DISORDER IN THE MINERAL BORNITE, Cu_5FeS_4

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ABSTRACT

X-ray data from a single crystal of Bristol, Connecticut, bornite shows that bornite is a pseudocubic orthorhombic crystal with the following cell dimensions.

$$a = 21.94 \text{ Å}$$
$$b = 21.94 \text{ Å}$$
$$c = 10.97 \text{ Å}$$

X-ray, thermal, and electrical evidences indicate that bornite can exist in both a low- and a high-temperature form, and that the structural difference between the forms is one of order-disorder. When thermally induced, the disorder first reaches a measurable magnitude at 170° C. and the critical temperature of complete disorder is reached at 220° C. By quenching in cold water the high or disordered form can be retained, but if cooled slowly from the elevated temperature the low form is regained.

The high-temperature form is cubic with a cell edge of 10.97 Å and belongs to one of the space groups: $F\bar{4}3m$, $F43$, $Fm3m$.

INTRODUCTION

At a recent meeting of the Crystallographic Society of America the author presented a paper on "Disorder in Bornite, Cu_5FeS_4." Shortly thereafter it was called to his attention by Professor George Tunell that there was a paper already in press on "The Symmetry and Crystal System of Bornite" by G. Tunell and C. E. Adams [1] in which some of the data seemed to be in disagreement with that reported by the author. Because of this disparity it seemed advisable to present a more detailed account of the study of disorder in this mineral at the present time.

HISTORICAL BACKGROUND

Bornite usually occurs as a hypogene mineral intimately associated with chalcocite (Cu_2S) and chalcopyrite ($CuFeS_2$) [2]. Many intergrowths of these minerals as well as intergrowths of tetrahedrite ($Cu_{12}Sb_4S_{13}$) and klaprothite ($Cu_6Bi_4S_9$) in bornite have been described in the literature [3, 4, 5, 6, 7, 8, 9] and the conclusion has invariably been reached that the intergrowth textures found are the result of the unmixing of these different minerals from bornite. In many instances heat-treating experiments were conducted to demonstrate that the exsolved plates could be redissolved in the bornite host at elevated temperatures and that subsequent exsolution would occur under the proper cooling or annealing

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conditions. G. M. Schwartz [4] showed that the chalcopyrite lamellae in a naturally occurring bornite sample would dissolve into the bornite when the temperature was raised to 475° C. and that by quenching in cold water the solid solution could be retained at room temperature. R. Latsky [6] demonstrated that exsolution occurs in bornite at a lower temperature than that at which dissolving takes place, and that a sample of bornite in which the lamellae of chalcopyrite have been completely dissolved and "quenched in" will, when held at 220° C. for seventy-two hours, exhibit exsolution blebs and minute specks of chalcopyrite. A. B. Edwards [7] was able to redissolve the lath shaped intergrowths of tetrahedrite existing in the bornite from Pine Valley, Australia, at a temperature between 250° and 285° C.

Thus it has been clearly demonstrated that at elevated temperatures the structure of bornite will accept additional iron and copper atoms, and will permit the diffusion of these atoms through it, and, that at lower temperatures there is a return to stoichiometric proportions by the expelling of any excess atoms in the form of exsolved material. Therefore, it might be expected that self diffusion may also occur in bornite at these elevated temperatures, and, as M. J. Buerger [10] has pointed out, "the process of ordinary self diffusion in a crystal resembles that of substitutional disorder."

A determination of the crystal structure of bornite was attempted but not completed by D. Lundqvist and A. Westgren [11] from powder photographs of synthetically prepared material. They found bornite to be cubic, space group *Fd*3*m*, with a cell edge of 10.93 Å. The structure they proposed is based upon sulfur atoms arranged in cubic close packing (face-centered cubic) with the metal atoms placed in the interstices. Several distributions of metal atoms were suggested but none of them could be definitely confirmed by *x*-ray intensity checks.

More recently G. Tunell and C. E. Adams [1] have obtained rotating crystal and Weissenberg data with a single crystal of bornite from the Carn Brea Mine, Illogan, Cornwall, and found the true cell edge to be 32.81 Å. By adopting a cubic cell of edge length 5.47 Å with the sulfur atoms at the origin and at the face centers (close packed cubic) they found reasonable intensity checks for all of the spots of strong and medium intensity and some of the spots of weak intensity when four copper or iron atoms were statistically distributed over the positions $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, and two copper or iron atoms were statistically distributed over the positions $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, the total number of copper and iron atoms averaging five per cell and one per cell respectively. However, a considerable number of spots of weak intensity were not accounted for by this approximate arrangement.

