

## Properties of Sb-compounds with Rutile-like Structures

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Powder X-ray diffraction, magnetic susceptibility, and <sup>121</sup>Sb Mössbauer measurements are reported for the so-called random-rutiles CrSbO<sub>4</sub>, FeSbO<sub>4</sub>, RhSbO<sub>4</sub>, AlSbO<sub>4</sub>, and GaSbO<sub>4</sub>, the tri-rutiles MgSb<sub>2</sub>O<sub>6</sub>, CoSb<sub>2</sub>O<sub>6</sub>, NiSb<sub>2</sub>O<sub>6</sub>, and ZnSb<sub>2</sub>O<sub>6</sub>, and the distorted tri-rutile CuSb<sub>2</sub>O<sub>6</sub>.

The rutile (TiO<sub>2</sub>-*r*) type structure and its closely related variants are frequently found among binary dioxides,<sup>1</sup> and substitutional TiO<sub>2</sub>-*r* type solid solution phases can often be prepared from mixtures of such dioxides. Rutile-like atomic arrangements are also found for apparently well-defined ternary Sb and Te compounds (*cf.*, *e.g.*, Ref. 2): MSbO<sub>4</sub> (*M*=Cr, Fe, Rh, Al, and Ga), MSb<sub>2</sub>O<sub>6</sub> (*M*=Mg, Co, Ni, Cu, and Zn), and M<sub>2</sub>TeO<sub>6</sub> (*M*=Cr, Fe, Al, and Ga). According to current classifications the MSbO<sub>4</sub> compounds belong to the random-rutiles, whereas MSb<sub>2</sub>O<sub>6</sub> and M<sub>2</sub>TeO<sub>6</sub> belong to the tri-rutiles (*cf.* Fig. 1). These series of compounds represent a hitherto little explored source of information on the bonding properties of Sb and Te. Since M<sub>2</sub>TeO<sub>6</sub> is better characterized,<sup>3-5</sup> the present work was concentrated on the Sb-compounds. A <sup>121</sup>Sb Mössbauer study<sup>6</sup> which includes all but two of these compounds was reported after the experimental part of this investigation was completed.

### EXPERIMENTAL

The samples were prepared by mixing appropriate amounts of the materials specified below in open porcelain crucibles (previously fired with Sb<sub>2</sub>O<sub>3</sub> at 1000 °C). The temperature was slowly raised to 800 °C where the first heat treatments ranged from 4 h to 3 weeks. The samples were crushed and reannealed at 900—

1000 °C for 4 h to 2 weeks, and finally, slowly cooled to room temperature.

For *M*=Cr and Fe in MSbO<sub>4</sub>, Cr flakes (99.999 %; Koch-Light Laboratories) and turnings from Fe rods (99.99+ %; Johnson, Matthey & Co.), respectively, and Sb<sub>2</sub>O<sub>3</sub> (A. R.; Riedel-de Haën AG) were initially dissolved in hydrochloric acid (G.R.; Merck). After treatment of these solutions with nitric acid (G.R.; Merck), hydrous oxides were precipitated with NH<sub>3</sub>(aq) (G.R.; Merck), filtered, washed with NH<sub>4</sub>NO<sub>3</sub>/NH<sub>3</sub> solution, and dried. (CrSbO<sub>4</sub> and FeSbO<sub>4</sub> can also be obtained through direct reactions between Cr<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub>, but this procedure requires considerably longer heating periods.) The sources of *M*=Al, Ga, and Rh in MSbO<sub>4</sub> were NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>3</sub>·12H<sub>2</sub>O (A. R.; Riedel-de Haën AG), Ga<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and Rh<sub>2</sub>O<sub>3</sub> (G.R.; K. & K. Laboratories, Inc.), respectively, and for *M*=Mg, Cu, and Zn in MSb<sub>2</sub>O<sub>6</sub>, MgO, CuO, and ZnO (G.R.; Merck) were used. The previously synthesized<sup>7</sup> products of CoSb<sub>2</sub> and NiSb<sub>2</sub> were used as starting materials for CoSb<sub>2</sub>O<sub>6</sub> and NiSb<sub>2</sub>O<sub>6</sub>.

