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CONCERNING THE α-AsS ⇄ REALGAR INVERSION

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ABSTRACT

The temperature of the α-AsS ⇄ realgar inversion is composition sensitive, occurring at 239 ± 3°C in the presence of As, at 252 ± 2°C for AsS prepared from a stoichiometric mix of As and S, and at 263 ± 3°C in the presence of As_2S_3 when vapour is present. The high-temperature phase (α-AsS) is monoclinic, $a = 9.92 \pm 0.03$, $b = 9.48 \pm 0.02$, $c = 8.91 \pm 0.04$ Å, $\beta = 101°50' \pm 15'$, Z = 16. The diffraction symbol is C^*/c.

INTRODUCTION

Realgar, β-AsS, is relatively common and widely distributed in ores. Not until recently, however, was its high-temperature structural modification, α-AsS, definitely identified as a mineral (Clark 1970), and, in fact, the existence of a high-temperature synthetic phase was not known with certainty until it was identified by Strathdee & Pidgeon (1961). The inversion temperature was reported to be 256±5°C (Hall 1966) or 252±2°C (Roland 1966) and α-AsS melts at 306±2°C (Roland 1966), these temperatures being determined in the presence of vapour. The only symmetry information reported for α-AsS is that it is probably triclinic (Cahoon 1965). The identification of α-AsS as a mineral at Mina Alacrán, Pampa Larga, Chile, as well as the associated mineral assemblages were described in detail by Clark (1970). Both α-AsS and realgar occur in the Mina Alacrán vein and the inversion temperature should prove to be a useful indicator in deciphering depositional temperatures in various parts of the deposit.

Additional experiments on the temperature of the α-AsS ⇄ realgar inversion and the single-crystal *x*-ray data for synthetic α-AsS are reported in this note.

DETERMINATION OF THE INVERSION TEMPERATURE

Most of the experiments conducted to define the temperature of the reaction α-AsS ⇄ realgar were performed using the silica tube quenching technique as previously described (Roland 1970). Reactant materials were prepared from elements of 99.999+ wt. % purity (ASARCO) and products were identified by *x*-ray powder-diffraction patterns. Heating temperatures were carefully controlled, but pressures were determined by the "pressure of the system", *i.e.*, the equilibrium vapour pressure over the particular phase assemblage present in the sample tubes. The powder patterns of the synthetic α- and β-AsS closely agree as to line position with the patterns obtained from the minerals by Clark (1970), although there is some discrepancy as to line intensity. The differences are not considered significant. A pattern of natural realgar from Mercur, Utah contained lines at 6.81, 3.80, 3.68, 3.44, 3.35, 3.15, 3.10, and 2.96 Å in addition to those observed for the synthetic low modification but it was not shown that these were realgar reflections and not due to some impurity phase.

The experiments performed in silica tubes are described in Table 1. These data show that the temperature of the α-AsS $\rightleftharpoons$ realgar inversion

TABLE 1. QUENCHING EXPERIMENTS CONDUCTED TO DEFINE THE TEMPERATURE OF THE α-AsS $\rightleftharpoons$ REALGAR INVERSION IN THE PRESENCE OF VAPOUR.

Reactants	Temp., ± 3°C	Time, hrs.	Products *
rl + orp (1)**	266	197	α-AsS + rl + orp
rl + orp (1)	260	360	rl + orp
rl + orp (1)	254	816	rl + orp
α-AsS (2)	254	141	α-AsS
rl (3)	254	978	α-AsS
α-AsS (2)	250	1440	rl
α-AsS (2)	248	323	α-AsS + rl
α-AsS + As (4)	242	165	α-AsS + As
rl + As (5)	242	212	α-AsS + As
α-AsS + As (4)	236	317	rl + As
rl + As (5)	236	317	rl + As
α-AsS + As (4)	230	192	rl + As
rl + As (5)	230	192	rl + As
ntural rl	254	978	α-AsS
natural rl	225	163	rl

