^{121}Sb Mössbauer Studies on Mo_3Sb_7 and $Nb_3Sb_2Te_5$

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^{121}Sb Mössbauer data for Mo_3Sb_7 and $Nb_3Sb_2Te_5$ have been obtained at 4.2 K and are discussed in relation to their crystal structures. The resolution of overlapping profiles arising from the two distinct Sb sites in Mo_3Sb_7 has been achieved through the use of a Fourier transform treatment. Sb has been assigned to the X_{II} site of the crystallographic formula $T_3(X_I)_3(X_{II})_4$ for $Nb_3Sb_2Te_5$.

By far the largest amount of experimental information on compounds in the solid state is concerned with structural data because any approach to bonding must begin with the atomic arrangement. For the transition metal pnictides and chalcogenides the amount of structural data at hand has attained a level where it is desirable to acquire supplementary information in order to proceed further with interpretations as to their bonding characteristics. Among the experimental techniques employed for this purpose, Mössbauer spectroscopy is particularly attractive because the probe nucleus reflects the electronic situation at the relevant site in the compound. Although the major part of such studies has been performed on ^{57}Fe and ^{119}Sn, the progress in data reduction (notably least squares fitting and Fourier transform procedures) is changing the situation and there is an increasing interest among chemists in alternative nuclei. The advances being made in ^{121}Sb Mössbauer methodology are typical of the development which is taking place. Even the complicating feature of a twelve line unresolved spectrum arising from a quadrupole splitting interaction of the $7/2 \rightarrow 5/2$ transition has its advantage in permitting the determination of the asymmetry parameter and sign of the quadrupole interaction.

The employment of the Fourier transform technique in the deconvolution of the source line-shape from the experimental absorption envelope provides the opportunity for examining antimonides which have structurally non-equivalent Sb atoms. Hence, as a continuation of previous studies [1-3] on transition metal antimonides we present here the results of an investigation of the isostructural [4,5] compounds Mo_3Sb_7 and $Nb_3Sb_2Te_5$.

EXPERIMENTAL

The experimental details concerning the purity of the elemental starting materials, sample preparation, characterization by X-ray diffraction, Mössbauer spectroscopic measurements and data reduction have been presented in previous communications.[1,6-9] (The Fourier transform computations were performed according to the programme of Ure and Flinn [10] and the experimental data least squares fitted to eight or twelve superimposed Lorentzian peaks employing the resonance line coefficients and transition probabilities of Shenoy and Dunlap.[11])

RESULTS AND DISCUSSION

Fig. 1 shows the ^{121}Sb Mössbauer spectra of Mo_3Sb_7 and $Nb_3Sb_2Te_5$. The Fourier transformed sharpened spectra (Fig. 2) reveal the presence of two different Sb sites in Mo_3Sb_7, but only one site in $Nb_3Sb_2Te_5$. In order to facilitate the discussion, a brief description is presented of the crystal structures of the compounds.