DTA/DTG data were collected with a Mettler Recording Vacuum Thermoanalyzer, using ~50 mg samples and silica (≤900 °C) and Al<sub>2</sub>O<sub>3</sub> (>900 °C) crucibles (Al<sub>2</sub>O<sub>3</sub> as reference). Experimental details concerning X-ray diffraction, magnetic susceptibility, and <sup>121</sup>Sb Mössbauer measurements with subsequent data reduction are described in Refs. 8–10.

### RESULTS AND DISCUSSION

(i) *The samples.* The present study was based on powder samples since attempts to make single crystals (at >1000 °C) were unsuccessful. Decompositions and/or reactions with the porcelain crucibles were observed in the range 1150–1250 °C. Decomposition temperatures and products could not be determined more accurately (by *e.g.*, DTA/DTG methods) be-

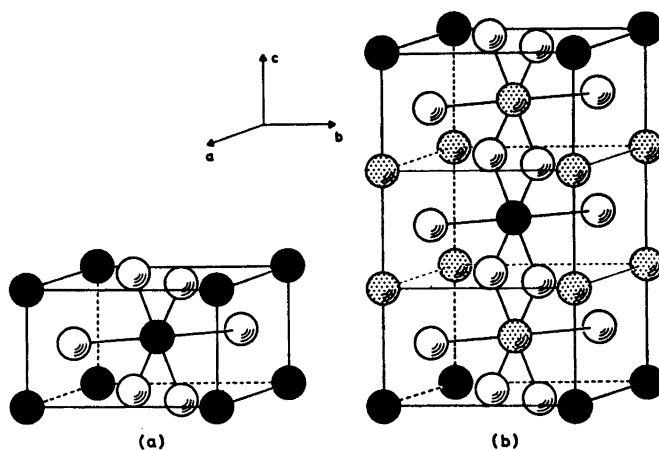


Fig. 1. Models emphasizing the main features of the (a) rutile or so-called random-rutile and (b) tri-rutile type structures.

Table 1. Room temperature tetragonal unit cell dimensions (with standard deviations) for  $MSbO_4$  and  $MSb_2O_6$ .

Random-rutiles			Tri-rutiles		
Compound	$a$ (Å)	$c$ (Å)	Compound	$a$ (Å)	$c$ (Å)
CrSbO <sub>4</sub>	4.5837(3)	3.0477(4)	MgSb <sub>2</sub> O <sub>6</sub>	4.6489(6)	9.2334(17)
FeSbO <sub>4</sub>	4.6347(3)	3.0732(3)	CoSb <sub>2</sub> O <sub>6</sub>	4.6535(4)	9.2804(18)
RhSbO <sub>4</sub>	4.6122(7)	3.1073(6)	NiSb <sub>2</sub> O <sub>6</sub>	4.6417(4)	9.2203(15)
AlSbO <sub>4</sub>	4.5300(4)	2.9731(4)	CuSb <sub>2</sub> O <sub>6</sub> <sup>a</sup>	4.6353(4)	9.2993(13)
GaSbO <sub>4</sub>	4.5986(9)	3.0349(10)	ZnSb <sub>2</sub> O <sub>6</sub>	4.6679(5)	9.2676(15)

<sup>a</sup> Monoclinically deformed;  $a=b$  (calculated, not fixed) and  $\beta=91.15(1)$ .

cause of disturbing reactions with all crucible materials tried.

