

## NQR Study of Ternary Chalcogenides $A_3BX_3$ , $ABX_2$ , and $ABX$ Where $A = \text{Cu, Ag, or Tl}$ , $B = \text{As or Sb}$ , and $X = \text{S or Se}$

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$^{121}\text{Sb}$ ,  $^{123}\text{Sb}$ ,  $^{75}\text{As}$ ,  $^{63}\text{Cu}$ , and  $^{65}\text{Cu}$  NQR resonances are reported for  $\text{CuSbSe}_2$ ,  $\text{Tl}_3\text{SbSe}_3$ ,  $\text{Tl}_3\text{SbS}_3$ ,  $\text{Tl}_3\text{AsS}_3$ ,  $\text{Tl}_3\text{AsSe}_3$ ,  $\text{Ag}_3\text{AsSe}_3$ ,  $\text{TlSbS}_2$ ,  $\text{CuAsS}$ ,  $\text{AgAsS}$ , and  $\text{Cu}_3\text{SbS}_3\text{I}_2$ .  $\text{Tl}_3\text{SbSe}_3$  is an incongruently melting compound not observed in an earlier phase-diagram study of the pseudobinary system  $\text{Tl}_2\text{Se}-\text{Sb}_2\text{Se}_3$ . For isostructural arsenic and antimony chalcogenides the ratio of  $^{75}\text{As}$  to  $^{121}\text{Sb}$  quadrupole coupling constants is 0.42, and for the  $BX_3$  group in binary or ternary corresponding pairs of sulfide and selenides the ratio of quadrupole coupling constants for  $^{75}\text{As}$  or  $^{121}\text{Sb}$  is 0.83. A reversible phase transition was observed at 130 K for  $\text{Ag}_3\text{AsSe}_3$ . Unit cell parameters are reported for crystals of  $\text{TlSbS}_2$  and  $\text{Cu}_3\text{SbS}_3\text{I}_2$ .

### Introduction

The ternary title compounds have tetrahedral structures related to zinc blende or wurtzite. Many of such compounds undergo phase changes from ordered structures to cation-disordered structures, and the disordered structures have potentially useful physical transport properties. Magnetic resonance in conjunction with diffraction study has proved to be an excellent tool for investigating detailed aspects of these ternary phases. For example, the variation of the NQR with temperature has been used to follow phase changes in  $\text{Cu}_3\text{SbS}_3$  (1, 2),  $\text{Ag}_3\text{AsS}_3$  (3), and  $\text{Ag}_3\text{SbS}_3$  (4). More generally, crystallographic information, such as site symmetry and site multiplicity of the asymmetric unit of the unit cell, can often be deduced from NQR spectra. This information may be a useful check on the indexing of X-ray powder patterns of compounds that are not readily prepared as

single crystals. (5) In the present paper we report results of a comparative study of a series of related ternary chalcogenides.

### Experimental

The series of ternary arsenic and antimony chalcogenides were prepared by the general method of reaction of their component elements in stoichiometric proportions in evacuated glass ampoules at temperatures above the melting point of the final product, followed by annealing at a temperature somewhat below the melting point for a time sufficient to give sharp X-ray diffraction patterns and strong NQR lines. We observed that an arsenic-rich glass such as  $\text{TlAsS}_2$  crystallizes more slowly than an arsenic-poor glass such as  $\text{Tl}_3\text{AsS}_3$ , and an arsenic glass crystallizes more slowly than the corresponding antimony glass.

The compounds were characterized by their X-ray powder patterns recorded on a

Rigaku Miniflex X-ray diffractometer using Ni-filtered Cu radiation. Nuclear quadrupole resonances were detected with a Zeeman-modulated noise-controlled super-regenerative oscillator which could be scanned from 4 to 150 MHz.

### Results and discussion

In Table I are listed the NQR frequencies observed for the title compounds together with previously published frequencies on some comparable compounds. For the anti-

mony resonances, the quadrupole coupling constants ( $QCC = e^2Qq/h$ ) and asymmetry parameters,  $\eta$ , have been calculated from the data. For the arsenic resonances the coupling constant is calculated for those compounds whose asymmetry parameters,  $\eta$ , are known to be zero from their crystal structures.

For all the antimony compounds, we observed that the most intense line arose from the  $^{121}\text{Sb}$  ( $\frac{1}{2}-\frac{3}{2}$ ) transition, and the next most intense line from the  $^{123}\text{Sb}$  ( $\frac{1}{2}-\frac{3}{2}$ ) transition.

