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THE USE OF ZONE THEORY IN PROBLEMS OF SULFIDE MINERALOGY, PART III; POLYMORPHISM OF Ag_2Te AND Ag_2S

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ABSTRACT

Three polymorphs of Ag_2Te exist between room temperature and the melting point. They are, in the order of increasing temperature: monoclinic, face-centered cubic, and body-centered cubic. The transformation temperature between the face-centered cubic and the body-centered cubic forms increases with a slight stoichiometric excess of Ag. The three polymorphs of Ag_2S are, in order of increasing temperature, monoclinic, body-centered cubic, and face-centered cubic. The transformation temperature between the body-centered cubic and the face-centered cubic forms decreases with a slight stoichiometric excess of Ag. An explanation, based on the relative shapes of the n (e) vs. E curves of the two cubic forms, is suggested to explain the increase of the stability range of the face-centered cubic structure with stoichiometric excess of Ag in both these compounds.

INTRODUCTION

The sulfides, selenides and tellurides of silver and copper have for many years been the subject of countless investigations by mineralogists and solid state workers. Some of the interest stems from the unusual property of combined electronic and ionic conductivity exhibited by these compounds. Of equal and related interest is the fact that each possesses a high-temperature or α-phase which is characterized by either a face-centered or body-centered array of anions, with a random or statistical distribution of the cations in the interstitial sites.

A now-classical structural investigation was conducted by Rahlfs (1935). He showed that the diffraction record of the high-temperature or α modifications of Ag_2S and Ag_2Se could be explained by placing the sulfur or selenium atoms at the nodes of a body-centered cubic lattice, and distributing 1.5 of the 4 silver atoms per cell in the 12(d) positions listed below and the remaining 2.5 silver atoms in the 24(h)+(6b) positions.

	(000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$+			
6(b)	$\frac{1}{2}00$	$0\frac{1}{2}0$	$00\frac{1}{2}$	
12(d)	$\frac{1}{2}0\frac{1}{2}$	$\frac{1}{4}\frac{1}{2}0$	$0\frac{1}{4}\frac{1}{2}$	
	$\frac{1}{2}0\frac{3}{4}$	$\frac{3}{4}\frac{1}{2}0$	$0\frac{3}{4}\frac{1}{2}$	
24(h)	uu0	u$\bar{u}$0	$\bar{u}$u0	$\bar{u}\bar{u}$0
	u0u	u0$\bar{u}$	$\bar{u}$0u	$\bar{u}$0$\bar{u}$
	0uu	0u$\bar{u}$	0$\bar{u}$u	0$\bar{u}\bar{u}$

where $u = \frac{5}{8}$.

Rahlfs further described the high-temperature or α modifications of Ag_2Te, $Cu_{1.8}S$ and Cu_2Se as structures in which the tellurium, selenium or sulfur atoms occupied the corners and face-centers of a cubic cell, and the silver or copper atoms were distributed amongst the octahedral holes, the tetrahedral holes, and the 16-fold positions ($\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$).

More thorough studies on the phase relations in the systems silver-sulfur and silver-tellurium by F. C. Kracek (1946), and by Kracek and Ksanda,* have revealed additional high-temperature phases. For the purposes of the present paper, the terms α and β will be dropped, and the nomenclature utilized by Kracek will be followed. The crystalline phase that can exist in equilibrium with the liquid will be assigned the Roman numeral I. Those phases stable at successively lower temperatures will be assigned numerals of increasing value.

POLYMORPHISM OF Ag_2S

The phase diagram in Fig. 1 shows the temperature range within which each of the three phases of Ag_2S is stable. The effect of stoichiometry on the temperature of phase change should be noted. A stoichiometric deficiency of Ag results in an increase in the temperature of the phase change from Ag_2S-II to Ag_2S-I from $586 \pm 3°$ C. to $622 \pm 3°$ C. A smaller but similar change is shown between Ag_2S-III and Ag_2S-II.

The structure of Ag_2S-III was shown by Frueh (1958) to be monoclinic, based upon a slightly distorted body-centered cubic array of sulfur atoms, with the silver atoms on two different but definite positions. One silver position lies between two sulfurs at 2.49 Å and 2.52 Å; the other between three sulfurs at 2.50 Å, 2.61Å and 2.69 Å.