MATERIAL

Material for the present investigation was obtained from the Harvard University mineralogy collection through the courtesy of Professor Clifford Frondel and was selected for *x*-ray, thermal, and electrical investigation only after polished section examination showed the material to be relatively homogeneous and free from exsolved or included extraneous matter. Only one locality, that of Bristol, Connecticut, provided single crystals of useful dimensions and quality; some additional, fairly pure bornite from Butte, Montana, was selected.

X-RAY INVESTIGATION

A complete diffraction record was taken of a single crystal from Bristol, by the rotating-crystal and Weissenberg methods. This record indicates that the Bristol bornite in its low-temperature form is a pseudo-cubic orthorhombic crystal with the following cell dimensions:

$a = 21.94$ Å
$b = 21.94$ Å
$c = 10.97$ Å

The *a* axis and the *c* axis rotation photographs are shown in Figs. 1*a*, and 1*b*, respectively. The rotation photograph of the *a* axis appears to be identical with that of the *b* axis, but a closer study of the upper levels of the *c* axis by the Weissenberg method indicates that the crystal does not possess a four-fold axis, but is based upon a primitive orthogonal cell. Due to the fortuitous lack of reflections on the zero and first levels, the presence or absence of glide planes and screw axes could not be determined with certainty by systematic extinctions.

The identical crystal used in obtaining the record described above was heated in a sealed evacuated pyrex tube to 225° C. and quenched in ice water. The crystal was mounted and oriented parallel to an axis previously identified in the low-temperature form as the *a* axis and a rotating crystal photograph was taken (Fig. 1*c*). From this photograph and the supporting Weissenberg photographs it is evident that through heat treatment the crystal becomes isometric with a cell edge of 10.97 Å. The diffraction symbol is *m3mF*— and hence there are three possible space groups under which the symmetry of the heat treated crystal may be classified: $F\bar{4}3m$; $F43$; and $Fm3m$.

Structurally the difference between the low-temperature and high temperature form of the Bristol bornite lies in the presence of a superstructure in the low form. Supported by the solid solution data in the literature as outlined above, and by the thermal and electrical evidences described below, this would indicate that self diffusion and subsequent