TABLE I  
NQR FREQUENCIES FOR ANTIMONY, ARSENIC, AND COPPER

		(a) Antimony resonances (MHz)								
		$^{121}\text{Sb}$		$^{123}\text{Sb}$			QCC	$\eta$	Ref.	
$T(\text{K})$		$\frac{1}{2}-\frac{3}{2}$	$\frac{3}{2}-\frac{5}{2}$	$\frac{1}{2}-\frac{3}{2}$	$\frac{3}{2}-\frac{5}{2}$	$\frac{5}{2}-\frac{7}{2}$				
$\text{CuSbS}_2$	295	55.46	110.69	33.68	67.34	101.00	369.7	<0.02	<sup>a</sup>	
	77	56.99	113.76	34.68	69.16	103.56	379.9	<0.02	<sup>a</sup>	
	77	56.92	113.80	34.58	69.07	103.63	379.3	0.016	(10)	
$\text{CuSbSe}_2$	295	46.94		28.49			312.9	<0.02	<sup>a</sup>	
	77	48.71		29.61	59.09		324.7	<0.02	<sup>a</sup>	
$\text{Cu}_3\text{SbS}_3$	Site 1	295	49.76	99.12	30.35		330.4	0.06	(1)	
	Site 2	295	51.10	100.43	31.98		335.3	0.12	(1)	
	77	52.30	103.26	32.53	62.45	94.12	344.9	0.10	(2)	
$\text{Ag}_3\text{SbS}_3$	77	49.84	99.70	30.28	60.52	90.78	323.3	0	(16)	
$\text{Cu}_3\text{SbS}_3\text{I}_2$	295	59.91		36.54					<sup>a</sup>	
	TlSbS <sub>2</sub>	Site 1	295	59.11						<sup>a</sup>
		Site 2		63.85						<sup>a</sup>
Tl <sub>3</sub> SbS <sub>3</sub>	Site 1	77	60.45						<sup>a</sup>	
	Site 2		65.55		75.46				<sup>a</sup>	
Tl <sub>3</sub> SbS <sub>3</sub>	295	50.85	101.65	30.89	61.76	92.58	339.0	<0.02	<sup>a</sup>	
	77	51.89	103.70	31.52	62.99	94.43	345.9	<0.02	<sup>a</sup>	
Tl <sub>3</sub> SbSe <sub>3</sub>	295	38.97	77.88	23.65	47.32	70.96	259.9	0	<sup>a</sup>	
	77	39.79	79.54	24.18	48.27	72.43	265.3	0	<sup>a</sup>	
$\text{Sb}_3\text{S}_3$	Site 1	77	47.70	95.36	28.96	57.91	86.83	317.9	0.009	(32)
	Site 2	77	42.97	73.24	32.26	42.91	67.45	250.54	0.377	(32)
$\text{Sb}_2\text{Se}_3$	Site 1	77	40.91	81.84	24.86	49.68	74.52	272.75	0.008	(32)
	Site 2	77	34.99	57.75	27.01	33.96	53.35	198.87	0.417	(32)
$\text{Sb}_4\text{O}_6$ (cubic)	77	83.21	166.45	50.511	101.01	151.89	554.83	0	(30)	

TABLE I—Continued

	T(K)	(b) Arsenic resonance (MHz)			QCC	$\eta$	Ref.
		<sup>75</sup> As					
Ag <sub>3</sub> AsS <sub>3</sub>	293	66.17			132.3	0	(16)
	77	67.31			134.6	0	(16)
Ag <sub>3</sub> AsSe <sub>3</sub>	295	53.62			107.2	0	<sup>a</sup>
	195	54.18			108.4	0	<sup>a</sup>
TlAsS <sub>2</sub>	77	81.20	84.61				(13)
Tl <sub>3</sub> AsS <sub>3</sub>	295	67.28			134.6	0	<sup>a</sup>
	77	68.93			137.9	0	<sup>a</sup>
Tl <sub>3</sub> AsSe <sub>3</sub>	295	57.20			114.4	0	<sup>a</sup>
	77	58.82			117.6	0	<sup>a</sup>
AgAsS <sub>2</sub>	77	68.00	68.64	71.65			(25)
AgAsS	295	76.58					<sup>a</sup>
	77	78.52					<sup>a</sup>
CuAsS	295	68.19					(22)
	77	69.23					(22)
As <sub>4</sub> S <sub>3</sub>	77	79.6					(27)
As <sub>4</sub> Se <sub>3</sub>	77	68.97					(28)
As <sub>2</sub> S <sub>3</sub>	4.2						
	Site (1)	70.38			138.1	0.343	(33)
	Site (2)	72.86			142.4	0.374	(33)
As <sub>2</sub> Se <sub>3</sub>	77	56.07,	60.25				(29)
As <sub>4</sub> O <sub>6</sub>	77	116.781			233.56	0	(31)
(c) Copper resonances (MHz)							
<sup>63</sup> Cu							
CuAsS	295	10.82					<sup>a</sup>
Cu <sub>3</sub> SbS <sub>3</sub>	77	21.84	22.38	24.81			(2)
<sup>a</sup> this work							

The other three resonances are very much less intense, and indeed the weaker resonances were not observed for some compounds.