Ag_2S-II is the same phase referred to previously as α-Ag_2S, and hence has the body-centered cubic structure as determined by Rahlfs and described above.

A face-centered cubic structure for Ag-S-I has been suggested by Djurle (1958). Due to a very high background blackening, only one line of a Debye-Scherrer powder pattern could be seen by that author. However, all the I-modifications (Cu_2S-I, Ag_3CuS_2-I, $Ag_6Cu_4S_5$-I, AgCuS-I) along the "quasi-binary" line Cu_2S- Ag_2S produce a diffraction record which can be indexed on the basis of a face-centered cubic cell with (220) as the most intense reflection. Djurle, assuming isomorphism in all the I-modifications, therefore suggested this same index (220) for the single discernible line of Ag_2S-I. This yields a cubic cell size at 600° C. of $6.269 \pm .02$ Å.

In the present investigation, three lines of *d* spacings, 3.17 Å, 2.24 Å and 1.819 Å, were obtained on a powder diffraction of Ag_2S-I from Kongsberg, Norway, by means of a Unicam high-temperature powder camera,

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* F. C. Kracek and C. J. Ksanda, A paper on the Ag-Te system in preparation, private communication.

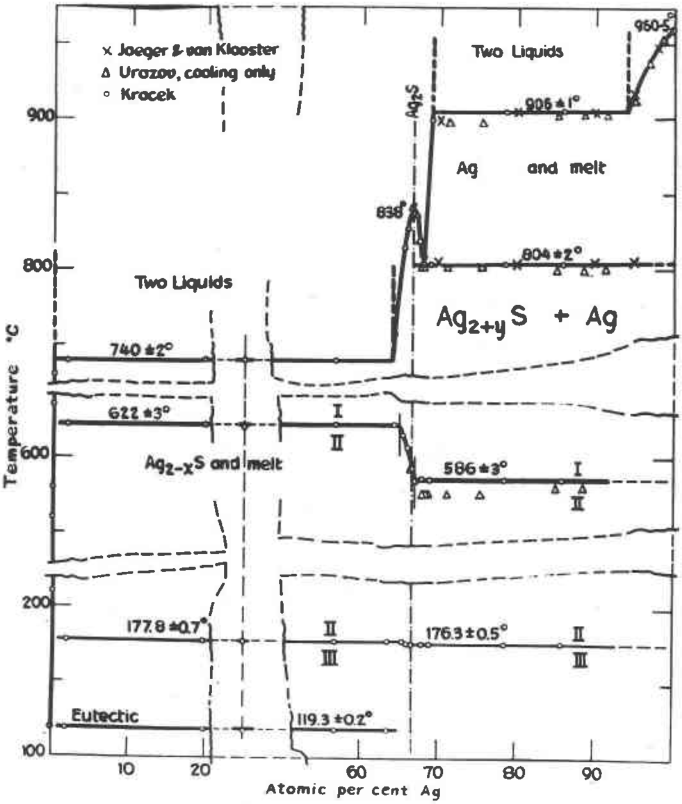

FIG. 1. Phase diagram of the system Ag-S from Kracek (1946).

at 650° C. These can be indexed either as the (100), (110) and (111) planes of a simple cubic cell of $a = 3.17$ Å, or as the (200), (220) and (222) planes of a face-centered cubic cell of $a = 6.34$ Å. Allowing but one formula weight of Ag_2S per unit cell, the calculated density of 12.84 makes the simple cubic cell of edge 3.17 Å an unlikely choice. On the other hand, the face-centered cubic cell of 6.34 Å edge could contain 4 formula weights and have a density of 6.42, which is a little less than the measured density of the room-temperature form (7.2).

POLYMORPHISM OF Ag_2Te

The phase diagram in Fig. 2 shows the temperature range of the stability of the three phases of Ag_2Te. Again, the effect of stoichiometry on the temperature of the phase change should be noted. In the case of the telluride, a stoichiometric deficiency of Ag results in a decrease in the temperature of the phase change Ag_2Te-II to Ag_2Te-I from 802.3° C. to less than 700° C. A similar change is shown between Ag_2Te-III and Ag_2Te-II, where the transition temperature is lowered from 145° on the silver-excess side to 105° on the silver-deficient side.

