\textbf{121}Sb Mössbauer Studies on Mo$_3$Sb$_7$ and Nb$_3$Sb$_2$Te$_5$

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$^{121}$Sb Mössbauer data for Mo$_3$Sb$_7$ and Nb$_3$Sb$_2$Te$_5$ 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$_3$Sb$_7$ has been achieved through the use of a Fourier transform treatment. Sb has been assigned to the X$_{II}$ site of the crystallographic formula $T_s(X_{I}S_{II})$ for Nb$_3$Sb$_2$Te$_5$.

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 $^{113}$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 nonequivalent 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$_3$Sb$_7$ and Nb$_3$Sb$_2$Te$_5$.

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.$^{1,4-9}$ (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 $^{113}$Sb Mössbauer spectra of Mo$_3$Sb$_7$ and Nb$_3$Sb$_2$Te$_5$. The Fourier transformed sharpened spectra (Fig. 2) reveal the presence of two different Sb sites in Mo$_3$Sb$_7$, but only one site in Nb$_3$Sb$_2$Te$_5$. In order to facilitate the discussion, a brief description is presented of the crystal structures of the compounds.

The Ir$_5$Ge$_3$ type structure of Mo$_3$Sb$_7$ and Nb$_3$Sb$_2$Te$_5$ contains two nonequivalent X atoms and the crystallographic formula is $T_s(X_{I}S_{II})$_4.$^{4,5}$ Those interatomic distances

Fig. 1. $^{125}$Sb Mössbauer spectra for Nb$_2$Sb$_2$Te$_5$ and Mo$_2$Sb$_7$. Smooth curves give calculated profiles.

Table 1. Bond distances and angles in Nb$_2$Sb$_2$Te$_5$, Mo$_2$Sb$_7$, and Re$_5$As$_7$, including average distortions from the tetrahedral angle of 109.47 for the bonds around $X_I$ and $X_{II}$.

<table>
<thead>
<tr>
<th>Distance (Å)</th>
<th>Nb$_2$Sb$_2$Te$_5$</th>
<th>Mo$_2$Sb$_7$</th>
<th>Re$_5$As$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 $T-X_I$, 4 $X_I-T$</td>
<td>2.900(5)</td>
<td>2.828(7)</td>
<td>2.584(4)</td>
</tr>
<tr>
<td>4 $T-X_{II}$, 3 $X_{II}-T$</td>
<td>2.878(8)</td>
<td>2.793(10)</td>
<td>2.559(19)</td>
</tr>
<tr>
<td>1 $T-T$</td>
<td>3.090(20)</td>
<td>3.015(25)</td>
<td>2.779(11)</td>
</tr>
<tr>
<td>1 $X_{II}-X_{II}$</td>
<td>2.890(13)</td>
<td>2.905(14)</td>
<td>2.482(26)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angle (°)</th>
<th>Nb$_2$Sb$_2$Te$_5$</th>
<th>Mo$_2$Sb$_7$</th>
<th>Re$_5$As$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 $T-X_I-T$</td>
<td>64.4(3)</td>
<td>64.4(4)</td>
<td>65.0(2)</td>
</tr>
<tr>
<td>4 $T-X_I-T$</td>
<td>135.7(2)</td>
<td>135.7(3)</td>
<td>135.3(1)</td>
</tr>
<tr>
<td>Deviation $\xi_I$</td>
<td>32.5</td>
<td>32.5</td>
<td>32.0</td>
</tr>
<tr>
<td>3 $T-X_{II}-T$</td>
<td>111.4(3)</td>
<td>112.2(2)</td>
<td>110.3(7)</td>
</tr>
<tr>
<td>3 $T-X_{II}-X_{II}$</td>
<td>107.5(3)</td>
<td>106.6(3)</td>
<td>108.7(8)</td>
</tr>
<tr>
<td>Deviation $\xi_{II}$</td>
<td>2.0</td>
<td>3.0</td>
<td>0.8</td>
</tr>
<tr>
<td>4 $X_I-T-X_I$</td>
<td>73.5(1)</td>
<td>73.5(2)</td>
<td>73.2(1)</td>
</tr>
<tr>
<td>8 $X_I-T-X_{II}$</td>
<td>81.2(1)</td>
<td>81.8(1)</td>
<td>80.5(4)</td>
</tr>
<tr>
<td>4 $X_{II}-T-X_{II}$</td>
<td>68.6(3)</td>
<td>67.6(3)</td>
<td>69.7(6)</td>
</tr>
</tbody>
</table>