For the compounds in Table I, the arsenic or antimony atoms are pyramidally coordinated to three sulfur or selenium atoms. Some general correlations between the coupling constants and coordination of the nuclei in this series of compounds are exemplified in Tables II and III.

First for the corresponding pairs of arsenic and antimony compounds listed in Table II the ratio of the <sup>75</sup>As and <sup>121</sup>Sb QCC is reasonably constant and close to the ratio

of the atomic coupling constants of <sup>75</sup>As (−412 MHz) and <sup>121</sup>Sb (954 MHz), namely, 0.43 (6). This is explicable in terms of Townes–Dailey theory, on the assumption that geometric similarity ensures the same bond populations for the *p* orbitals on the antimony and arsenic atoms, and that bond ionicities are similar. For the pyramidally coordinated Group V metal atom, Townes–Dailey theory gives for the metal atom coupling constant

$$\frac{e^2qQ}{h} = -3(1 + I) \frac{\cos \alpha}{1 - \cos \alpha} \frac{e^2qQ}{h} \text{ atomic,}$$

where  $\alpha$  is the chalcogen–metal–chalcogen

TABLE II

Compounds	<i>T</i> (K)	Ratio of QCC (As/Sb)
Ag <sub>3</sub> AsS <sub>3</sub> , Ag <sub>3</sub> SbS <sub>3</sub>	77	0.416
Tl <sub>3</sub> AsS <sub>3</sub> , Tl <sub>3</sub> SbS <sub>3</sub>	77	0.399
Tl <sub>3</sub> AsSe <sub>3</sub> , Tl <sub>3</sub> SbSe <sub>3</sub>	77	0.443
Cubic As <sub>4</sub> O <sub>6</sub> , Sb <sub>4</sub> O <sub>6</sub>	77	0.421

bond angle and *I* is the bond ionicity, conventionally written

$$I = \frac{1}{2}(X_A - X_B),$$

where  $X_A$  and  $X_B$  are the electronegativities of the atoms *A* and *B* forming the bond.

For the pairs of compounds listed in Table III, the ratio of the QCC values of a selenide and its corresponding sulfide of similar local geometry is close to 0.85. This agrees with earlier observations on the  $AsX_3$  moiety in binary arsenic chalcogenides (7). With electronegativities such as those given by Pauling (8) the factors (1 + *I*) for the As–S, As–Se, Sb–S, and Sb–Se bonds are 1.5, 1.4, 1.6, and 1.5, respectively, yielding a ratio for corresponding selenides and sulfides of approximately 0.93. The slightly greater bond angles for the selenium compounds would account for the observed lower value of 0.85.

Finally for corresponding ternary compounds of silver and thallium, the arsenic or antimony coupling constant for the thallium compound is greater than the coupling constant for the silver compound.

### Compounds $ABX_2$

CuSbS<sub>2</sub>, chalcostibite or wolfsbergite, is orthorhombic, space group *Pnma*, and has one antimony in its asymmetric unit (9). This antimony is pyramidally coordinated to three sulfur atoms and within the experimental error of the structure determination the SbS<sub>3</sub> moiety had  $C_{3v}$  symmetry. However, the point group symmetry at the anti-

mony site is only *m* and so the asymmetry parameter for the NQR spectrum will be nonzero by symmetry. Penkov *et al.* (10) calculate a value of  $\eta = 0.016$  from their NQR data. Our experimental data indicate that  $\eta$  is less than 0.02 at both 77 and 295 K.

Electron diffraction photographs from CuSbSe<sub>2</sub> thin films were shown to be in accord with it being isostructural with CuSbS<sub>2</sub> (11). Our NQR data show one antimony site with an asymmetry parameter not detectably different from zero.

The mineral lorandite, TlAsS<sub>2</sub>, is monoclinic (12) and shows two NQR lines (13) in accord with the two arsenic atoms in the asymmetric unit of its unit cell.