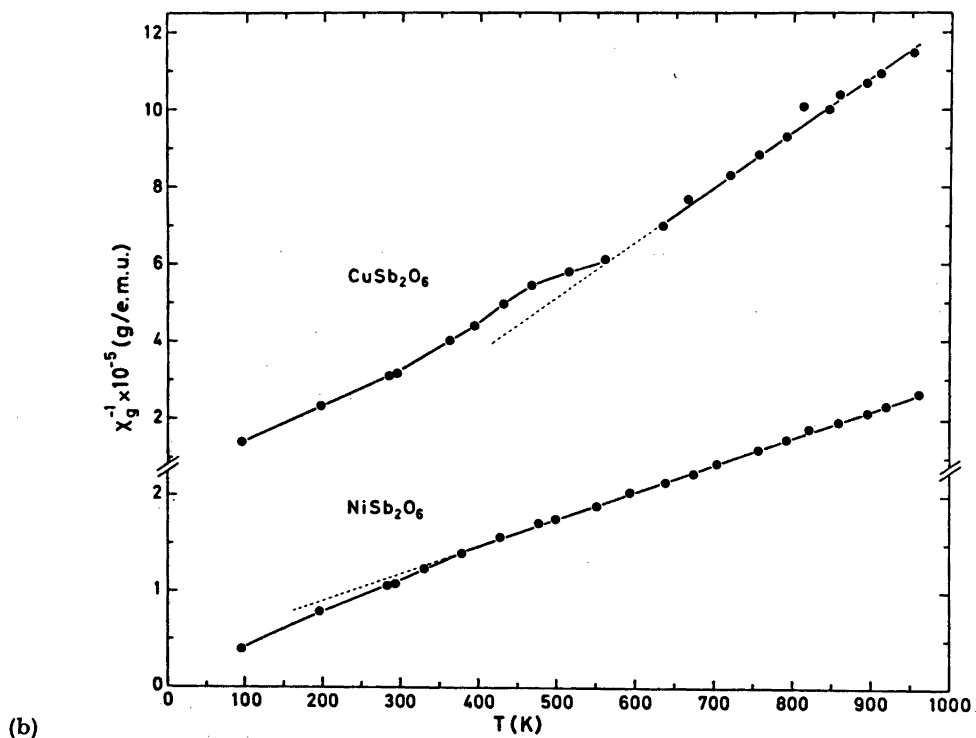
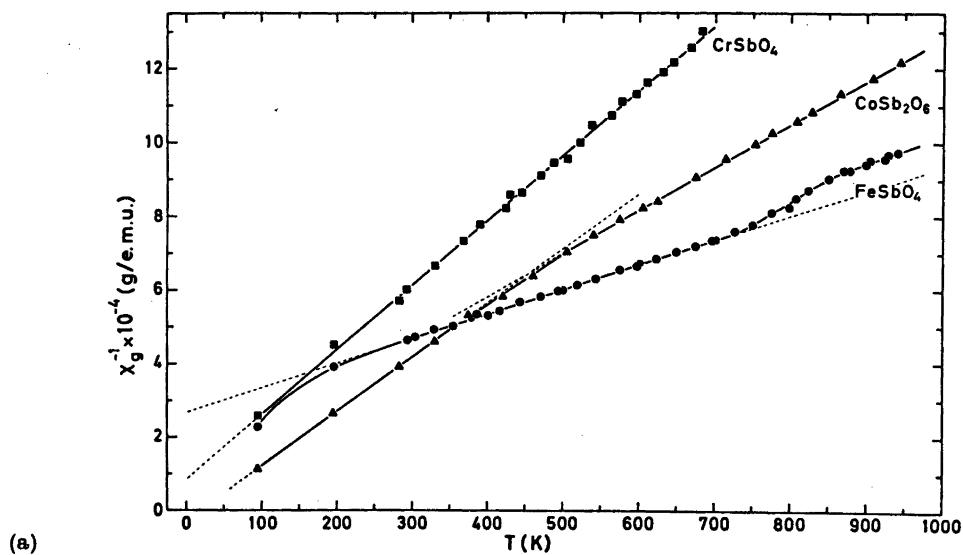
The present samples are conveniently characterized by the unit cell dimensions recorded in Table 1; these data also serve to establish identity with those studied in Refs. 11, 12.