The monoclinic structure of Ag_2Te-III was determined by Frueh (1959). Some shifting of tellurium as well as of silver atoms is necessary to transform this structure to the face-centered cubic structure of Ag_2Te-II, or α-phase, that was suggested by Rahlfs and described above.

The structure of Ag_2Te-I has not previously been determined. The powder diffraction record from a Unicam high-temperature camera at

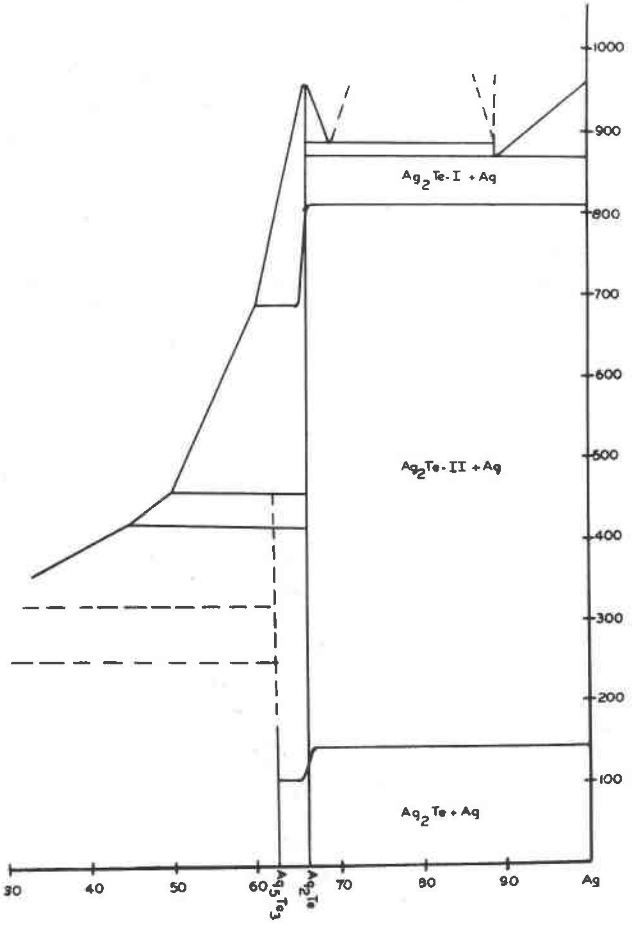

FIG. 2. Tentative phase diagram of the system Ag-Te after Kracek and Ksanda (private communication).

825° C. of a sample of hessite (Ag_2Te) from Bótes, Transylvania, revealed three diffraction lines of about equal intensity above an intense background. These lines had *d* spacings of 3.74 Å, 2.65 Å and 2.16 Å respectively, and could be indexed as the (110), (200) and (211) planes of a body-centered cubic cell of $a = 5.29$ Å.

It would be unreasonable to suppose that a higher-temperature, and hence higher-entropy, form of Ag_2Te would have greater order with respect to the silver positions. Therefore, it is suggested that the structure of Ag_2Te-I is a body-centered arrangement of Te atoms (000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$), with the silver atoms randomly distributed about the interstitial positions. The randomness of the silver positions, rather than a statistical distribution amongst certain select positions, is borne out by the uniformity of the intensity, albeit weak, of the first three powder lines.

It was noted above that a deficiency of silver in Ag_2S increased the stability range of Ag_2S-II at the expense of Ag_2S-I, while a silver deficiency of Ag_2Te increased the range of Ag_2Te-I at the expense of Ag_2Te-II. However, in both cases the deficiency of silver increases the range of the body-centered phase, while a silver excess favors the face-centered phase.

In seeking a structural explanation for this phenomenon, one would expect that, as the cations are distributed in the interstices of the anion structure, the structure with the greater pore space would be favored when an excess of cations is present. This, however, does not seem to be the case, for the face-centered cell is more efficiently packed, having a pore space of only 26%, while the body-centered cell has a pore space of 32%. Nor is it likely that a treatment based upon packing of spheres and filling of holes would be valid for crystals as far from ideally ionic as Ag_2S and Ag_2Te.

A possible explanation of the phenomenon lies in a semi-quantitative interpretation of the possible band structure of the different phases. Of most interest is the Brillouin zone whose boundaries lie in the vicinity of the Fermi level and delimit the valence band. This particular zone has been referred to recently by Junod (1959) as the Jones zone. If we assume that all the outer-shell electrons contribute to the valence band, then the electron-to-atom ratio of the stoichiometric compounds of Ag_2S and Ag_2Te will be 8/3 or 2.67. The most intense line on the diffraction record of the face-centered phases is always the (220) reflection. The volume of the zone in *k* space bounded by the dodecahedron comprising this form in terms of electron-to-atom ratio is exactly 8/3.