* rl = realgar, orp = orpiment. The products always include vapour.
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(1) Crystallized from $As_{0.9}S_{1.1}$ glass annealed at 250°C for 504 hours.
(2) Chilled AsS liquid.
(3) Prepared by heating α-AsS at 250°C for 515 hours.
(4) Crystallized from As_4S_3 glass at 247°C.
(5) Crystallized from As_4S_3 glass in 157 hours at 188°C.

is sensitive to composition, occurring at 239 ± 3°C in the presence of elemental As and at 263 ± 3°C in the presence of orpiment (As_2S_3). The inversion in microscopically pure AsS prepared from a stoichiometric mix of As and S occurred at 252 ± 2°C. The reaction is reversible and was observed to occur when natural as well as synthetic realgar was used as a reactant. From these experimental data, it can be inferred that either α-AsS or realgar (or both) have a composition range although the extent of the variation is not known, and indeed, would be time-consuming to define because equilibrium is reached very slowly. The composition range is small however, certainly much less than 5 at. %, a conclusion in agreement with the electron microprobe analyses of Clark (1970). It is tempting to speculate that the disparity in the observations of the behaviour of realgar on exposure to light or infrared radiation (Clark 1970) is due to a variation in stability of realgar of different compositions (*i.e.*, different As:S ratio). This was not experimentally investigated.

Four experiments (Table 2) were performed to determine the inversion temperature under a confining pressure of 2 kilobars. Welded gold sample containers were used and pressures were applied in standard cold seal pressure vessels heated in muffle furnaces. Stoichiometric α-AsS, the reactant, remained unchanged at 285° but inverted to realgar at 269°C. The inversion temperature is taken to be 277 ± 8°C at 2 kb. If it is assumed that the AsS inversion temperature was not altered by dissolved gold (seemingly a valid assumption because no reaction was observed between container and reactant), then pressure raises the inversion temperature, *i.e.*, the temperature stability range of realgar is increased relative to that of α-AsS. It is quite possible that realgar might crystallize directly from liquid at some high pressure, but certainly that pressure would greatly exceed pressures inferred to exist (< 1 kb) during the deposition of hypogene mineral assemblages which include realgar.

TABLE 2. EXPERIMENTS CONDUCTED TO DEFINE THE TEMPERATURE OF THE α-AsS ⇄ REALGAR INVERSION AT 2 KILOBARS CONFINING PRESSURE.

Reactant*	T, °C	Time, hrs.	Product
α-AsS	297	120	α-AsS
α-AsS	285	141	α-AsS
α-AsS	269	264	realgar
α-As-S	240	166	realgar

* Chilled AsS liquid.

SINGLE CRYSTALS : GROWTH AND X-RAY STUDY

Small crystals of α-AsS for *x*-ray study were grown by reacting sulphur with liquid of As_4S_8 composition. A one-gram portion of As_4S_8 glass (prepared by rapidly chilling liquid from 650°C) was kept physically separated by silica wool from a few mg. of sulphur and sealed under vacuum in an 8 mm ID silica glass tube. The finished charge was about 5 cm long. The tube was heated at 280°C for six days during which time the sulphur was transported via a vapour phase and reacted with the liquid to form α-AsS. Most of the reaction product was a fine-grained polycrystalline mass, but a few small single crystals were present on the inside wall of the tube, apparently where small beads of liquid had initially been present. Several subhedral crystals in the size range 0.1 to 0.5 mm in their maximum dimension were separated when the tube was opened.

The crystals were studied using a Buerger precession *x*-ray camera with Zr-filtered Mo radiation. They are monoclinic, Laue Class $2/m$, with $a = 9.92 \pm 0.03$, $b = 9.48 \pm 0.02$, $c = 8.91 \pm 0.04$ Å, $\beta = 101° 50' \pm 15'$. The measured density is 3.46 ± 0.02 gms/cc (pycnometer) which gives $Z = 16$ ($D_{\text{calc.}} = 3.46$). The observed extinction criteria are $h\ k\ l$ when $h + k$ is odd, $h0l$ when h or l is odd, and $0k0$ when k is *odd*, so that the diffraction symbol (Donnay & Kennard 1964) is C^*/c, and $C\ 2/c$ or Cc are possible space groups. A test for piezoelectricity was negative.

