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Compounds with the Skutterudite Type Crystal Structure

II. The ^{121}Sb Mössbauer Effect in $CoSb_3$, $Fe_{0.5}Ni_{0.5}Sb_3$, $RhSb_3$, and $IrSb_3$

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^{121}Sb Mössbauer spectra of $CoSb_3$, $Fe_{0.5}Ni_{0.5}Sb_3$, $RhSb_3$, and $IrSb_3$ have been obtained at 4.2 K and are discussed in relation to their $CoAs_3$ type structure. The data provide additional evidence in support of the bonding being predominantly of a covalent nature in these compounds.

The application of ^{121}Sb Mössbauer spectroscopy has, in recent years, stimulated studies on the bonding properties of antimony compounds. Of particular interest in this connection are a number of binary antimonides whose accurately determined crystal structures facilitate the interpretation and permit semi-quantitative comparisons between the crystallographic and electronic environments of antimony. As an example of such an investigation reference [1] is made to a recent discussion on the ^{121}Sb Mössbauer parameters for a series of diantimonides with the pyrite, marcasite, or arsenopyrite type crystal structures. We report here corresponding data for $CoSb_3$, $Fe_{0.5}Ni_{0.5}Sb_3$, $RhSb_3$, and $IrSb_3$ with the $CoAs_3$ (skutterudite) type crystal structure.

EXPERIMENTAL

The compounds were prepared by heating stoichiometric quantities of the elements (in the form of turnings from Fe, Co, and Ni rods and Rh, Ir, and Sb powders all from Johnson, Matthey & Co; spectroscopically standardized and of purity better than 99.99 %) in evacuated, sealed quartz tubes. The binary samples were maintained for one week at 750 ($CoSb_3$) or 850°C ($RhSb_3$ and $IrSb_3$), crushed, reannealed for a further week at the same temperature, and finally cooled to room temperature over a period of three days. The ternary sample $Fe_{0.5}Ni_{0.5}Sb_3$ was prepared similarly at 650°C, crushed and subjected to three further annealings at 600°C with intermediate crushings.

The experimental details concerning the X-ray diffraction and ^{57}Fe and ^{121}Sb Mössbauer measurements have been presented in previous communications.[1,2]

RESULTS AND DISCUSSION

The identity and homogeneity of the compounds were ascertained from Guinier photographs, which gave the unit cell dimensions $a = 9.0347(6)$, 9.2322(6), 9.2533(5), and 9.0904(5) Å for $CoSb_3$, $RhSb_3$, $IrSb_3$, and $Fe_{0.5}Ni_{0.5}Sb_3$, respectively, in good agreement with earlier findings.[3–9]

The room temperature ^{57}Fe Mössbauer spectrum for $Fe_{0.5}Ni_{0.5}Sb_3$ consists of a single absorption peak of line-width $\Gamma = 0.64$ mm/s which is positioned at a chemical shift value of $\delta = 0.29 \pm 0.01$ mm/s relative to metallic iron.

The magnitude of δ is consistent with the Fe atoms attaining a formal low-spin $3d^6$ electron configuration (*vide infra*). In compounds with the $CoAs_3$ type structure the metal (T) atoms are octahedrally coordinated to six non-metal (X) atoms, the T site being only slightly distorted from O_h symmetry (*cf.*, *e.g.*, Refs. 10 – 12). The lack of a resolvable quadrupole interaction reflects this high crystallographic symmetry at the Fe site since for low-spin Fe(II) there is no contribution arising from the non-bonding d electrons.

Fig. 1 shows the ^{121}Sb Mössbauer spectra of $Fe_{0.5}Ni_{0.5}Sb_3$, $CoSb_3$, $RhSb_3$, and $IrSb_3$ taken at 4.2 K.

The Mössbauer transitions in ^{121}Sb occur between the nuclear spin states $7/2 \rightarrow 5/2$. The presence of an electric field gradient at the antimony nucleus will remove some of the degeneracies of these transitions although the short half-life of the excited state usually results in unresolved quadrupole split spectra. The relative line positions are determined by the eigenvalues of the ground and excited state Hamiltonians which involve the ratio ($R = 1.38$ [13]) of the excited and ground state quadrupole coupling constants and the asymmetry parameter η. For $\eta = 0$ the selection rules restrict the number of possible transitions to eight.