Among the  $MSbO_4$  and  $MSb_2O_6$  compounds reported earlier, only  $M=Fe$  was claimed in both variants. For this reason considerable efforts were made to duplicate the preparation of  $FeSb_2O_6$ , using the original recipe,<sup>11</sup> coprecipitation reactions (see Experimental), as well as oxidation experiments on  $FeSb_2$ . According to Ref. 11,  $FeSb_2O_6$  should be obtainable at 1000 °C, but even systematic variation of the reaction and annealing temperatures between 600 and 1100 °C did not result in the desired compound. As a matter of fact,  $FeSbO_4$  was invariably obtained, and

as the only product at ~1000 °C (more specifically  $900 \leq t \leq 1100$  °C), where the excess antimony oxide originally present in the crucible was observed to volatilize. These findings do not finally reject  $FeSb_2O_6$  as non-existent, since the synthesis of the related  $FeTa_2O_6$  could only be obtained<sup>13</sup> through a careful control of the oxygen partial pressure.

Contrary to the suggestion in Ref. 6, no indication of a homogeneity range has been observed for  $NiSb_2O_6$ . (The distinction between brown and green reaction products consists in different crystallite size, the former being presently observed for roughly amorphous products.)

(ii) *Magnetic susceptibilities.* The sign of the magnetic susceptibilities divides the compounds under consideration into a diamagnetic and a paramagnetic class. The fact that the present



*Fig. 2.* The reciprocal magnetic susceptibility of (a)  $\text{CrSbO}_4$ ,  $\text{FeSbO}_4$ , and  $\text{CoSb}_2\text{O}_6$  and (b)  $\text{NiSb}_2\text{O}_6$  and  $\text{CuSb}_2\text{O}_6$  as a function of temperature.

Table 2. Susceptibilities of diamagnetic  $MSbO_4$  and  $MSb_2O_6$  expressed according to  $(1/\chi_g) \times 10^{-6} = AT - B$  ( $90 \leq T \leq 950$  K).

Compound	$A \times 10^6$ (g/e.m.u.K)	$B$ (g/e.m.u.)
$AlSbO_4$	0.1	3.0
$GaSbO_4$	3.4	5.5
$RhSbO_4$	0.0	8.1
$MgSb_2O_6$	1.5	3.5
$ZnSb_2O_6$	4.3	7.4

Table 3. Evaluated parameters ( $\theta$ ,  $\mu_p$ ,  $2S$ ) for temperature intervals ( $T_i$  to  $T_f$ ) where Curie-Weiss Law is satisfied for  $MSbO_4$  and  $MSb_2O_6$ . Estimated uncertainties in  $\mu_p$  are  $\pm 0.1$  B.M.; correspondingly in  $2S$ .

Compound	$T_i - T_f$ (K)	$\theta$ (K)	$\mu_p$ (B.M.)	$2S$	$n$
$CrSbO_4$	90–950	$-50 \pm 10$	3.3	2.5	3
$FeSbO_4$	250–730	$-400 \pm 60$	5.4	4.5	5
$CoSb_2O_6$	90–375	$-20 \pm 5$	4.6	3.7	3
	500–950	$-110 \pm 20$	5.3	4.4	—
$NiSb_2O_6$	90–375	$-15 \pm 5$	3.0	2.2	2
	375–950	$-110 \pm 20$	3.3	2.5	—
$CuSb_2O_6$	90–300	$-50 \pm 10$	1.9	1.1	1
	560–950	$+140 \pm 30$	1.5	0.8	—

data are uncorrected for induced diamagnetism (due to the lack of reliable corrections) does not alter this classification.

The reciprocal susceptibility ( $1/\chi$ ) of the diamagnetic compounds  $MgSb_2O_6$ ,  $ZnSb_2O_6$ ,  $AlSbO_4$ ,  $GaSbO_4$  and  $RhSbO_4$  show a linear dependence on temperature ( $T$ ) to a reasonable approximation. These relationships are conveniently used to present our results for the compounds in Table 2.

