An Antimony-121 Mössbauer and Electron Spin Resonance Study of Some Antimony–Molybdenum–Oxygen and Antimony–Tungsten–Oxygen Compounds

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121-Antimony Mössbauer and e.s.r. spectroscopies have been used to examine Sb_2WO_6, Sb_2MoO_6, and $Sb_2Mo_3O_{12}$. In Sb_2WO_6 the cations are Sb^{III} and W^{VI}, but in Sb_2MoO_6 and $Sb_2Mo_3O_{12}$ the antimony is present as both Sb^{III} and Sb^{V}. This implies that some of the Mo exists in an oxidation state, or states, lower than VI. This is confirmed by e.s.r. spectroscopy.

The antimony–molybdenum–oxygen and antimony–tungsten–oxygen systems have been used as selective oxidation catalysts for the conversion of olefins to partially oxidized products, such as acrolein[1] and methacrolein.[2] Despite the commercial development of these solids there have been few attempts to investigate the solid-state properties of molybdenum or tungsten antimonates. Indeed while Parmentier *et al.* reported the preparation and powder *X*-ray data of the tungsten antimonate Sb_2WO_6[3] and molybdenum antimonates[4] described as Sb_2MoO_6 and $Sb_2Mo_3O_{12}$ between 1974 and 1975, the structure of Sb_2MoO_6 has been determined only recently.[5,6] However, no attempt has been made to characterize the oxidation states of the cations in these mixed-metal oxides. Mössbauer spectroscopy is well suited to the investigation of the electronic environments of Mössbauer-active cations, while e.s.r. spectroscopy is sensitive to paramagnetic molybdenum and tungsten species. Hence, the tungsten antimonate, Sb_2WO_6, and the molybdenum antimonates, Sb_2MoO_6 and $Sb_2Mo_3O_{12}$, have been examined by Mössbauer spectroscopy, complimented by e.s.r. spectroscopy, in an attempt to characterize the oxidation states of the cations present in these solids.

Experimental

The molybdenum and tungsten antimonates were supplied by E. I. du Pont de Nemours. The samples were prepared by heating the required proportions of Sb_2O_3 and MoO_3 (or WO_3) in a sealed tube under argon at 750 °C according to the procedure of Parmentier *et al.*[3]

Powder *X*-ray diffraction patterns were recorded using a horizontal goniometer and copper K_α radiation, samples being intimately mixed with an internal standard of KCl.

Mössbauer spectra were recorded on apparatus which has been described.[7] Absorbers were prepared by intimately mixing the finely powdered sample with grease and enclosing the mixture between thin aluminium sheets in a copper holder. The samples contained 6 mg of Sb per cm^2. The $Ba^{121m}SnO_3$ (^{121}Sb) source was maintained at room temperature while the sample was cooled. Approximately 150 000 counts per channel, after folding, were accumulated, using the escape peak of a Xe–CO_2 proportional counter, and the chemical isomer shifts were measured relative to InSb at 4 K.

The antimony-121 Mössbauer spectra were fitted using the transmission integral procedure,[8] in which the source and absorber linewidths were constrained to equal the natural linewidth. Allowing the absorber linewidth to vary resulted in a fitted linewidth of 1.09 ± 0.05 mm s^{-1} which is indistinguishable from the natural linewidth of 1.05 mm s^{-1}. The Debye–Waller factor of the source was estimated by a procedure in which an InSb spectrum was fitted to a single Lorentzian line of width Γ_0. The effective sample thickness (t_a) was then calculated from: $\Gamma_0 = 2r(1 + 0.27t_a)$, in which Γ_0 is the natural linewidth. This value was then used as a constant in a transmission integral fit of the same InSb spectrum to obtain the Debye–Waller factor of the source. This parameter was then used as a constant in all other fits.

Electron spin resonance spectra were recorded using a Bruker ER 100 D spectrometer. The frequency (ν) of the microwave radiation was determined using a Bruker FR 040X microwave bridge and the *g* values determined from $g = h\nu/\mu_\beta B$, where *B* is the magnitude of the static magnetic field at resonance, *h* is Planck's constant, and μ_β the Bohr magneton. Spectra were recorded at temperatures between 77 K and room temperature.

