate that the twinning mechanism which has been proposed for the transition from the high-temperature form to the 5*a* type structure is not tenable. A similar conclusion has been drawn for the formation of intermediate bornite (Allais, 1968; Putnis and Grace, 1976) for which a similar twinning hypothesis had been proposed.

The evolution of the diffraction pattern implies that several discrete rate-controlling processes are involved in the mechanism of the transformation. The development of satellites about the subcell reflections may be ascribed to a spinodal clustering mechanism for vacant sites, which at this stage would be statistically distributed. The subsequent development of additional superstructure spots along [111] then accords with further local ordering of vacancies and tetrahedral sites. Morimoto and Gyobu (1971) have demonstrated that the presence of iron stabilizes the structure, and the full development of the 5*a* superlattice may be due to the differentiation of copper and iron atoms over specific sites.

The irreversible process resulting from heat treatment of the digenite is probably due to the differential diffusion of iron atoms across a temperature gradient in the grain. Such a loss of iron from the area being heated is consistent with the formation of the 6*a* superlattice spots along [111], as an iron-free composition equivalent to natural digenite could form a 6*a* superstructure (Morimoto and Koto, 1970). The differential diffusion of iron has also been observed in the breakdown of bornite (Grace and Putnis, 1976), in which iron diffuses away from the heat source forming structures with compositions along the bornite–digenite join.

Transformations in this heat-treated digenite well illustrate the general principles of behavior in a phase transformation. The high-temperature disordered structure has a stability field above about 75°C (Morimoto and Koto, 1970), and the anilite superstructure is apparently the stable phase below this temperature. The transformation to the anilite structure appears to be first-order. If the transformation is carried out irreversibly (in the thermodynamic sense) the high-temperature form is retained below the transformation temperature, and alternative metastable second-order processes may take place to lower the free energy of the system. In this case the metastable behavior involves the formation of the 6*a* superlattice spots.

Since the sequence of processes leading to a 6*a* type superstructure is clearly metastable relative to the formation of the anilite structure, the very similar behavior of natural digenite may also be metastable. The behavior of natural digenite is however in some way modified by the presence of iron in that the 5*a* superstructure is retained at room temperatures. Whether this structure is stable in the strict sense or whether it is a 'frozen-in' metastable phase unable to transform to a more stable phase due to kinetic constraints is as yet unanswered, although the pattern of behavior suggests that the latter may be the case. The analogous formation of modulated structures of different periodicities along the entire digenite–bornite join (Morimoto and Kullerud, 1966) should also be reconsidered in terms of possible metastability.

The composition of anilite is not known with precision, as analyses have been carried out on two-phase assemblages (Morimoto *et al.*, 1969; Morimoto and Koto, 1970). The present work shows that the 6*a* type metastable structure is isochemical with the anilite structure, and according to Morimoto and Koto (1970) the 6*a* type is limited to a composition of $Cu_{1.80}S$. These authors have also noted a transformation from the 6*a* type to anilite, and it is therefore possible that the anilite superstructure may exist over a wider range of composition than that implied by the nominal formula, Cu_7S_4.

Acknowledgments

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