The Ir_3Ge_7 type structure of Mo_3Sb_7 and $Nb_3Sb_2Te_5$ contains two non-equivalent X atoms and the crystallographic formula is $T_3(X_I)_3(X_{II})_4$.[4,5] Those interatomic distances
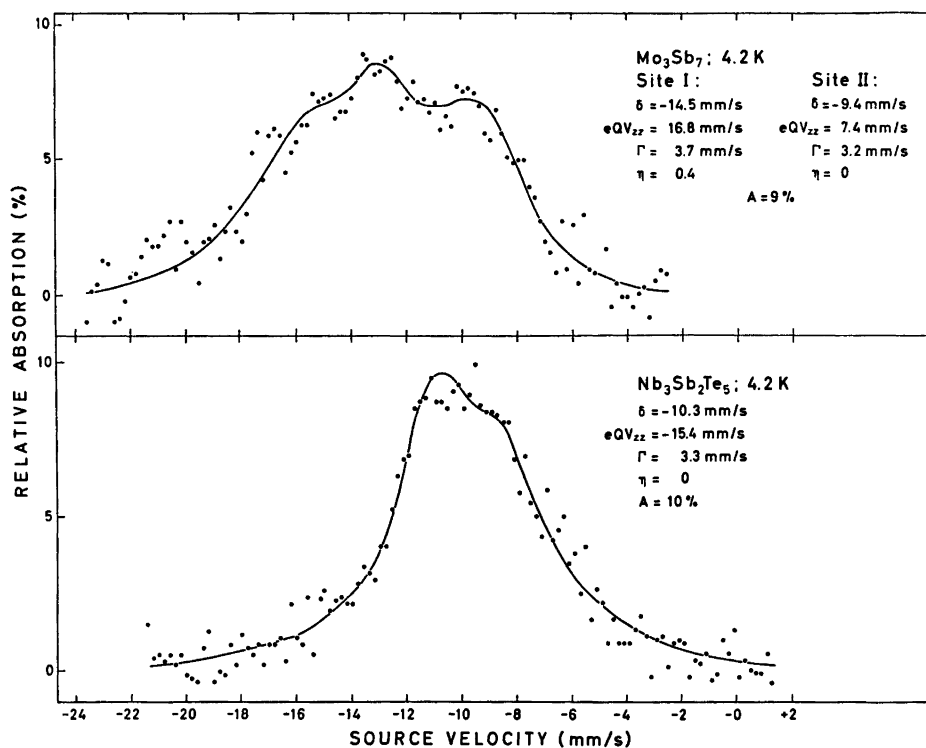
Fig. 1. ^{121}Sb Mössbauer spectra for $Nb_3Sb_2Te_5$ and Mo_3Sb_7. Smooth curves give calculated profiles.

Table 1. Bond distances and angles in $Nb_3Sb_2Te_5$, Mo_3Sb_7, and Re_3As_7, including average distortions from the tetrahedral angle of 109.47 for the bonds around X_I and X_{II}.

Distance (Å)	$Nb_3Sb_2Te_5$	Mo_3Sb_7	Re_3As_7
$4\ T-X_I,\ 4\ X_I-T$	2.900(5)	2.828(7)	2.584(4)
$4\ T-X_{II},\ 3\ X_{II}-T$	2.878(8)	2.793(10)	2.559(19)
$1\ T-T$	3.090(20)	3.015(25)	2.779(11)
$1\ X_{II}-X_{II}$	2.890(13)	2.905(14)	2.482(26)

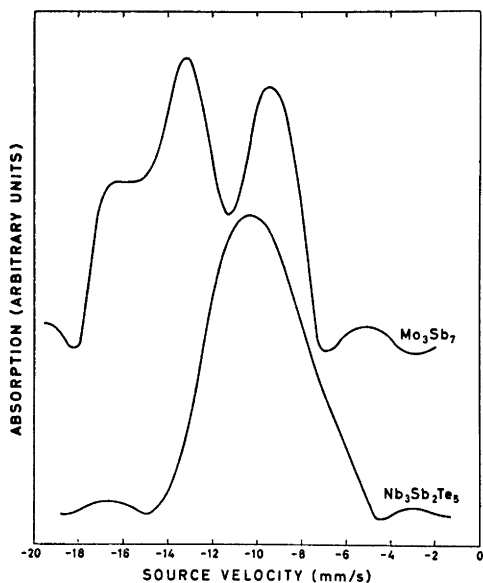| Angle (°)	$Nb_3Sb_2Te_5$	Mo_3Sb_7	Re_3As_7
$2\ T-X_I-T$	64.4(3)	64.4(4)	65.0(2)
$4\ T-X_I-T$	135.7(2)	135.7(3)	135.3(1)
Deviation ξ_I	32.5	32.5	32.0
$3\ T-X_{II}-T$	111.4(3)	112.2(2)	110.3(7)
$3\ T-X_{II}-X_{II}$	107.5(3)	106.6(3)	108.7(8)
Deviation ξ_{II}	2.0	3.0	0.8
$4\ X_I-T-X_I$	73.5(1)	73.5(2)	73.2(1)
$8\ X_I-T-X_{II}$	81.2(1)	81.8(1)	80.5(4)
$4\ X_{II}-T-X_{II}$	68.5(3)	67.6(3)	69.7(6)