Table. Antimony-121 Mössbauer parameters of molybdenum and tungsten antimonates

Sample	Site	Isomer shift[a]	Quadrupole interaction eq^2Q[b]	Asymmetry parameter[c]	Contribution[d]	Degrees of freedom (χ^2)
Sb_2O_4[e]	1	−6.21	16.4			
	2	+8.76	−6,1			
Sb_2WO_6	1	−5.07	17.7		100	1.49
	1	−5.05	17.3	0.25	100	1.46
Sb_2MoO_6	1	−5.57	18.0		87	1.26
	2	+7.91			13	
$Sb_2Mo_3O_{12}$	1	−5.06	17.6		76	0.9
	2	+7.84	4.7		24	

[a] In mm s^{-1} (±0.04 mm s^{-1}) relative to InSb. [b] In mm s^{-1} (±0.3 mm s^{-1}). [c] ±0.05. [d] ±2%. [e] Ref. 11.

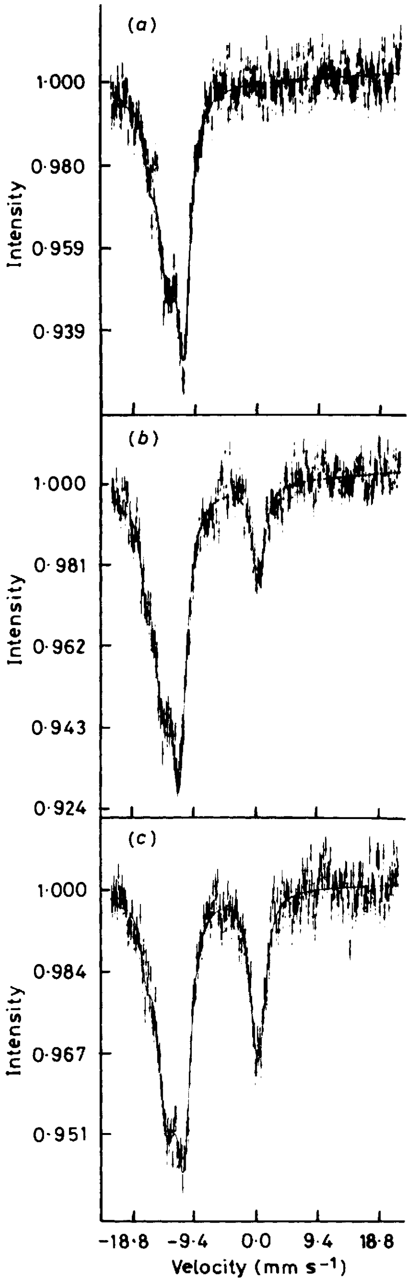

Figure 1. Antimony-121 Mössbauer spectra recorded at 77 K of (*a*) Sb_2WO_6, (*b*) Sb_2MoO_6, and (*c*) $Sb_2Mo_3O_{12}$

Results and Discussion

The antimony-121 Mössbauer data recorded from the tungsten and molybdenum antimonates are summarized in the Table. Fitted Mössbauer spectra are shown in Figure 1.

A powder *X*-ray diffraction pattern obtained from the sample of tungsten antimonate was similar to that reported by Parmentier *et al.*,[3] as being characteristic of Sb_2WO_6. The Mössbauer spectrum from tungsten antimonate [Figure 1(*a*)] consisted of a single broad peak which was fitted to a quadrupole-split resonance. The chemical isomer shift, −5.07 mm s^{-1}, is in the range (−3 to −6 mm s^{-1}) characteristic[9] of antimony(III) and is less negative than that associated with the Sb^{III} in Sb_2O_4. Since $\Delta R/R$ is negative for antimony[10] it is apparent that there is a lower *s*-electron density at the nucleus of Sb in Sb_2WO_6 than is found in Sb_2O_4.[9,11] The quadrupole interaction, e^2qQ, is large and reflects the highly distorted environment, typical of antimony(III). In this respect it is notable that a significant asymmetry parameter could be fitted to the spectrum resulting in a slight improvement of the statistical fit. Hence the Mössbauer spectra show that tungsten antimonate prepared by the reaction of equimolar mixtures of Sb_2O_3 and WO_3 contains antimony(III) and the data are therefore consistent with the proposed formula Sb_2WO_6.

