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Pressure-induced phase transformations in the chalcopyrite-structure compounds: $CuGaS_2$ and $AgGaS_2$

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Pressure-induced phase transformations have been found in $CuGaS_2$ and $AgGaS_2$ by high-pressure x-ray-diffraction studies, using the energy dispersion technique. $CuGaS_2$ transforms from the chalcopyrite to the NaCl type near 16 GPa. $AgGaS_2$ undergoes three pressure-induced phase changes: (1) from chalcopyrite to a hexagonal lattice near 5 GPa, (2) from chalcopyrite and hexagonal to α-$NaFeO_2$ type near 12 GPa, and (3) to the NaCl type at pressures above 15 GPa. These results confirm the pressure-induced phase transitions indicated by the phonon behavior in a recent high-pressure Raman study of $CuGaS_2$ and $AgGaS_2$. From the high-pressure x-ray data on the chalcopyrite phase, the following bulk modulus B_0 and dB_0/dP were obtained by fitting the data to the Murnaghan equation of state: $CuGaS_2$, $B_0 = 96 \pm 10$ GPa, $B_0' = 6.5$; $AgGaS_2$, $B_0 = 60 \pm 8$ GPa, $B_0' = 6$.

INTRODUCTION

The I-III-VI_2 ternary semiconductors crystallize in the chalcopyrite structure, which may be regarded as a superstructure of the zinc-blende type.[1] As in the latter, the ions in the chalcopyrite structure are tetrahedrally coordinated and hence the packing efficiency is low. Therefore under high pressure chalcopyrite-structure compounds are expected to transform to denser structures with higher coordination. Earlier x-ray studies on pressure-quenched products[2] of several I-III-VI_2 compounds have shown that the chalcopyrite lattice transforms to the NaCl type, or to the related α-$NaFeO_2$-type structure at high pressure. An *in situ* high-pressure x-ray-diffraction study[3] on $AgInSe_2$, $AgInTe_2$, and $CuInSe_2$ has indicated a transformation to the NaCl-type phase at high pressure. However, it has not been clearly demonstrated that the α-$NaFeO_2$-structure phase is an equilibrium phase at high pressure.

In a recent Raman scattering study[4] of zone-center phonons in $CuGaS_2$ and $AgGaS_2$ as a function of pressure, evidence for pressure-induced phase transformations has been seen. In the case of $CuGaS_2$ a phase transition near 16 GPa and in the case of $AgGaS_2$ two phase transitions, one near 4.5 GPa and another near 12 GPa, are indicated by the pressure dependence of Raman-active modes. The present high-pressure x-ray study on $CuGaS_2$ and $AgGaS_2$ was stimulated by these findings. We have investigated both these compounds to about 25-GPa pressure, by *in situ* high-pressure x-ray-diffraction techniques and have been able to determine the nature of these phase transitions. The experiments and the results will be presented and discussed.

EXPERIMENTS

Samples were from the same batch, grown at Bell Laboratories and used in the aforementioned high-pressure Raman study. $CuGaS_2$ was orange in color and $AgGaS_2$ was light yellow. These were powdered fine for the pressure studies. A gasketed diamond anvil cell was used for generating the high pressure.[5] The pressure medium was a 4 : 1 mixture of methanol and ethanol and the pressure generated was measured using the well known ruby fluorescence technique.[6] X-ray powder-diffraction patterns were obtained using the energy dispersion technique. The details of this technique adapted to high-pressure investigations have been described in earlier publications.

RESULTS AND DISCUSSION

$CuGaS_2$

In Fig. 1 we have plotted the $d(hkl)$ values of the observed reflections of $CuGaS_2$ as a function of pressure. The (200), (004) and the (220), (024) reflections of the chalcopyrite structure are not resolved by the presently used energy dispersion technique, because the c/a ratio in the case of $CuGaS_2$ is nearly 2 ($c/a = 1.96$). The lines, connecting the data points of the different reflections of the chalcopyrite structure were obtained as follows: Firstly, the data for the (112) reflection were fitted with a polynomial of second degree, under the assumption that $c/a = 2$, and from this the pressure variations of the lattice parameter for the other reflections were calculated. At about 16 GPa three new reflections begin to appear, in addition to those of the chalcopyrite structure, and these reflections are identified as the (111), (200), and the (220) of the NaCl-