Fig. 2. The Fourier transform sharpened spectra from Fig. 1.

which are presumed to be bond lengths are summarized in Table 1 together with the relevant angles. The corresponding data for Re_3As_7[12] are included for the purpose of comparison. Each T is coordinated to eight near X (four X_I and four X_{II}) at the corners of a somewhat distorted square antiprism. Each X_I is surrounded by four near T tetrahedrally arranged. The distortion of these T_4 tetrahedra produces $T-T$ pairs, and although their interatomic distance is about $2-10$ % longer than the shortest interatomic distances in the corresponding metals[13] a $T-T$ bonding interaction within the pairs strongly suggests itself as the cause of the distortion. The X_{II} atoms are coordinated to three near T and one near X_{II} and the resulting $X_{II}-X_{II}$ pairs have short interatomic distances closely matching the corresponding expectation values[14] for single $X-X$ bonds.

The composition $Nb_3Sb_2Te_5$ raises an interesting crystallographic problem associated with the distribution of Sb on the positions X_I and X_{II}. Due to the very small difference in the X-ray scattering factors of Sb and Te it could not be distinguished (*viz.* significantly) between the three simple alternatives: all Sb in X_I, all Sb in X_{II}, and a statistical distribution of Sb over

the X_I and X_{II} sites. However, the least squares refinements appeared[5] to show a slight preference for the second alternative.

In addition to revealing the presence of two sites in Mo_3Sb_7 the Fourier transform reduced spectra (Fig. 2) provide preliminary estimates for input parameters for the least squares fitting procedure. The final values for the chemical shifts (δ), quadrupole splittings (eQV_{zz}), line widths (Γ), and asymmetry parameters (η) are contained on Fig. 1, probable experimental errors being ± 0.1 mm/s in δ, ± 0.5 mm/s in eQV_{zz} (± 1 mm/s for site II in Mo_3Sb_7), ± 0.2 mm/s in Γ (± 0.4 mm/s for site II in Mo_3Sb_7), and ± 0.2 in η for site I in Mo_3Sb_7 ($\eta < 0.2$ for site II in Mo_3Sb_7 and in $Nb_3Sb_2Te_5$; fixed at zero during the final computations). (A δ value of -9.0 mm/s is obtained for the reference compound InSb at 4.2 K.)

The chemical shift which is directly governed by the *s* electron distribution over the bonds originating from Sb, is expected to be quite different for Sb_I and Sb_{II} in Mo_3Sb_7 (*vide supra*). This expectation is indeed confirmed by the shifts for the two sites in this compound which take the values -14.5 and -9.4 mm/s, both being in the region for Sb(III) valence states.[8,15]

At first sight it might have seemed natural to attempt an identification of the two contributions to the overall profile on the basis of the relative concentration of Sb atoms in the individual sites. However, such a naive approach appears somewhat dubious in this case where the bonding situations for the two kinds of Sb atoms are substantially different. This environmental distinction is bound to be reflected in the recoil free fractions for the two sites. The fact that X-ray diffraction sees[4] (within standard deviation) equal isotropic thermal vibration at room temperature is misleading in this connection. The Mössbauer experiments were performed at 4.2 K and on going from room to liquid helium temperature the vibrational characteristics for the two Sb sublattices are almost certainly no longer equal. Hence, identification must be based on the expected quadrupole interactions for the two sites.

In covalent compounds of the type studied here, the major contribution to quadrupole interactions at the Sb probe nuclei arises from the imbalances in $5p$ orbital occupation caused by deviations of the electronic environment

from cubic symmetry. It has previously been shown [1] that, for a series of ten structurally closely related antimonides, the average angular distortion (ξ) from the tetrahedral value of 109.47° for the bond angles subtended at Sb provides a relative measure for the deformation through its correlation with the eQV_{zz} values.