X-ray single-crystal precession photographs of TlSbS<sub>2</sub> showed it to be triclinic with unit cell parameters  $a = 11.812 \text{ \AA}$ ,  $b = 6.320 \text{ \AA}$ ,  $c = 6.131 \text{ \AA}$ ,  $\alpha = 104.00^\circ$ ,  $\beta = 98.25^\circ$ , and  $\gamma = 101.45^\circ$ . These values are slightly different from those reported by the previous workers (14). NQR lines from two or four antimony sites are expected according to whether the triclinic cell has a center of symmetry or not (i.e.,  $P1$  or  $P\bar{1}$ ). We observe a doublet which we assign to the  $^{121}\text{Sb} (\frac{1}{2} - \frac{3}{2})$  transitions of two sites, in agreement with the centric space group ( $P\bar{1}$ ).

TABLE III

Compounds	<i>T</i> (K)	Ratio of QCC (Se/S)
CuSbS <sub>2</sub> , CuSbSe <sub>2</sub>	77	0.855
Ag <sub>3</sub> AsS <sub>3</sub> , Ag <sub>3</sub> AsSe <sub>3</sub>	295	0.810
Tl <sub>3</sub> AsS <sub>3</sub> , Tl <sub>3</sub> AsSe <sub>3</sub>	77	0.853
Tl <sub>3</sub> SbS <sub>3</sub> , Tl <sub>3</sub> SbSe <sub>3</sub>	77	0.767
As <sub>4</sub> S <sub>3</sub> , As <sub>4</sub> Se <sub>3</sub> apical As	77	0.866 <sup>a</sup>
As <sub>2</sub> S <sub>3</sub> , As <sub>2</sub> Se <sub>3</sub>		
Site 1	77	0.828 <sup>a</sup>
Site 2	77	0.797 <sup>a</sup>
Sb <sub>2</sub> S <sub>3</sub> , Sb <sub>2</sub> Se <sub>3</sub>		
Site 1	77	0.858
Site 2	77	0.794

<sup>a</sup> Ratio of frequencies as  $\eta$  not known for these resonances.

### Compounds $A_3BX_3$

$Ag_3AsS_3$  is the well-characterized mineral proustite. Its space group at room temperature is  $R\bar{3}c$ . There is one arsenic atom in the asymmetric unit of its unit cell of dimensions  $a = 10.78 \text{ \AA}$  and  $c = 8.682 \text{ \AA}$  (15). The NQR spectrum (16) shows a single line whose asymmetry parameter is taken as zero from the point group symmetry,  $3m$ , of the lattice site. The quadrupole coupling constant for the arsenic atom in  $Ag_3AsS_3$  is thus exactly twice the observed NQR frequency. At low temperature  $Ag_3AsS_3$  undergoes a phase transition which has been studied by the technique of NQR (3).

The  $Ag_3AsSe_3$  X-ray powder diffraction pattern can be indexed in terms of a hexagonal unit cell with parameters  $a = 11.28 \text{ \AA}$  and  $c = 8.80 \text{ \AA}$ ;  $Ag_3AsSe_3$  is probably isostructural with  $Ag_3AsS_3$  (17). We observe a reversible phase change at 130 K for  $Ag_3AsSe_3$ ; the NQR signal disappears abruptly on cooling below 128 K and reappears on warming above 132 K. We were not able to detect any NQR signal for  $Ag_3AsSe_3$  between 77 and 130 K.

$Ag_3SbS_3$ , the mineral pyrrargyrite, has space group  $R\bar{3}c$  with cell dimensions  $a = 11.05 \text{ \AA}$  and  $c = 8.74 \text{ \AA}$  and is isostructural with  $Ag_3AsS_3$  (15). It gives a five-line antimony spectrum (16) with a zero asymmetry parameter in accord with the point group symmetry  $3m$  at the antimony lattice site. At lower temperatures  $Ag_3SbS_3$  undergoes a phase change which has been investigated by studying the NQR resonances from the antimony atoms (4).

The mineral ellisite (18),  $Tl_3AsS_3$ , has recently (19) been shown by X-ray single-crystal diffraction to be rhombohedral, space group  $R\bar{3}m$ , hexagonal cell parameters  $a = 9.5707 \text{ \AA}$  and  $c = 6.9888 \text{ \AA}$ . There is one arsenic in the asymmetric unit of the cell at a lattice point of point group symmetry  $3m$ . The NQR shows one line as expected and the asymmetry parameter,  $\eta$ , is

zero by symmetry.