Using the same procedure as that outlined previously,[1] the observed spectra were initially least squares computer fitted to eight Lorentzians on a parabolic base line with $\eta = 0$. This resulted, however, in unsatisfactory fits for all the compounds. When η was allowed to vary in the least squares fitting procedure, the values listed in the diagram were obtained.

The spectral line shapes are broad and symmetrical for all compounds. There are a number of reasons to which line broadening can be attributed, *e.g.*, non-homogeneity, non-stoichiometry, more than one crystallographic Sb environment, and/or an internal magnetic field induced at the Sb site by the metal atoms. None of these factors, however, is relevant for these particular samples. Thus an explanation as to the line broadening must be sought elsewhere.

Inspection of the atomic arrangement of the $CoAs_3$ type structure [12] reveals that η must differ from zero since the immediate environment of the Sb atoms is of lower symmetry than C_{2v}. In fact, for a site of symmetry C_{2v}, in which all the bond angles attain the ideal tetrahedral value, η is expected to approach unity. For finite values of η all twelve possible Mössbauer transitions become allowed and the ratios of the individual peak intensities are modified. As an example of this effect we refer to Nichols *et al.*[14] who studied the influence of the asymmetry parameter on unresolved quadrupole splittings of the $7/2 \rightarrow 5/2$ Mössbauer transitions in ^{151}Eu showing that $\eta > 0.5$ causes significant spectral

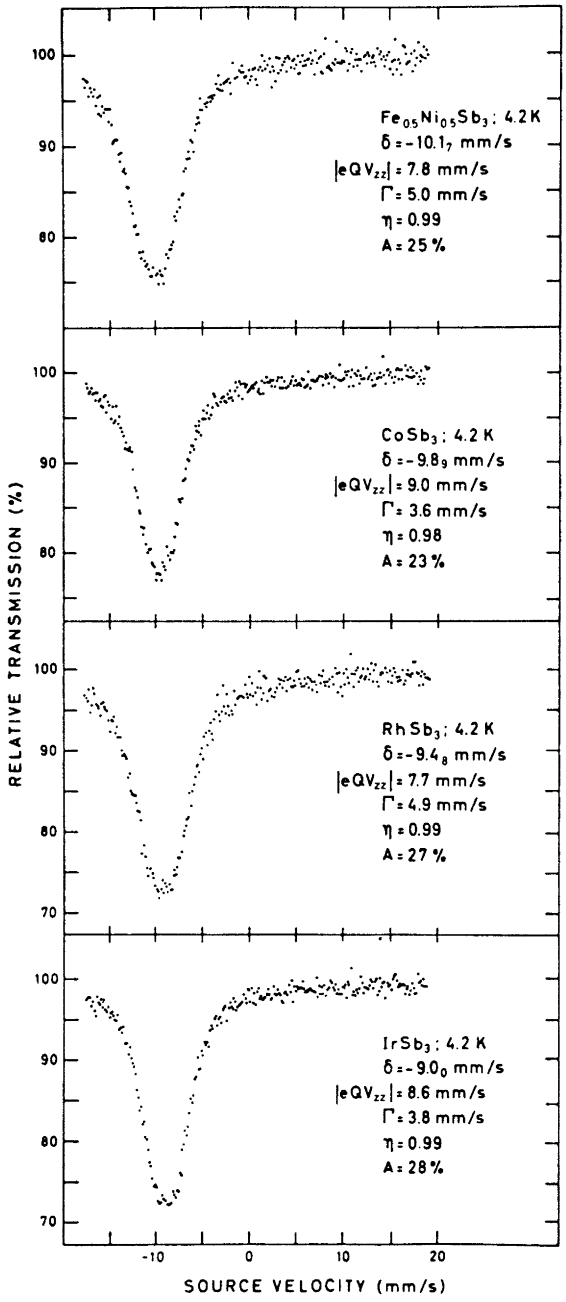

Fig. 1. ^{121}Sb Mössbauer spectra of $Fe_{0.5}Ni_{0.5}Sb_3$, $CoSb_3$, $RhSb_3$, and $IrSb_3$ at 4.2 K.

broadening. It is thus apparent that the fitting to eight Lorentzians for the present ^{121}Sb Mössbauer spectra is not a reasonable approximation.