The coordination around Sb_{II} (cf. Table 1) takes C_{3v} symmetry and hence this site can be unambiguously identified with that having a calculated η value of zero and the small eQV_{zz}, V_{zz} being located along the $Sb_{II}-Sb_{II}$ bond. The actual value for the coupling constant for this site should be regarded as somewhat inaccurately determined because of its small magnitude and the appreciable overlap of a significant part of the envelope. Nevertheless, it is interesting to note that the definitely small eQV_{zz} value is consistent with an almost negligible ξ value of 3.0° for this site. Although the crystallographic symmetry of Sb_{II} is lowered from T_d to C_{3v} the p electron imbalance is not substantial because of the small eQV_{zz}. This suggests that there is no great difference between the p characters of the $Sb_{II}-Sb_{II}$ and $Sb_{II}-Mo$ bonds.

Although the four Sb_I-Mo bond lengths are constrained by symmetry to be equal, the coordination around Sb_I is heavily deformed from T_d symmetry in the bond angles. Moreover, since the six $Mo-Sb_I-Mo$ bond angles split into two groups of two and four, C_{3v} symmetry no longer applies. In line with this a finite η value has been derived for this site. Stronger evidence is provided by the large quadrupole coupling constant which is fully consistent with the remarkably high ξ value of 32.5° for the Sb_I site.

When the absorption envelope is unsymmetrical, the sign of eQV_{zz}, and hence, that of V_{zz} can be deduced. For Mo_3Sb_7 the sign of the quadrupole coupling constant is positive for the Sb_I site whereas that for Sb_{II} cannot be considered reliably determined. Since Q for ^{121}Sb is negative, V_{zz} for the Sb_I site is negative, which implies that the degree of electron delocalization from the Sb_I $5p_z$ orbital into the relevant "molecular orbitals" is lower than those from the $5p_x$ and $5p_y$ atomic orbitals.

It is worth noting that the small, but significant shortening of the $Sb-Mo$ bond on going from Sb_I to Sb_{II} corresponds to an increase in

the overall contribution from the Sb (in particular s) electrons to the bonding. This would effectively lower the total s electron density at the Sb nucleus and matches the smaller negative shift assigned to site II.

Turning now to the data for $Nb_3Sb_2Te_5$, the fact that its spectrum (cf. Figs. 1 and 2) shows apparently only one site eliminates the possibility of a statistical distribution of Sb on sites X_I and X_{II}. The question then arises as to which of these is occupied by Sb. The decision is taken on the basis of the reasonably close proximity of the δ values for $Nb_3Sb_2Te_5$ with that for the Sb_{II} site in Mo_3Sb_7. Hence, the conclusion from the ^{121}Sb Mössbauer data concurs with the indications from X-ray diffraction (cf. Ref. 5 and *vide supra*). Support for Sb being located in the X_{II} site is also provided by assuming similar electronic configurations of Mo in Mo_3Sb_7 and Nb in $Nb_3Sb_2Te_5$.

The accurately determined crystal structures of $Nb_3Sb_2Te_5$, Mo_3Sb_7, and Re_3As_7 show that the X_{II} sites are very similar in the crystallographic sense (cf. Table 1). Hence, the larger and positive value of V_{zz} for $Nb_3Sb_2Te_5$ must arise from electronic differences at the Sb_{II} site. This would indicate that the Sb $5p_z$ orbital is participating more strongly in Sb—Te bonding in $Nb_3Sb_2Te_5$ than in Sb—Sb bonding in Mo_3Sb_7, which, in turn, would be consistent with the slightly higher s electron density at Sb_{II} in $Nb_3Sb_2Te_5$ than Mo_3Sb_7 as reflected by the δ values. (We have also observed a positive sign for V_{zz} in the ^{121}Sb Mössbauer spectrum of SbTeI.[16])

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