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

In addition to revealing the presence of two sites in Mo$_5$Sb$_7$, 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 ($\delta$), quadrupole splittings ($eQV_{zz}$), line widths ($\Gamma$), and asymmetry parameters ($\eta$) are contained on Fig. 1, probable experimental errors being $\pm 0.1$ mm/s in $\delta$, $\pm 0.5$ mm/s in $eQV_{zz}$ ($\pm 1$ mm/s for site II in Mo$_5$Sb$_7$), $\pm 0.2$ mm/s in $\Gamma$ ($\pm 0.4$ mm/s for site II in Mo$_5$Sb$_7$), and $\pm 0.2$ in $\eta$ for site I in Mo$_5$Sb$_7$, $\eta < 0.2$ for site II in Mo$_5$Sb$_7$, and in Nb$_3$Sb$_7$Te$_5$; fixed at zero during the final computations. (A $\delta$ 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$_7$ and Sb$_{II}$ in Mo$_5$Sb$_7$ (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.

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 see 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 5$p$ orbital occupation caused by deviations of the electronic environment.
from cubic symmetry. It has previously been shown 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 eQV₄ values.

The coordination around Sb₁₁ (cf. Table 1) takes C₃ᵥ symmetry and hence this site can be unambiguously identified with that having a calculated η value of zero and the small eQV₄, V₄ being located along the Sb₁₁–Sb₁₁ 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 eQV₄ value is consistent with an almost negligible ξ value of 3.0° for this site. Although the crystallographic symmetry of Sb₁₁ is lowered from T₄ to C₃ᵥ the p electron imbalance is not substantial because of the small eQV₄. This suggests that there is no great difference between the p characters of the Sb₁₁–Sb₁₁ and Sb₁₁–Mo bonds.

Although the four Sb₁–Mo bond lengths are constrained by symmetry to be equal, the coordination around Sb₁ is heavily deformed from T₄ symmetry in the bond angles. Moreover, since the six Mo–Sb₁–Mo bond angles split into two groups of two and four, C₃ᵥ 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 Sb₁ site.

When the absorption envelope is unsymmetrical, the sign of eQV₄, and hence, that of V₄, can be deduced. For Mo₃Sb₁, the sign of the quadrupole coupling constant is positive for the Sb₁ site whereas that for Sb₁₁ cannot be considered reliably determined. Since eQ for ¹¹⁹Sb is negative, V₄ for the Sb₁ site is negative, which implies that the degree of electron delocalization from the Sb₁ ⁵p₂ orbital into the relevant “molecular orbitals” is lower than those from the ⁵p₂ and ⁵p₃ atomic orbitals.

It is worth noting that the small, but significant, shortening of the Sb–Mo bond on going from Sb₁ to Sb₁₁ 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 Nb₃Sb₁₁Te₅, 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 X₁ and X₁₁. 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 Nb₃Sb₁₁Te₅ with that for the Sb₁₁ site in Mo₃Sb₁. Hence, the conclusion from the ¹¹⁹Sb Mössbauer data concurs with the indications from X-ray diffraction (cf. Ref. 5 and vide supra). Support for Sb being located in the X₁₁ site is also provided by assuming similar electronic configurations of Mo in Mo₃Sb₁ and Nb in Nb₃Sb₁₁Te₅.

The accurately determined crystal structures of Nb₃Sb₁₁Te₅, Mo₃Sb₁, and Re₃As₃ show that the X₁₁ sites are very similar in the crystallographic sense (cf. Table 1). Hence, the larger and positive value of V₄ for Nb₃Sb₁₁Te₅ must arise from electronic differences at the Sb₁₁ site. This would indicate that the Sb ⁵p₀ orbital is participating more strongly in Sb–Te bonding in Nb₃Sb₁₁Te₅ than in Sb–Sb bonding in Mo₃Sb₁, which, in turn, would be consistent with the slightly higher s electron density at Sb₁₁ in Nb₃Sb₁₁Te₅ than Mo₃Sb₁ as reflected by the δ values. (We have also observed a positive sign for V₄ in the ¹¹⁹Sb Mössbauer spectrum of SbTeI.)

REFERENCES


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