The band structure of the body-centered phase of Ag_2S has been investigated by Junod (1959) who found that the cube bounded by the (200) form would have a volume of 8/3 electrons to atoms. If this form alone determined the Jones zone, Ag_2S-II would be a semiconductor. As

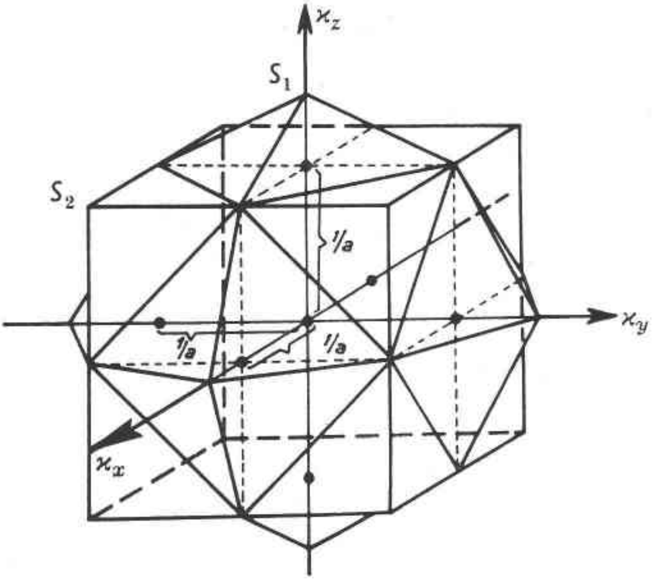

FIG. 3. "Jones" zone of Ag_2S-II, from Junod (1959).

this is in contradiction to observed electrical properties, Junod suggests that there is some overlap, and that the true Jones zone must be constructed with the help of the (200) and (211) forms (Fig. 3).

Because a dodecahedron more closely approaches the shape of a sphere than does a cube, the Fermi body will more quickly assume a spherical shape as it recedes from the zone boundary, and the slope of the N(e) vs. E curve in the vicinity of the zone boundary will be much steeper for the face-centered cubic cell than for the body-centered structure. The effect of the overlap in the body-centered phase will further extend the curve to include more high-energy states. The approximation of these curves is illustrated in Fig 4.

A deficiency of silver in either Ag_2S or Ag_2Te will result in a deficiency of electrons in the valence band. The presence of the excess anions will serve to extend the framework of the solid, while the holes, in the form of Schottky defects, will be distributed throughout the structure. These defects or holes can be considered as atoms that contribute *no* valence electrons. Hence, the electron-to-atom ratio of the solid will diminish. With a reasoning similar to that used by Jones (1937) to explain the phase boundaries in the Hume-Rothery or electron phases of intermetallic compounds, we can see that the removal of a given number of electrons from under the curve of gentler slope will result in a greater lowering of the enegy of the electrons at the top of the band than if an equal number were removed from under the curve of steeper slope.

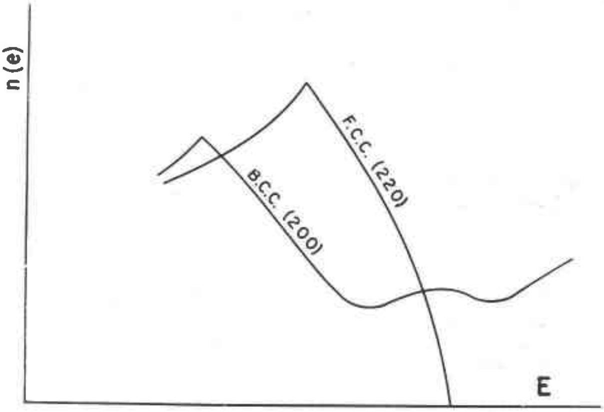

FIG. 4. Approximate n(e) vs E cirve for face-centered and body-centered cubic structures.

Thus, because more electrons are contained at a lower energy level in the body-centered phase when there is a silver deficiency, the stable range of this phase is increased at the expense of the face-centered phase.

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