An inspection of the antimony-121 Mössbauer spectrum of the molybdenum antimonate prepared by reacting equimolar quantities of Sb_2O_3 and MoO_3, and described as Sb_2MoO_6, reveals the presence of two peaks [Figure 1(*b*)]. The chemical isomer shift of the major component may be attributed[9,11] to Sb^{III}, whilst the isomer shift of the less intense peak indicates the presence of some Sb^{V}. Since the relative recoil-free fractions of Sb^{III} and Sb^{V} in molybdenum antimonate are unknown, it was not possible to obtain accurately the concentrations of Sb^{III} and Sb^{V}. Indeed the relative areas of the Sb^{III} and Sb^{V} peaks as determined from the fit may be subject to considerable uncertainty since the fitted position of the baseline would critically influence the contribution of the minor peak.

The chemical isomer shift of the Sb^{III} site in this molybdenum antimonate is more negative than that of Sb_2WO_6, indicating a greater *s* electron density on the antimony. It is also interesting to compare the data with those from α-Sb_2O_4, since the Sb^{III} site of Sb_2MoO_6 has a larger quadrupole interaction (18 mm s^{-1}) than α-Sb_2O_4 (16.4 mm s^{-1}),[9,11] whilst displaying a less negative chemical isomer shift (−5.57 mm s^{-1}). This would indicate a more active participation of the 5*s* electron pair of the Sb^{III} in the Sb–O bonds in Sb_2MoO_6 relative to Sb_2O_4. The antimony(V) site gives rise to a less positive isomer shift than that of Sb^{V} in Sb_2O_4 whilst the narrow linewidth seems to preclude a significant quadrupole interaction.

The detection, by Mössbauer spectroscopy, of low concentrations of Sb^{V} in this sample of molybdenum antimonate is interesting since a recent single-crystal *X*-ray diffraction, and powder neutron diffraction study,[6] of Sb_2MoO_6 described the oxidation states as close to Sb^{III} and Mo^{VI}. It would seem relevant that the *X*-ray diffraction and neutron diffraction data arise from cationic oxidation states which have been averaged over the whole structure, such that small concentrations of oxidized antimony species could remain undetected. In contrast, Mössbauer spectroscopy examines the *s*-electron density at each antimony nucleus and would be expected to be more sensitive to low concentrations of oxidized species. Hence it is possible that monophasic Sb_2MoO_6 contains oxidized antimony(V) cations, and therefore also some molybdenum in an oxidation state lower than Mo^{VI}.

However, it is relevant to note that vanadium antimonates prepared by the reaction of Sb_2O_3 with V_2O_5 have been reported[12] to be extremely sensitive to the preparative conditions and, in particular, to low concentrations of oxygen, such that small amounts of the oxidized antimony oxide Sb_2O_4 were detected[12] by scanning electron microscopy, even in materials prepared in commercially produced oxygen-free nitrogen. Given the high sensitivity of Mössbauer spectroscopy to Sb^{V}, low concentrations of Sb_2O_4 which were undetected by powder *X*-ray diffraction could be observed in the Mössbauer spectrum of Sb_2MoO_6 as an Sb^{V} resonance. The Sb^{III} resonance of Sb_2O_4 would overlap that of the main Sb^{III} component. Thus this material might also be considered to be a multiphasic system containing a molybdenum antimonate of composition close to Sb_2MoO_6, and an oxidized antimony oxide. The reported purity of the samples of molybdenum antimonate studied by Hewat and co-workers[5,6] seems likely to be more quantitative, given the high quality of the profile refinement of their data to a monophasic material.[6] The differences between the present data and those of Hewat and co-workers are most likely to reflect variations in preparative procedure, and it seems that the present sample of molybdenum antimony oxide is a more complex, partially oxidized, system. Further studies of these solids seem warranted.

A further molybdenum antimonate of nominal composition $Sb_2(MoO_4)_3$ was reported by Parmentier *et al.*[4] The sample of this composition, examined here, consisted of small blue-black crystals. The Mössbauer spectrum [Figure 1(*c*)] contained two peaks which were attributed to Sb^{III} and Sb^{V}. It is notable that a much more intense Sb^{V} resonance was detected in our sample of $Sb_2Mo_3O_{12}$ than was found in the solid of nominal composition Sb_2MoO_6. The relative peak areas for Sb_2O_4, which contains a 1:1 ratio of Sb^{III} and Sb^{V}, are approximately 0.91 as determined by ^{121}Sb Mössbauer spectroscopy.[11] Using this ratio as much as 21% antimony might be present as Sb^{V} in $Sb_2Mo_3O_{12}$. Since powder *X*-ray diffraction could be reasonably expected to detect similar levels of a contaminant antimony oxide phase, it is significant that the powder *X*-ray diffraction pattern from $Sb_2Mo_3O_{12}$ resembled that reported by Parmentier *et al.*[4] with no evidence for an impurity phase. Hence it seems that the oxidized antimony is a constituent of a monophasic molybdenum antimonate. The Mössbauer data therefore indicate that the reaction of Sb_2O_3 and MoO_3, in the molar ratio 1:3, gives rise to an apparently complex solid containing Sb^{III}, Sb^{V}, and hence, presumably more than one oxidation state of molybdenum.