In view of the time required to prepare a programme dealing with the considerably more complex general case for $\eta > 0.5$ it was decided to evaluate the computer data already at hand. In this situation the chemical shift values are taken to be meaningful because of the symmetric line shapes. Moreover, since the compounds are closely related the line widths of the individual transitions are assumed to be similar and the overall values for Γ provide at least an order for the magnitudes of the quadrupole interactions $|eQV_{zz}|$. There is of course a sign uncertainty in V_{zz} as a result of $\eta = 1$, because then $V_{yy} = -V_{zz}$.

The ^{121}Sb chemical shift values listed on Fig. 1 confirm the bonding to be of a predominantly covalent nature in the TSb$_3$ compounds. These δ values are more negative than that for the reference InSb (-8.9_3 mm/s at 4.2 K) implying higher total s electron densities at the Sb nuclei in the present compounds. The chemical shifts for CoSb$_3$, RhSb$_3$, and IrSb$_3$ are similar to, and show the same trend as, the corresponding compounds CoSb$_2$, RhSb$_2$, and IrSb$_2$ with the arsenopyrite type crystal structure.[1] The latter compounds have distorted tetrahedral environments around the Sb atoms in common with the TSb$_3$ compounds. Whilst the Sb atoms in the TSb$_2$ compounds are coordinated to one Sb and three T the Sb atoms in the TSb$_3$ compounds are coordinated to two Sb and two T. The observed variations in δ for the different chemical and crystallographic environments result from changes in population of the valence orbitals, the p and/or d orbitals affecting the overall s electron density at the Mössbauer nucleus by virtue of their shielding properties. The fact that substitution of a T by a Sb atom on going from the TSb$_2$ to the TSb$_3$ series does not cause large variations in δ lends support to the already inferred covalent nature of the bonding.

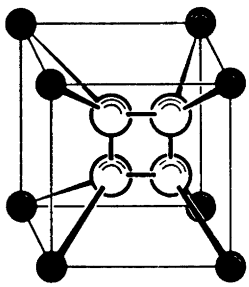

Fig. 2. Model showing a rectangular Sb$_4$ group bonded to two T atoms at each corner.

As illustrated in Fig. 2 the most striking feature of the CoAs$_3$ type structure is the collection of the non-metal atoms into planar X_4 groups. There is a rectangular distortion from an ideal square arrangement of these X_4 groups which is of the order of 5 %. This rectangular distortion is imposed by the crystal structure and is attributed to anisotropic interactions arising from the non-metal sublattice and not to any differences in covalency between the Sb–T and Sb–Sb bonds or to the T sublattice.[12]

The Sb and T atomic wave functions of the molecular fragment SbT_2Sb_2 (Fig. 2) transform to a first approximation as described by the irreducible representations of point group C_{2v}. The bonding orbitals are envisaged as linear combinations taken over a Sb and its surrounding two Sb and two T atoms using s, p, and d atomic wave functions for T and s and p atomic wave functions for Sb. The magnitude of the $T-Sb-T$ bond angle reflects the mixing of the $5p_z$ and $5s$ contributions. The fact that the $Sb-Sb-Sb$ bond angle is fixed at 90° implies that the contribution to the $Sb-Sb$ bonds comes from the $5p_x$ and $5p_y$ orbitals only.

The rectangular distortion of the Sb_4 groups which causes two different $Sb-Sb$ bond lengths is not insignificant.[15] The effect of this is to decrease orbital overlap in the longer $Sb-Sb$ bond with respect to the shorter. However, these bond differences do not vary significantly within the TSb_3 series and this suggests that the rectangular distortion is not the major cause of the variation in δ values. Thus, within this series of compounds the changes in δ, which parallel those found for the corresponding TSb_2 compounds, mainly reflect the different bonding characteristics of the T atoms, notably the differences in the principal quantum number which causes significant variations in $Sb-T$ orbital overlaps.