As illustrated in Fig. 2, the paramagnetic compounds  $CrSbO_4$ ,  $FeSbO_4$ ,  $CoSb_2O_6$ ,  $NiSb_2O_6$ , and  $CuSb_2O_6$  satisfy Curie-Weiss Law [ $\chi^{-1} = C^{-1}(T - \theta)$  where  $C$  and  $\theta$  are the Curie and Weiss constants, respectively] over various temperature intervals. The  $1/\chi_g$  versus  $T$  curve for  $CrSbO_4$  is linear (90–950 K; the part from 650 to 950 K being omitted in order to compress the diagram), that for  $NiSb_2O_6$  consists of two linear spans, whereas those for  $FeSbO_4$ ,  $CoSb_2O_6$ , and  $CuSb_2O_6$  reveal addi-

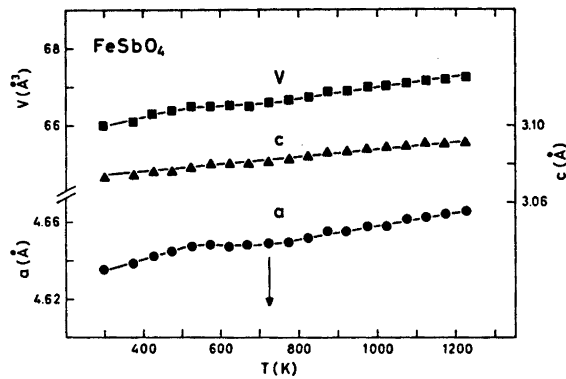
tional curved sections. The characteristic magnetic parameters [ $\theta$ ,  $\mu_p = \sqrt{8C_{mol}} =$  paramagnetic moment, and  $S =$  spin quantum number according to the "spin only" approximation  $\mu_p = g\sqrt{S(S+1)}$  with  $g = 2$ ] are listed in Table 3. The last column of the table gives the number of unpaired electrons ( $n$ ) predicted from ionic models ( $M^{3+}$ ,  $Sb^{5+}$ ,  $4O^{2-}$  and  $M^{2+}$ ,  $2Sb^{5+}$ ,  $6O^{2-}$ ) with completely quenched orbital momenta for the  $M$  atoms. The discrepancies between these and the "observed" values ( $2S$ ) are no more than one would expect from the crudeness of the models, and the findings concur to that extent with those for other compounds when compared with unrealistic ionic models.

The changes in the "number of unpaired electrons" as functions of temperature, as brought out in Fig. 2 and Table 3, appear to be of different origin. As discussed in section (iii), the thermomagnetic behaviour of  $CuSb_2O_6$  below 560 K has its parallel in structural alterations. The deviation from Curie-Weiss Law for  $FeSbO_4$  above 725 K may also be correlated with structural features. The changes at 375–500 and 375 K (Fig. 2) in  $CoSb_2O_6$  and  $NiSb_2O_6$ , respectively, are, on the other hand, not correlated with observable structural effects.

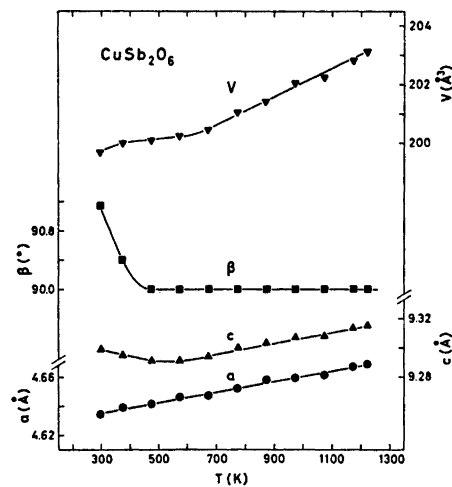
Concerning the possibility of cooperative magnetic ordering in these compounds at low temperatures, no definite conclusion can be drawn from the present thermomagnetic data. The most interesting candidate for a low temperature neutron diffraction study is  $FeSbO_4$ , with  $\theta = -400$  K and a curved  $1/\chi$  versus  $T$  portion below 250 K.

(iii) *Structural aspects.* The room temperature structures of the compounds under consideration divide into three categories:  $MSbO_4$  (tetragonal),  $MSb_2O_6$  (tetragonal), and  $CuSb_2O_6$  (monoclinic); cf. Table 1.