The Mössbauer parameters of the Sb^{III} site resemble those of Sb_2WO_6 and Sb_2MoO_6 and are therefore also consistent with the presence of a stereochemically more active lone pair than is detected in Sb_2O_4.[9,11] Whilst the isomer shift of the Sb^{V} species resembles that of Sb^{V} in antimony molybdate, indicating a higher *s*-electron density at the antimony nuclei of $Sb_2Mo_3O_{12}$ than is observed in Sb_2O_4, it is notable that a significant quadrupole splitting could be fitted to this resonance. This seems to indicate that Sb^{V} occupies a distorted lattice environment in this compound.

It is interesting that the blue-black colour of this compound is similar to that reported for other materials in which Sb^{III}–Sb^{V} charge transfer occurs.[13] However, this property is more likely to be related to the presence of reduced molybdenum species (see below).

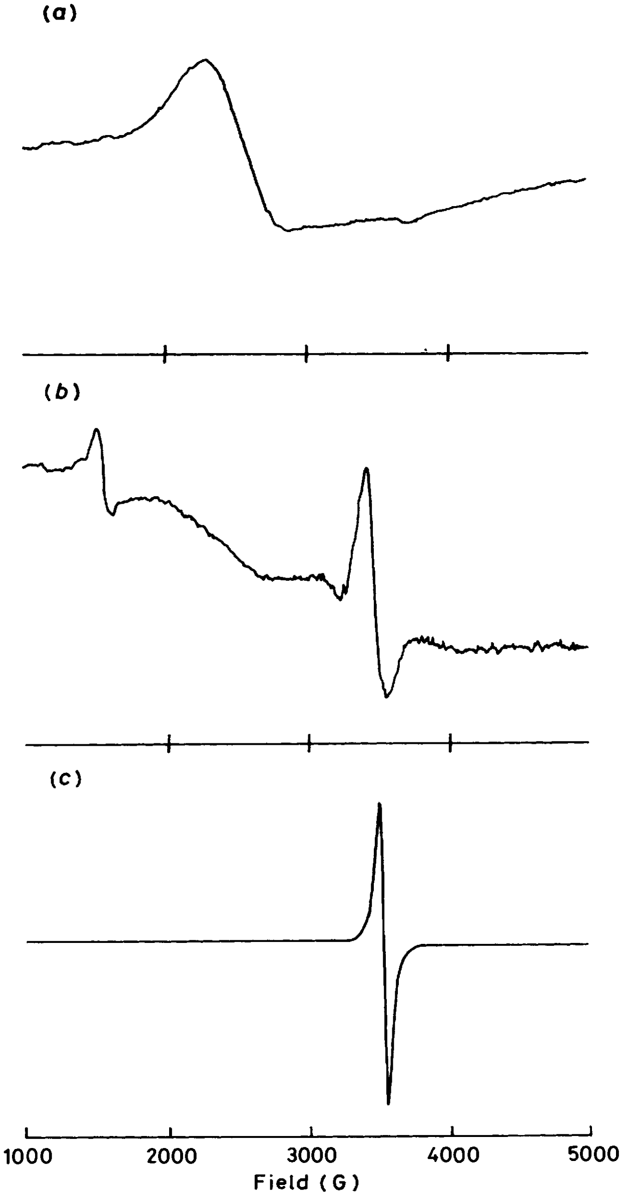

Figure 2. E.s.r. spectra (G = 10^{-4} T) of (*a*) Sb_2MoO_6 at room temperature, (*b*) Sb_2MoO_6 at 77 K, and (*c*) $Sb_2Mo_3O_{12}$ at 77 K