In a previous paper [1] it is shown that a measure of the angular part of the distortion from cubic (T_d) symmetry is given by the average deviation (ξ) of the bond angles from the tetrahedral value of 109.47°. For the TSb_2 compounds the values of ξ (ranging between 8.3 and 13.6°) have been found to correlate well with the ^{121}Sb Mössbauer quadrupole coupling constants. Largely because of the restrained $Sb-Sb-Sb$ bond angle (90°) ξ is virtually constant for compounds with the $CoAs_3$ type structure. Hence, a corresponding relationship is unobservable for the TSb_3 series and any variation in $|eQV_{zz}|$ is attributable to dissimilar electron imbalances in the Sb $5p_z$ orbital.

It is characteristic for compounds with the $CoAs_3$ type structure that the T atoms attain a formal low-spin d^6 (t_{2g}^6) configuration. The apparent exception provided by NiP_3,[10] in which the Ni atoms are formally d^7, is explained by the seventh electron being delocalized over the macromolecule. The ternary series [16-18] produced by substituting Co by Fe or Ni are additional pieces of the "jigsaw puzzle" which fall into position. The limit to which the apparently incompatible Ni atoms are tolerated by the $CoAs_3$ type structure without destroying its basic stability decreases in the sequence CoP_3, $CoAs_3$, and $CoSb_3$. The opposite trend is evident on substitution of Co by Fe.

As for the non-metal atoms the $CoAs_3$ type structure appears to be limited to pnictides and there are no reports concerning the existence of corresponding compounds with Group IVB or VIB elements. Regarding the t_{2g}^6 configuration of T as being a significant feature of the skutterudites, then the hypothetical chalcogenides would be restricted to Cr, Mo, or W in a formally zero valence state. Because of the large diffuse d orbitals on the non-metal atoms [19] π back-bonding is presumably ineffective and hence, such low valence states on T would be unstable. On the other hand, hypothetical Group IVB skutterudites would require an unusually high valence state of T (*e.g.* Zn(VI), Cd(VI), or Hg(VI)).

REFERENCES

1. Donaldson, J. D., Kjekshus, A., Nicholson, D. G. and Tricker, M. J. *Acta Chem. Scand.* **26** (1972) 3215.

2. Kjekshus, A., Nicholson, D. G. and Mukherjee, A. D. *Acta Chem. Scand.* **26** (1972) 1105.
3. Rosenqvist, T. *Acta Met.* **1** (1953) 761; *N.T.H.-Trykk*, Trondheim 1953.
4. Zhuravlev, N. N. and Zhdanov, G. S. *Kristallografiya* **1** (1956) 509.
5. Dudkin, L. D. and Abrikosov, N. Kh. *Zh. Neorgan. Khim.* **1** (1956) 2096.
6. Hulliger, F. *Helv. Phys. Acta* **34** (1961) 782.
7. Kjekshus, A. and Pedersen, G. *Acta Cryst.* **14** (1961) 1065.
8. Kuz'min, R. N. and Snovidov, V. M. In Sirota, N. N., Ed., *Chemical Bonds in Semiconductors and Solids*, Consultants Bureau, New York 1967, p. 257.
9. Bjerkelund, E. and Kjekshus, A. *Acta Chem. Scand.* **24** (1970) 3317.
10. Rundqvist, S. and Ersson, N.-O. *Arkiv Kemi* **30** (1968) 103.
11. Mandel, N. and Donohue, J. *Acta Cryst.* **B 27** (1971) 2288.
12. Kjekshus, A., Nicholson, D. G. and Rakke, T. *Acta Chem. Scand.* **27** (1973) 1307.
13. Ruby, S. L., Kalvius, G. M., Snyder, R. E. and Beard, G. B. *Phys. Rev.* **148** (1966) 176.
14. Nichols, A. L., Large, N. R. and Lang, G. *Chem. Phys. Letters* **15** (1972) 598.
15. Kjekshus, A., and Rakke, T. *To be published.*
16. Roseboom, E. H. *Am. Mineralogist* **47** (1962) 310.
17. Pleass, C. M. and Heyding, R. D. *Can. J. Chem.* **40** (1962) 590.
18. Kuz'min, R. N. In Sirota, N. N., Ed., *Chemical Bonds in Semiconductors and Solids*, Consultants Bureau, New York 1967, p. 265.
19. Craig, D. P., Maccoll, A., Nyholm, R. S., Orgel, L. E. and Sutton, L. E. *J. Chem. Soc.* **1954** 332.

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