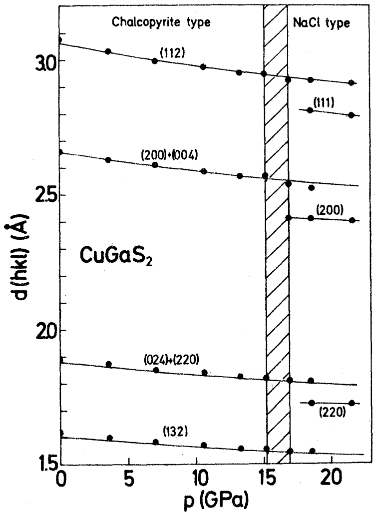

FIG. 1. Pressure dependence of the $d(hkl)$ values of the observed reflections in CuGaS$_2$. The hatched area indicated the region of uncertainty of the phase transformation from chalcopyrite to NaCl structure.

type phase. At about 22 GPa, the highest pressure applied on CuGaS$_2$, the powder pattern is almost entirely from the NaCl phase. The (112) of the chalcopyrite phase is still weakly present, as this is the strongest reflection of the latter phase. We believe that the chalcopyrite structure becomes unstable with respect to the NaCl-type structure at about 16 GPa. However, both phases coexist over the pressure range 16–20 GPa. This is to be expected since the chalcopyrite to NaCl-type structure transformation involves a drastic change in the primary coordination as well as the bonding characteristics and would therefore be a very sluggish phase transition at room temperature. Pertinent data on CuGaS$_2$ are given in Table I. The high-pressure phase reverts to the chalcopyrite structure on release of pressure.

According to the earlier study, the sample turns black near 16 GPa, and the Raman peaks disappear. This was attributed to a phase transition which was speculated to be to the NaCl structure. Further, the softening of the lowest-mode phonon frequency was taken as additional evidence for an impending phase transition. The absence of any Raman peaks in the new phase would be consistent with the formation of an NaCl-type phase, since first-order Raman activity in the latter phase would be prohibited by symmetry. Although in the present case it would be allowed because of cationic disorder in the lattice, it would still be a very weak effect and hence unobservable under the conditions in the diamond cell. Thus the Raman behavior is consistent with the phase transition at 16 GPa to the NaCl-type phase, a result obtained in the present study.

TABLE I. Relevant data on phase transitions, structures, lattice parameters, volume changes, and bulk moduli of CuGaS$_2$ and AgGaS$_2$.

Pressure range (GPa)	Transition pressure (GPa) x ray determination	Transition pressure (GPa) Raman determination	Structure	Lattice parameter (Å)	Volume change	Bulk modulus (GPa)
	CuGaS$_2$					
0–15.1			Chalcopyrite type	$a = 5.29–5.10$ $c = 2a$		96 ± 10^{a} ($dB_0/dp = 6.3$)
	15.1–16.9	~16			16.1%	
16.9–22.5			Chalcopyrite type NaCl type	a (16.9 GPa)$=4.81$		94 ± 15^{b} ($dB_0/dp = 4.3$)
	AgGaS$_2$					
0–5			Chalcopyrite type	$a = 5.76–5.69$ $c = 10.30–9.90$		60 ± 8^{a} ($dB_0/dp = 6$)
	~5	4.5				
5–10.5			Chalcopyrite type + Hexagonal type	$a = 5.69–5.64$ $c = 9.90–9.79$		
	10.5–12.1	11.6			14.5%	59.6^{c}
12.1–20		15	α-NaFeO$_2$ type	$a = 3.36$ $c = 20.42$ (12.1 GPa)	2.5%	
>15	15		NaCl type	$a = 5.02$ (18.1 GPa)		

[a] Values taken from present paper.
[b] Value taken from Ref. 8.
[c] Value taken from Ref. 7.