E.S.R. Spectroscopy.—Tungsten antimonate failed to give an e.s.r. signal at room temperature. It therefore seems that the the possible presence in tungsten antimonate of paramagnetic tungsten species, such as tungsten(V), can be discounted. Hence the e.s.r. and ^{121}Sb Mössbauer data indicate that tungsten antimonate prepared by the reaction of Sb_2O_3 and WO_3 *in vacuo* is best considered to contain Sb^{III} and W^{VI}. No redox processes involving tungsten or antimony seem to have occurred during the solid-state preparation, and this is consistent with the behaviour of other tungstates.[14]

However, it is interesting to note that on cooling to 150 K an e.s.r. signal was observed. The low-temperature signal consisted of a broad resonance extending across a magnetic field range of greater than 6 000 G and persisted on further cooling to 77 K. Similar e.s.r. signals have been observed from other mixed-metal oxides and reported to be characteristic of exchange interactions in an antiferromagnetic material.[15] It seems surprising that such interactions should be a property of this tungsten antimonate since both Sb^{III} and W^{VI} are diamagnetic. Moreover, antimony-121 Mössbauer spectra recorded from a vanadium antimonate[16] were sensitive to the presence of magnetic fields on neighbouring sites and it is relevant that no transferred field was detected at Sb^{III} in tungsten antimonate. Thus, while doubt remains as to the cause of the broad e.s.r. resonance recorded from tungsten antimonate, the Mössbauer spectrum indicates that if antiferromagnetism is a feature of this compound Sb^{III} is less amenable than Sb^{V} to the transference of magnetic fields from other cations.

Since ^{121}Sb Mössbauer spectroscopy detected the presence of some antimony(V) in the molybdenum antimonate, described by Parmentier *et al.*[4] as Sb_2MoO_6, it seems reasonable that this phenomenon would be associated with the reduction of some Mo^{V}. Therefore, the material was examined by e.s.r. which has been shown to be a sensitive probe for reduced molybdenum species, such as Mo^{V} and Mo^{III}.[17]

Electron spin resonance spectra recorded on Sb_2MoO_6 at ambient temperature and at 77 K are depicted in Figure 2. The ambient-temperature spectrum consists of a broad resonance at 2 300 G. The signal is very similar to those, recorded in the presence of other well-resolved signals, from $TeMo_5O_{16}$, oxidized $MoTe_2$, and reduced Te_2MoO_7 by Bart and co-workers[15,18] who interpreted their data in terms of antiferromagnetic electronic exchange through oxygen atoms.

However we note that in a more recent study of $TeMo_5O_{16}$, by ^{125}Te Mössbauer spectroscopy and e.s.r., other workers have attributed[19] the broad e.s.r. spectra of $TeMo_5O_{16}$ to the delocalization of molybdenum *d* electrons, and commented on the consistency of this argument with the chemical isomer shift of the Mössbauer spectrum and with the colour of the solid. It is possible that the e.s.r. spectra from Sb_2MoO_6 could also reflect similar processes.

It is significant that distinctly different e.s.r. spectra were obtained on cooling the sample of Sb_2MoO_6. While the broad resonance observed at room temperature was detected with diminished intensity at 150 K, and had suffered almost complete collapse at 77 K, the low-temperature spectra were dominated by two intense, well-resolved signals with average *g* values of 4.22 and 1.91. The attenuation of the broad resonance at low temperatures resembles[18] the temperature-dependent spectrum of $TeMo_5O_{16}$, which was compared with the behaviour of an antiferromagnetic species.[18]