According to a more detailed description,  $MSbO_4$  should belong<sup>12</sup> to the  $TiO_2$ - $r$  type structure [space group  $P4_2/mnm$ :  $M$  and  $Sb$  randomly distributed in  $2(a)$ ,  $O$  in  $4(f)$ ]. As also illustrated in Fig. 1, the tri-rutiles  $MSb_2O_6$  should have<sup>11</sup> an ordered rutile-like atomic arrangement [space group  $P4_2/mnm$ :  $M$  in  $2(a)$ ,  $Sb$  in  $4(e)$ ,  $O_I$  in  $4(f)$ , and  $O_{II}$  in  $8(j)$ ] with trebled  $c$  axis. The structure of  $CuSb_2O_6$  at room temperature is registered<sup>11</sup> as a monoclinically distorted variant [space group  $P2_1/c$ :



(a)



(b)

Fig. 3. Unit cell dimensions of (a)  $\text{FeSbO}_4$  and (b)  $\text{CuSb}_2\text{O}_6$  versus temperature.

Cu in 2(a), Sb in 4(e),  $\text{O}_I$  in 4(e),  $\text{O}_{II}$  in 4(e), and  $\text{O}_{III}$  in 4(e)] of the tri-rutile type.

Common for all these compounds is that no proper structure determination has been carried out. The structural assignments have merely been done on the basis of rather superficial tests, in which only a selected value (set of values) for the variable positional parameters have been used to calculate X-ray intensities for comparison with visually estimated powder data. For this reason, all these compounds are candidates for structural reinvestigations.

The demand for anewed attention is greater for  $\text{MSbO}_4$  than for the others since the hitherto assumed complete crystallographic equivalence of  $M$  and Sb appears difficultly reconcilable. [The situation for  $\text{MSbO}_4$  may, in many re-

spects, be a parallel to that for  $\text{TeO}_2$  prior to 1961 (*cf.* Ref. 14), and the interesting findings for the latter compound should stimulate anewed attention on  $\text{MSbO}_4$ .] In view of the experimental difficulties encountered in attempts to prepare single crystals of  $\text{MSbO}_4$ , the powder neutron diffraction technique lends itself as the most suitable means of investigation.

If one accepts as a working hypothesis that  $M$  and Sb really are distributed at random in  $\text{MSbO}_4$ , it is pertinent to ask whether randomization of  $M$  and Sb also occurs in  $\text{MSb}_2\text{O}_6$  at high temperatures (*viz.* search for a tri-rutile to random-rutile type, order/disorder transformation in the latter class of compounds). For this reason  $\text{MSb}_2\text{O}_6$  and  $\text{MSbO}_4$  (for com-

parison purposes) were subjected to differential thermal analysis, high temperature X-ray diffraction, and quenching experiments (see Ref. 15) between room temperature and 1100 °C. None of the  $MSb_2O_6$  compounds showed any sign of an order/disorder transformation. This finding makes the assumed disordered status of  $MSbO_4$  even more intriguing.

The thermal expansion curves of  $FeSbO_4$  and  $CuSb_2O_6$  are presented in Fig. 3, since the thermomagnetic curves (Fig. 2) for these compounds showed somewhat abnormal behaviours. Fig. 3a demonstrates changes in the slopes of  $a$  and  $V$  at 725 K, which is just the temperature for the commencing anomaly in the magnetic susceptibility. Whereas the significance of the coincidences for  $FeSbO_4$  may well be argued, the correlation between structural and magnetic behaviour of  $CuSb_2O_6$  appears to be more clear-cut. As evident from Fig. 3b,  $CuSb_2O_6$  undergoes a structural alteration above room temperature, where the symmetry changes from monoclinic to tetragonal. The monoclinic angle ( $\beta$ ) for the distorted tri-rutile type modification of  $CuSb_2O_6$  is not sensitive enough for a stipulation of the temperature for the reversible, second (or higher) order phase transition. The minimum (at  $\sim 550$  K) in the thermal expansion curve for  $c$  (Fig. 3b) may provide a better measure for the conversion temperature; it is interesting to note that this matches the upper temperature of the non-linear  $\chi^{-1}(T)$  section (Fig. 2b and Table 3).