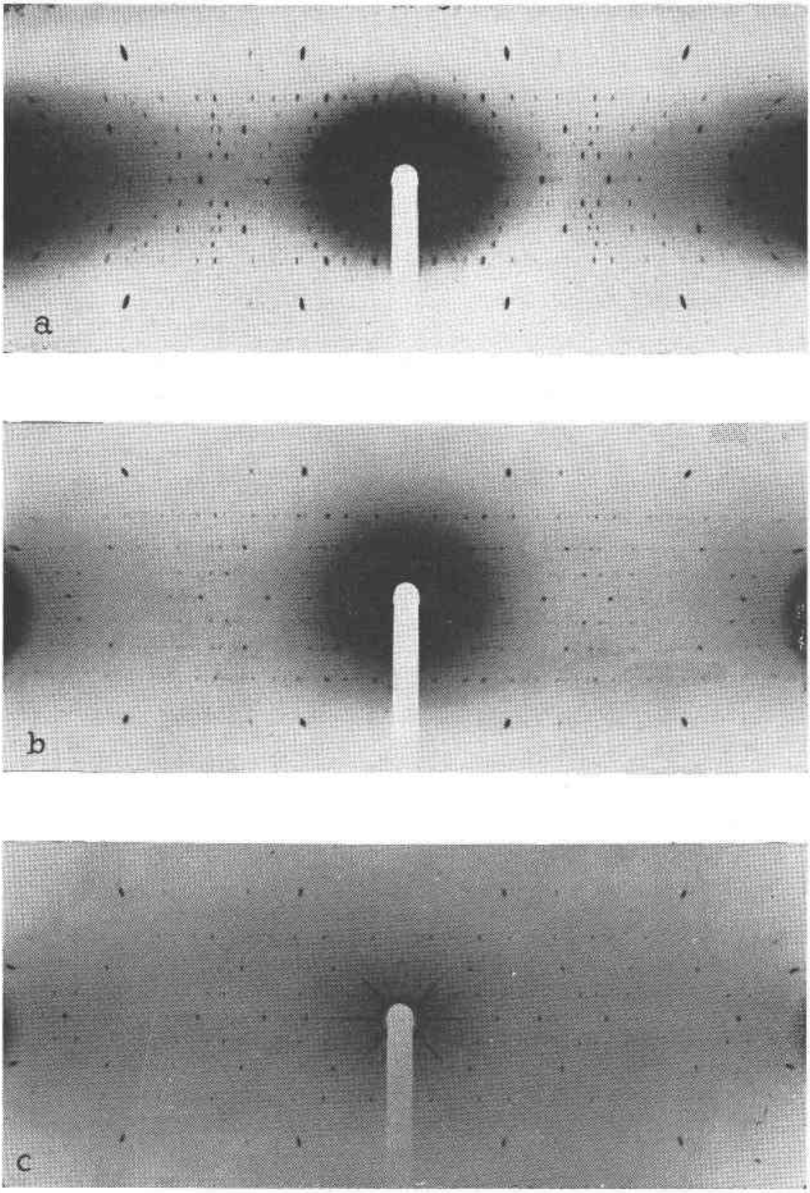

FIG. 1. Rotating-crystal photographs of bornite from Bristol, Connecticut, made with cobalt Kα radiation (Iron filter). (*a*) Rotated about the *a* axis. (*b*) Rotated about the *c* axis. (*c*) Identical rotation as (*a*) above only after crystal had been heated to 225° C. and quenched.

substitutional disorder is occurring at the elevated temperature. That the difference between the high and low forms is just one of simple substitutional disorder between the iron and copper atoms is unlikely. If this were the case then all the reflections that disappear as a result of the heat treatment, and which constitute the superstructure reflections, would owe their intensity to the difference in scattering power between iron and copper atoms. It would normally be expected that these reflections would all be very weak, as the difference in scattering factor between iron and copper is only 10% at low Bragg angles increasing to 14% at higher angles. Such strong spots as those that exist on the third and fifth levels of the ordered crystal are difficult to justify in view of this small difference in scattering power. Therefore, either slight shifts of atomic parameters within the cell might also be expected, or vacant sites or interstitial spaces are also involved in the disordering.

Lundqvist and Westgren [11] have already suggested the possibility that the metal atoms are distributed at random throughout the interstices of the close packed sulfur structure. However, as the cell edge of the high-temperature form has been reduced to 10.97 Å, rather than to 5.49 Å the edge length of a single close packed sulfur cell, either a selected number of interstitial sites must be involved or a selected number of atoms are involved while the others remain in definite positions. An example of the latter case would be realized if the iron atoms remained fixed in position while the copper atoms are statistically distributed throughout the remaining interstices.

THERMAL INVESTIGATION

As crystals in their disordered form are at a higher energy level than when in their ordered form, the change of bornite from ordered to disordered with increasing temperature is accompanied by a gain in energy that is evidenced by the absorption of heat by the crystal from its surroundings. Thus the differential thermal analyzer record for both Bristol and Butte bornite showed a definite endothermic saw-tooth shaped peak that would be expected to accompany disorder (Fig. 2). The deflection of the peak first starts at about 170° C. and is completed by 220° C. At 260° C. a rather broad exothermic peak is produced. From the presence of sulfur dioxide fumes and from the appearance on the *x*-ray powder record of the product of additional reflections representing new phases, it is evident that the exothermic peak is due to the dissociation and subsequent oxidation of the sulfide. If the sample is rapidly cooled from a little above 220° C. the endothermic peak is not present when the run is repeated. However, if the sample is cooled slowly from 220° C. the run can be repeated with the record being reproduced identically except for a slight loss in the amplitude of the endothermic peak.