$Tl_3AsSe_3$  also crystallizes in the space group  $R\bar{3}m$  and its cell parameters are  $a = 9.870 \text{ \AA}$  and  $c = 7.094 \text{ \AA}$  (20). The single arsenic atom in the asymmetric unit of the unit cell is coordinated to three selenium atoms with  $C_{3v}$  point group symmetry and one strong arsenic resonance is found in the NQR spectrum. By symmetry its  $\eta$  is zero.

The X-ray powder pattern of  $Tl_3SbS_3$  has been indexed in terms of a monoclinic (14) unit cell of dimensions  $a = 11.28 \text{ \AA}$ ,  $b = 9.65 \text{ \AA}$ ,  $c = 7.45 \text{ \AA}$ , and  $\beta = 104^\circ$ . We observed a complete set of five antimony NQR lines indicating only one antimony site per asymmetric unit. The asymmetry parameter for this site was not detectably different from zero, indicating a very small distortion from trigonal symmetry of the  $SbS_3$  grouping.  $Tl_3SbSe_3$  has not been previously reported. A phase-diagram study of the pseudobinary system  $Tl_2Se-Sb_2Se_3$  (21) showed the existence of only three compounds— $TlSb_3Se_5$ ,  $TlSbSe_2$ , and  $Tl_9SbSe_8$ —the first two of which melt incongruently and the third congruently. By rapid cooling of a melt of stoichiometric composition  $Tl_3SbSe_3$  we obtained a two-phase mixture with a powder X-ray pattern in agreement with previous work (21). However, on heating this mixture at 550 K in an evacuated ampoule for 48 hr, a solid-state reaction occurs, resulting in a new phase which we believe is  $Tl_3SbSe_3$ . The antimony NQR of this powder shows one antimony site with an asymmetry parameter not detectably different from zero. The ratio of the QCC to that of  $Tl_3AsSe_3$  (Table II) strongly suggests that  $Tl_3SbSe_3$  contains antimony pyramidally coordinated to three selenium atoms with  $3m$  point group symmetry.

### Compounds $ABX$

We observe a three-line NQR spectrum for synthetic lautite,  $CuAsS$ . One line is

assigned to  $^{75}\text{As}$  in accord with previous work (22). The two low frequencies are assigned to the single copper atom of the asymmetric unit of the unit cell of lautite (23). The ratio of the frequencies of these two lines is in accord with the ratio of the quadrupole moments of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , and the line intensities are in accord with the abundance ratio of the two isotopes. The low QCC for copper in  $\text{CuAsS}$  supports the structural evidence (23) that the Cu is in a spherically symmetric  $d^{10}$  configuration of Cu(I). Cu NQR lines have previously been observed in another ternary copper sulfide, namely,  $\text{Cu}_3\text{SbS}_3$ , at considerably higher frequencies. The copper atoms in this latter compound occupy lattice sites of lower symmetry than in  $\text{CuAsS}$ , and the higher NQR frequency reflects the increased distortion from the spherical symmetry of the isolated Cu(I) state. We also searched for NQR resonances in  $\text{CuAsSe}$ ,  $\text{AgAsS}$ , and  $\text{AgAsSe}$ , which have been reported as isostructural with lautite on the basis of X-ray diffraction from powder samples (24). We observed a single resonance attributed to  $^{75}\text{As}$  for  $\text{AgAsS}$ , at a frequency higher than the resonances in  $\text{Ag}_3\text{AsS}_3$  and  $\text{AgAsS}_2$  (25), but observed no resonances from the selenium compounds  $\text{CuAsSe}$  and  $\text{AgAsSe}$ . A single-crystal X-ray structure determination of  $\text{CuAsSe}$  (26) showed our sample has a structure different from though related to lautite with three molecules in the asymmetric unit of its unit cell, of space group  $Pbcn$  with cell parameters  $a = 11.73 \text{ \AA}$ ,  $b = 6.78 \text{ \AA}$ , and  $c = 19.18 \text{ \AA}$ .

A quaternary antimony compound,  $\text{Cu}_5\text{SbS}_3\text{I}_2$ , was prepared in the course of attempts to grow crystals of  $\text{Cu}_3\text{SbS}_3$  from a CuI flux. X-Ray single-crystal precession photographs showed that the crystals are orthorhombic, space group  $Pnmm$ , with unit cell parameters  $a = 12.65 \text{ \AA}$ ,  $b = 10.51 \text{ \AA}$ , and  $c = 7.34 \text{ \AA}$ . The measured density  $D_m = 5.29 \text{ g cm}^{-3}$  indicates that there are four molecules per unit cell. This com-

pound showed two NQR lines at frequencies characteristic of the pyramidal  $\text{SbS}_3$  grouping.

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