A detailed structural investigation of  $CuSb_2O_6$  at low and high temperatures is highly desirable, but, it is nevertheless tempting to present some naive considerations on the present findings. The distorted tri-rutile type structure for  $CuSb_2O_6$  is perhaps not unexpected in view of the fact that high-spin Cu(II) compounds frequently exhibit so-called Jahn-Teller distortions of their octahedral coordination. The situation in low temperature  $CuSb_2O_6$  may thus be analogous to that in  $CuF_2$ , where the regular  $TiO_2$ - $r$  type structure is also monoclinically distorted.<sup>16</sup> However, if a Jahn-Teller mechanism could be held responsible for the distortion in monoclinic  $CuSb_2O_6$  relative to tetragonal  $CuSb_2O_6$ , another mechanism [*e.g.*, (partial) delocalization of the unpaired electron] would have to be invented to account for the occurrence of the latter variant.

Table 4.  $^{121}Sb$  Mössbauer parameters for  $CrSbO_4$ ,  $FeSbO_4$ ,  $GaSbO_4$ ,  $MgSb_2O_6$ ,  $CoSb_2O_6$ , and  $CuSb_2O_6$  at 4.2 K; chemical shifts with respect to  $Ba^{121}SnO_3$ . Probable experimental errors are  $\pm 0.01$  mm/s in  $\delta$ ,  $\pm 1.0$  mm/s in  $eQV_{zz}$ , and  $\pm 0.05$  mm/s in  $\Gamma$  (width at half maximum).

	$\delta$ (mm/s)	$eQV_{zz}$ (mm/s)	$\Gamma$ (mm/s)	$\eta$	A (%)
$CrSbO_4$	-0.18	0 (fixed)	4.99	—	14.8
	-0.19	7.8	4.35	0.94	14.8
$FeSbO_4$	-0.07	0 (fixed)	6.59	—	15.3
	-0.06	5.1	3.87	0.90	15.3
$GaSbO_4$	+0.35	0 (fixed)	3.50	—	23.4
	+0.34	1.5	3.35	—	23.4
$MgSb_2O_6$	+0.17	0 (fixed)	3.00	—	15.1
	+0.15	3.8	2.75	—	15.1
$CoSb_2O_6$	-0.17	0 (fixed)	3.85	—	15.8
	-0.16	2.7	3.35	—	15.8
$CuSb_2O_6$	+0.13	0 (fixed)	2.92	—	22.5
	+0.13	1.3	2.89	—	22.5

(iv)  $^{121}Sb$  Mössbauer spectroscopy. The  $^{121}Sb$  Mössbauer parameters for  $CrSbO_4$ ,  $FeSbO_4$ ,  $GaSbO_4$ ,  $MgSb_2O_6$ ,  $CoSb_2O_6$ , and  $CuSb_2O_6$  derived from computer fitting of data collected at 4.2 K are contained in Table 4. The chemical shifts ( $\delta$ ) are given with respect to  $Ba^{121}SnO_3$  source and when converted to shifts relative to the InSb standard, the present  $\delta$  values are in excellent agreement with those obtained by Wooten *et al.*<sup>8</sup> at 77 K. The quadrupole interaction ( $eQV_{zz}$ ) is small for all compounds and is hardly significant for  $MgSb_2O_6$  and insignificant for  $GaSbO_4$ ,  $CoSb_2O_6$ , and  $CuSb_2O_6$ .

Neither the present results nor those of Wooten *et al.*<sup>8</sup> give any definite indication of spectral line broadening or splitting originating from magnetic coupling between the  $M$  atoms in the compounds referred to as paramagnetic in section ii.

There is some correlation between  $\delta$  and structure, which Wooten *et al.* couple to charges on the  $M$  atoms according to a formal ionic model. However, the magnitude of  $\delta$  appears to be more typical of covalently bonded Sb(V). Other aspects are taken up in Ref. 6.

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Received March 25, 1975.