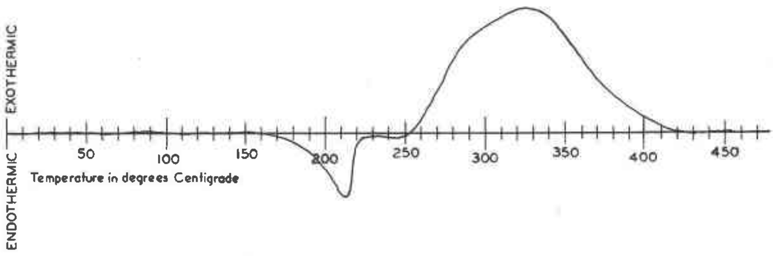

FIG. 2. Thermograph of bornite from Bristol, Connecticut. Recorded during a thermal rise of 12° C. per minute.

RESISTIVITY

Changes in electrical properties can be expected to accompany an order-disorder change [12, 13]. Although marked changes can also be expected in thermoelectric potential, resistivity is the electrical property most amenable to measurement at elevated temperatures. Little blocks of bornite 7 mm. × 1 mm. × 1 mm. were formed on the polishing lap from samples of both Bristol and Butte material. Resistivity measurements were made on these blocks over a range of temperature from 30° to 260° by measuring the voltage drop across a constant section of the block with a potentiometer while the current through the block was maintained at a constant level. A plot of temperature versus resistance (Fig. 3) exhibits a smooth curve of decreasing resistance with increasing temperature until 170° C. is reached, thus indicating that bornite throughout this temperature range behaves as a semi-conductor [14]. At 170° there is an increase in the rate of decrease of the resistance, smoothing out again after 220° C. is reached.

REVERSIBILITY

The ability for the disordered compound to reorder upon slow cooling was indicated by the reproduceability of the thermal record after slow cooling as described above. This reversibility has been verified by means of *x*-ray powder photographs. On the complete powder diffraction record, when taken with cobalt radiation, there are only two superstructure lines, 362 and 347, that are of sufficient intensity to show above the background. These two reflections are missing from the diffraction record of bornite after the powder has been quenched from 225° C. in a manner identical to that described for a single crystal. When the bornite powder

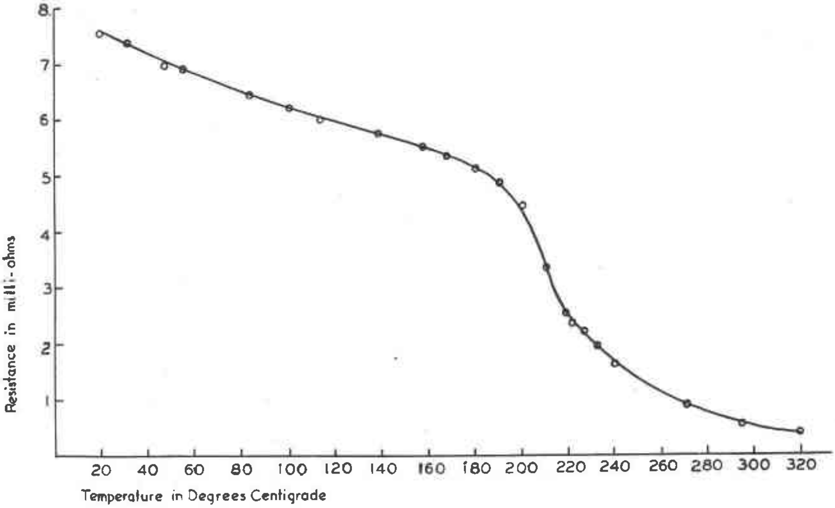

FIG. 3. Resistivity versus temperature of bornite from Butte, Montana. Measurements made across a constant section of material at a constant current of 12 milli-amperes.

in which the disorder has been "quenched in" is reheated to 225° C. and allowed to cool at the rate of 10° C. per hour to room temperature the x-ray powder diffraction record shows the reappearance of the superstructure lines, thus indicating a return to the low temperature form.

SUMMARY

From the results of this investigation it is evident that bornite can exist in at least two structurally different forms, and that the relation between these forms is one of order-disorder of the metal atoms. When thermally induced the disorder reaches observable proportions at 170° C. and the critical point of complete disorder is reached at 220° C. The disorder can be accounted for by one of the following mechanisms:

1. Substitutional disorder between some or all of the metal atoms with slight readjustments of the atomic parameters to account for the changes in the intensities of some of the x-ray reflections.
2. Substitutional disorder between some or all of the metal atoms and some or all of the interstitial openings in the close packed sulfur structure.

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