$AgGaS_2$

In Fig. 2 the $d(hkl)$ of the observed x-ray powder lines are plotted as a function of pressure. Different symbols indicate measurements at different angles. These changes in the diffraction angle were necessary to sort out the problem of superposition of true Bragg reflections and the characteristic lines of Ag. In contrast to $CuGaS_2$ the c/a ratio in $AgGaS_2$ is substantially smaller than 2 ($c/a = 1.79$). Hence the (200), (004) and (220), (024) reflections are well separated. The (200) and (004) reflections were fitted with a polynomial of second degree in the range 0–10.5 GPa. From these data d values for other reflections were calculated and are shown by the lines connecting the actual data points of the chalcopyrite structure. The (220) reflection appears too close to the strongest reflection of Inconel which is used as gasket material and hence could not be followed. Noteworthy is the behavior of the (004) reflection (very weak). In the range 0–5 GPa the $d(004)$ value decreases markedly with increasing pressure but remains nearly constant above 5 GPa. In the region of 5 to 10 GPa an additional line appears along with the chalcopyrite lines. We have fitted this to the (101) of a hexagonal lattice which would have nearly the same density as the chalcopyrite. At pressures above 12 GPa new powder lines emerge which we have indexed on the basis of α-$NaFeO_2$ structure, with very good agreement. The strongest chalcopyrite line (112) is observed up to about 17.5 GPa, along with the α-$NaFeO_2$ lines. At pressures above 20 GPa only three peaks are seen, which fits very well the (111), (200), and (220) of the NaCl-type structure. Between 15 and 20 GPa α-$NaFeO_2$ and NaCl-type phases coexist. The x-ray data thus indicate three pressure-induced phase transitions in $AgGaS_2$, near 5 GPa from chalcopyrite to hexagonal, near 12 GPa from chalcopyrite and hexagonal to α-$NaFeO_2$, and near 15 GPa to the NaCl type, with the latter two phases coexisting over the region of 15 to 20 GPa. The relevant data on the phase transitions, volume changes, and lattice parameters at several pressures are given in Table I. On release of pressure the chalcopyrite is obtained, indicating complete reversibility of the phase changes.

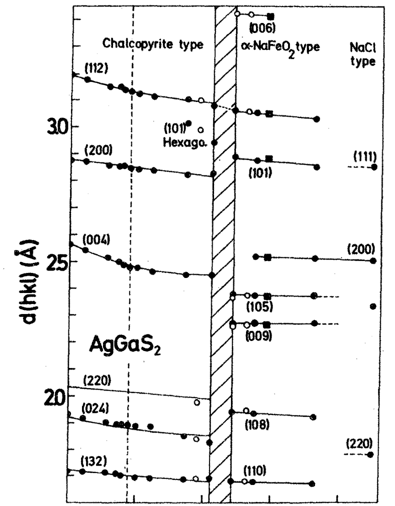

FIG. 2. Pressure dependence of the $d(hkl)$ values of the observed reflections in $AgGaS_2$. The hatched area indicates the region of uncertainty of phase transformation from chalcopyrite and hexagonal to α-$NaFeO_2$ type of structure. The dashed line indicates the phase transformation from the chalcopyrite to a hexagonal structure. (The transformation pressure of 4.4 GPa is from Ref. 4.) Different symbols indicate measurements at different angles: ●, $2\theta = 8.5°$; ○, $2\theta = 11°$; ■, $2\theta = 7.5°$.

It has been inferred from the high-pressure Raman study on $AgGaS_2$ that two phase transitions occur in the system, in the 0–20 GPa range. The lowest-frequency Raman mode exhibits a striking softening behavior and near 5 GPa a new phonon branch emerges which increases in frequency with pressure. It has been suggested that this behavior around 5 GPa is due to a subtle pressure-induced phase transition in $AgGaS_2$. We believe that this phase transition is to a phase with hexagonal symmetry, probably wurtzite or a wurtzitelike structure. At present more cannot be said on this phase because of insufficient data. At pressures above 11.6 GPa new Raman peaks were seen, although the sample began to darken. Above a pressure of 16 GPa it became increasingly difficult to obtain Raman data. Again this would be consistent with the findings of the present study. The α-$NaFeO_2$ phase is rhombohedral and hence first-order Raman lines would be present. However when the latter phase changes gradually to the NaCl-type structure, the Raman spectrum may be expected to disappear.