The e.s.r. spectrum obtained from Sb_2MoO_6 at 77 K closely resembles that obtained from Te_2MoO_7 after reduction by hydrogen at 350 °C.[18] Bart and co-workers[18] attributed the signal at $g = 4.2$ to Mo^{III} and the resonance at $g \simeq 1.9$ to Mo^V. Indeed the signal observed at $g = 1.91$ is very similar to others reported in e.s.r. studies of Mo^V species.[15,20–24] Hence the present spectra may indicate that Sb_2MoO_6 contains Mo^V and Mo^{III}, and that some electronic exchange processes prevent the detection of the paramagnetic electrons until suppressed at low temperature. Such an assignment of the e.s.r. spectrum of this molybdenum antimonate would be consistent with the reduction of two Mo^{VI} cations to form Mo^V and Mo^{III} in order to compensate for the oxidation of two Sb^{III} cations to Sb^V. However, it seems significant that e.s.r. failed to detect the well resolved resonances at room temperature, since, although Mo^{III} is difficult to detect by room-temperature e.s.r.,[25] several investigations have reported that Mo^V is observed readily at this temperature.[15,21] Although it is difficult to discount the possible delocalization of the single *d* electron of Mo^V at room temperature, which could broaden the spectrum,[18,19] there would appear to be some doubt about the assignment of the $g = 1.91$ signal to Mo^V. This spectrum requires further attention. Thus, while we do not dispute the assignment[18] of the e.s.r. signals from reduced Te_2MoO_7, to Mo^{III} and Mo^V, it would seem that the e.s.r. data from Sb_2MoO_6 may be amenable to a different interpretation. The d^3 ion of Mo^{III} has been reported to give e.s.r. spectra characterized by two resonances at $g = 1.94$ and 3.94, whilst Orme-Johnson *et al.*[17] have recorded e.s.r. spectra from several Mo^{III} compounds which consisted of resonances at $g \simeq 2$ and $g \simeq 4$. It is also worth noting that the e.s.r. signals of Mo^{III} species have been reported to be difficult to detect at room temperature.[25] It therefore seems reasonable to consider the low-temperature e.s.r. spectra of Sb_2MoO_6 in terms of the presence of Mo^{III} as the only paramagnetic ion, whilst the room-temperature spectra may reflect antiferromagnetic behaviour discussed above and which decreases at lower temperatures.[15,18] Hence the current data indicate that the oxidation of Sb^{III} to Sb^V detected by ^{121}Sb Mössbauer spectroscopy is accompanied by the reduction of Mo^{VI} to Mo^{III}.

The reduction of molybdenum during the reaction of MoO_3 with Sb_2O_3 might seem surprising, since the preparation of tungsten antimonate, by an analogous reaction, gives a product which appears to contain only W^{VI} and Sb^{III}. However, it should be noted that whilst the tin tungstate, $SnWO_4$, is formed by the reaction of tin(II) oxide and molybdenum(VI) oxide, attempts to prepare $SnMoO_4$ by similar methods yielded tin(IV) oxide and molybdenum(IV) oxide.[14]

The antimony molybdate which has been reported[4] to be $Sb_2Mo_3O_{12}$ gave a room-temperature e.s.r. spectrum which consisted of a single, broad resonance with a *g* value of 1.92. The intensity of the signal increased at decreasing temperatures, an observation which seems consistent with the temperature-dependent Boltzman distribution of spins. No hyperfine structure was detected at room temperature or at 77 K. In the absence of paramagnetic antimony species the spectra of $Sb_2Mo_3O_{12}$ might be best considered in terms of paramagnetic molybdenum species. It is, therefore, significant that the spectra closely resemble others[15,20–24] which have been attributed to molybdenum(V) and are dissimilar to those assigned[17,18,25,26] to molybdenum(III). Moreover the *g* value observed for $Sb_2Mo_3O_{12}$ compares with those examples reported for Mo^V.[15,20–24]

The lack of hyperfine structure in e.s.r. spectra from molybdenum(V) has been reported on studies of other mixed-oxide systems.[15,18,19] It could appear that the phenomenon may result from a variety of mechanisms, including interactions between high concentrations of paramagnetic ions[27] and the delocalization of the single *d* electron of Mo^V,[19] possibly over Mo^{VI}–O–Mo^V sites.[18] It seems reasonable to expect the presence of considerable concentrations of Mo^V in $Sb_2Mo_3O_{12}$ to contribute towards the charge balance of the Sb^V detected by ^{121}Sb Mössbauer spectroscopy, whilst in addition, much of the residual molybdenum might be expected to exist as Mo^{VI}. Thus the e.s.r. spectra from $Sb_2Mo_3O_{12}$ are consistent with contemporary models describing the e.s.r. spectra of Mo^V.

The current results indicate that the molybdenum antimonate previously described[4] as $Sb_2Mo_3O_{12}$ is a complex material. E.s.r. and ^{121}Sb Mössbauer data have revealed the presence of Mo^V, Sb^{III}, and Sb^V which probably coexist with Mo^{VI}. Although powder *X*-ray diffraction data detected only peaks which have been assigned to the phase $Sb_2Mo_3O_{12}$, it would seem that further studies of this system are required to establish whether the Mössbauer and e.s.r. spectroscopy data emanate from an equilibrated monophasic material or some other type of solid. In this respect it is pertinent to note that a single-crystal *X*-ray diffraction study of $Sb_2Mo_3O_{12}$ indicated the existence of considerable bulk disorder.[28]

Acknowledgements

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