As an added check on the cell size and symmetry determined for α-AsS. the cell dimensions measured on the precession photographs were used to index an *x*-ray diffraction powder pattern obtained with Cu*K*α(Ni) radiation. The agreement between the observed and calculated *d* values is good (Table 3). A least squares refinement of the cell dimensions would almost certainly result in more precise agreement, although such a refinement was not undertaken in this study.

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TABLE 3. α-AsS : X-RAY POWDER DATA
INDEXED WITH $a = 9.92$, $b = 9.48$, $c = 8.91$ Å, $\beta = 101°50'$.

I	$d_{\text{meas.}}$ (Å)	$d_{\text{calc.}}$ (Å)	$h\ k\ l$
1	6.76	6.78	1 1 0
8	5.75	5.77	1 1 $\bar{1}$
4	5.01	5.02	1 1 1
2	4.85	4.85	2 0 0
2	4.69	4.74	0 2 0
2	4.15	4.16	0 2 1
7	3.93	3.93	1 1 $\bar{2}$
1	3.44	3.45	1 1 2
½	3.39	3.39	2 2 0
1	3.33	3.33	2 2 $\bar{1}$
8	3.20	3.21	0 2 2
7	3.08	3.08	3 1 $\bar{1}$
		3.06	3 1 0
10	3.01	3.00	1 3 0
3	2.95	2.96	2 0 2
10	2.89	2.90	1 3 $\bar{1}$
		2.88	2 2 $\bar{2}$
6	2.82	2.82	1 1 $\bar{3}$
1	2.76	2.77	3 1 $\bar{2}$
1	2.74	2.73	3 1 1
3	2.53	2.54	1 1 3
2	2.50	2.51	2 2 2
½	2.47	2.48	0 2 3
1	2.44	2.43	4 0 0
3	2.39	2.37	0 4 0
2	2.25	2.26	3 3 0
2	2.21	2.22	4 0 1
2	2.17	2.18	0 0 4
2	2.15	2.16	1 3 $\bar{3}$
		2.16	2 0 4
		2.16	4 2 0
1	2.11	2.12	3 3 1
		2.11	2 4 $\bar{1}$
½	2.01	Broad, not indexed.	

Additional lines at lower d values.

REFERENCES

CAHOON, B.G. (1965) : Polymorphism of Arsenic Sulphide (AsS). In : *Research on Chemistry and Physics of Inorganic Systems Under Extreme High Pressure and Temperature* ; Final Report. C.S. Hurlbut, Jr., Principal Investigator. Available from The National Technical Information Service, Springfield, Virginia, 22151. Document AD 633148.

CLARK, A.H. (1970) : Alpha-Arsenic Sulphide, from Mina Alacrán, Pampa Larga, Chile, *Am. Mineral.*, **55,** 1338-1344.

DONNAY, J.D.H. & KENNARD, O. (1964) : Diffraction Symbols, *Acta Cryst.*, **17,** 1337-1340.

HALL, H.T. (1966) : The Systems Ag-Sb-S, Ag-As-S, and Ag-Bi-S : Phase Relations and Mineralogical Significance. *Unpubl. doctoral thesis, Brown University,* 172 pp.

ROLAND, G.W. (1966) : Phase Relations and Geological Application of the System Ag-As-S. *Unpubl. doctoral thesis, Lehigh University,* 191 pp.

——— (1970) : Phase Relations Below 575°C in the System Ag-As-S. *Econ. Geol.*, **65,** 241-252.

STRATHDEE, B.A. & PIDGEON, L.M. (1961) : Thermal Decomposition and Vapor Pressure Measurements on Arsenopyrite and an Arsenical Ore. *Trans. Can. Inst. Min. and Met. and the Min. Soc. of N.S.*, **54,** 506-510.

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