PRESSURE-VOLUME RELATIONSHIP AND BULK MODULUS

The pressure-volume relationship for $CuGaS_2$ and $AgGaS_2$ are shown in Figs. 3 and 4. In the case of $CuGaS_2$ the discontinuity in volume is due to the chalcopyrite–NaCl-type structural phase transition. The volume change ΔV for this transition evaluated at the transition pressure is found to be 16%. In Fig. 3 the overlapping of the two phases are clearly seen. In Fig. 4 the pressure-volume relationship for $AgGaS_2$ shows the chalcopyrite to the α-$NaFeO_2$ transition, which is

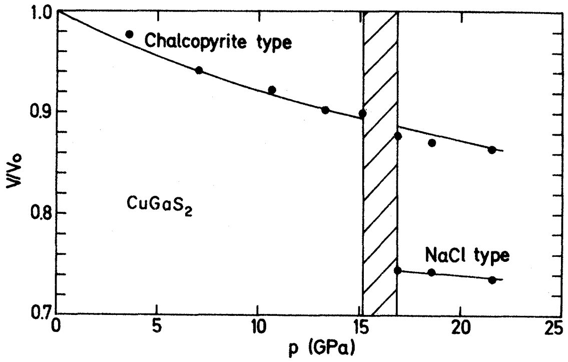

FIG. 3. Pressure-volume data for $CuGaS_2$. The hatched area indicates the region of phase transformation from the chalcopyrite structure to the NaCl-type structure. The solid line connecting the data points of the chalcopyrite structure is from the Murnaghan equation of state, with the parameter listed in Table I.

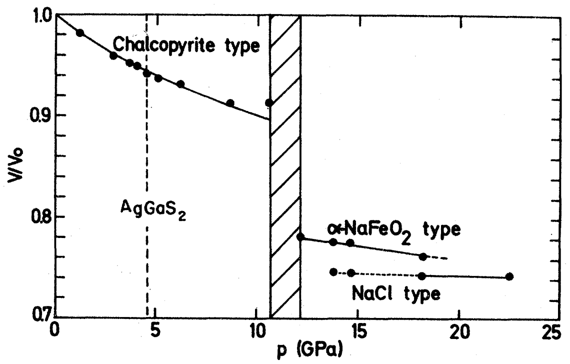

FIG. 4. Pressure-volume data for $AgGaS_2$. The hatched area indicates the region of phase transformation from (chalcopyrite and hexagonal) to α-$NaFeO_2$-type structure. The dashed line indicates the phase transformation from chalcopyrite to a hexagonal structure. The points in the range 0–10.5 GPa represent only the pressure-volume data of the chalcopyrite structure. The solid line connecting these data points is from the Murnaghan equation of state, with the parameter listed in Table I.

accompanied by a volume change of 14.5% near the transition pressure taken to be near 11 GPa. The NaCl-type phase has a slightly larger density and the volume change evaluated at about 18 GPa is 2.5%. We have not differentiated between the chalcopyrite and the hexagonal phases in the pressure-volume plot, since the densities are believed to be almost equal.

For both $CuGaS_2$ and $AgGaS_2$ the pressure-volume relationship in the chalcopyrite phase was fitted to the Murnaghan equation of state. From this fitting, the bulk modulus B_0 and the dB_0/dp have been obtained. These are given in Table I. The values appearing below the presently obtained values are from Koschel and Bettini[7] for $AgGaS_2$ from elastic constant data, and from Bettini and Holzapfel[8] for $CuGaS_2$ from high-pressure x-ray data. The agreement between our values and the values of bulk modulus from earlier studies is very good. Unfortunately neither the bulk moduli nor the elastic constant data for other chalcopyrite-structure compounds are available for a wider comparison to be made, especially to check the linear relationship one might expect between the log of B_0 and the log of specific volume for related substances, as the one proposed by Anderson and Nafe.[9]

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