NOTES

Antimony-121 Mössbauer Spectra of the Uranium–Antimony Oxides, $USbO_5$ and USb_3O_{10}

INTRODUCTION

The uranium–antimony–oxide system has been examined by Aykan and Sleight (1), who were able to prepare two compounds, namely, $USbO_5$ and USb_3O_{10}. It was concluded on the basis of magnetic measurements that the uranium, and hence the antimony, was in the +5 oxidation state in these two compounds. Grasselli et al. (2) have come to similar conclusions. Several groups (3–5) have demonstrated the usefulness of ^{121}Sb Mössbauer spectroscopy in establishing the oxidation states of antimony in a variety of chemical systems. Recently Evans (6) has applied this method to the U–Sb–O system and confirmed that the oxidation state of the antimony was indeed +5. It was concluded (6) that the covalency of the Sb–O bonds in $USbO_5$ and USb_3O_{10} was higher than in pure Sb–O systems and that this increased covalency was important in accounting for the higher catalytic activity of the U–Sb–O phases. However, since the Mössbauer parameters reported for these systems were obtained from rather poor quality spectra and in view of the importance of the materials, a reinvestigation of these compounds seemed to be warranted.

EXPERIMENTAL

The compounds were prepared as described previously (1). Mössbauer spectra were recorded on equipment described previously (7). The samples, containing 8 mg of Sb/cm^2 intimately mixed with apiezon grease, were held in Cu holders between thin aluminum foil windows and were cooled to liquid nitrogen temperature: The source, 0.5 mCi of $Ba^{121m}SnO_3$, was maintained at room temperature. The spectra obtained contained between 50 and 80,000 counts per channel and were computer fitted both to a single Lorentzian line using the program described by Bancroft et al. (8) and to the eight-line quadrupole split routine of Shenoy et al. (9), modified to include a variable asymmetry parameter (10) and the transmission integral procedure of Cranshaw (11). Typical spectra are shown in Fig. 1, and the parameters abstracted are summarized in Table 1 and discussed below.

RESULTS AND DISCUSSION

In ^{121}Sb Mössbauer spectroscopy, the observed transition is between an excited state ($I = 7/2$) and the ground state ($I = 5/2$), and in the absence of an electric field gradient at the antimony nucleus only one spectral line is allowed. The width at half-height of this observed Lorentzian line should be close to the natural linewidth, that is, 2.1 mm/sec, but, in practice, is slightly greater than this, being governed by the source as well as the absorber linewidth. In cases when the site symmetry deviates from cubic, the degeneracy of the ground and excited states is partially removed, a quadrupole
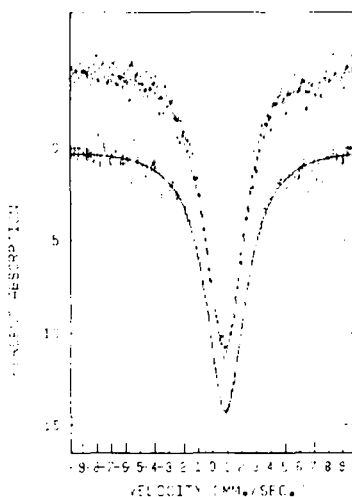
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FIG. 1. The ^{121}Sb Mössbauer spectrum of USb$_3$O$_{10}$. Upper curve fitted to an eight-line pattern, lower curve fitted to a single Lorentzian line.

interaction occurs, and an unresolved eight-line spectrum results (3). The spectral shape will no longer be Lorentzian, the overall width of the absorption band will be greater than the natural linewidth, and the peak minimum will no longer give the isomer shift. An eight-line computer fit must then be carried out in order to obtain the Mössbauer parameters (9). When the quadrupole coupling constant is large, as for example in Sb$_2$O$_3$, there is an obvious asymmetry to the spectrum (3), and the sign of the quadrupole coupling constant is obtained by inspection. However, when e^2qQ is small, i.e., $< \sim 8$ mm/sec, the sign and magnitude are often difficult to determine with certainty (12). One must therefore resort to fitting the spectrum in

TABLE 1

^{121}Sb Mössbauer Parameters for the U–Sb–O and Related Systems at 77 K

Compound	Isomer shift difference (mm/sec)	Quadrupole coupling constant (e^2qQ) (mm/sec)	Width (mm/sec)			χ^2/degrees of freedom		Ref.
Sb$_2$O$_4$	0.61	−6.1						(3)
	−14.36	16.4						
	0.3	.						(4)
	−14.5	.						
Sb$_2$O$_3$	1.06	−4.3						(3)
	0.1	..						(4)
USbO$_5$[a]	−0.53	– –	3.19					(6)
USb$_3$O$_{10}$[a]	−0.57	–	4.28					(6)
USbO$_5$[a]	0.43	—	3.26			269/256		This work
USb$_3$O$_{10}$[a]	0.75	–—	3.28			340/256		This work
			Γ	T$_a$	Convolution		M	
USbO$_5$	0.30	(−) −3.80[b]	1.31	0.47	0	264/254	0.026	This work
	0.30	(−) −3.93	1.53	0.42	1	264/254	0.027	This work
	0.28	(+) 3.04	1.41	0.47	0	268/254	0.037	This work
	0.27	(+) 3.09	1.64	0.43	1	269/254	0.037	This work
USb$_3$O$_{10}$	0.58	(−) 3.96	1.30	0.44	0	331/254	0.125	This work
	0.57	(+) 4.27	1.47	0.40	1	331/254	0.125	This work
	0.60	(−) −3.14	1.39	0.45	0	338/254	0.135	This work
	0.60	(−) −3.05	1.62	0.41	1	339/254	0.136	This work

[a] Lorentzian fit.

[b] Signs in parentheses indicate signs of initial estimates of e^2qQ.

a variety of ways and to compare them carefully before commenting on the meaning of the parameters obtained.

The spectra obtained for each of the two compounds studied appear as relatively sharp resonances. Computer fits to a single Lorentzian line shape resulted in small positive isomer shifts relative to the source. The overall width of each line was 3.3 mm/sec, which is greater than that expected for a thin absorber in a cubic environment. Fits to eight-line quadrupole split spectra were then tried both without and with the convolution routine, which does the transmission integral properly. Again small positive isomer shifts were obtained together with small quadrupole coupling constants. Unfortunately the signs of the e^2qQ values varied depending upon the signs of the initial estimates, and there was no difference in x^2 or Misfit (13) values for the various fits tried for each compound. The x^2 and Misfit values were however higher for USb_3O_{10} than for $USbO_5$. It is also apparent from Table 1 that the calculated widths, using the transmission integral procedure, are still higher than theoretical (1.05 mm/sec, i.e., 2.1/2) (9).

Attempts were also made to fit these spectra using a variable η as well as variable e^2qQ, but reliable fits could not be obtained. It is not clear to us why USb_3O_{10} consistently gave higher x^2 values than $USbO_5$ when the two spectra appeared comparable. It is tempting to conclude that the Sb(V) in $USbO_5$ exists in only one near cubic environment while a number of slightly different environments are present in USb_3O_{10}. This would certainly be consistent with the conclusions of Grasselli and co-workers (2).

The isomer shift difference between $USbO_5$ and USb_3O_{10} appears to be significant no matter how the spectral fitting is carried out. Both shifts are positive with respect to Ba $^{121m}SnO_3$ and are similar to the values obtained for the Sb(V)

site in Sb_2O_4 and Sb_2O_5 (Table 1). The negative values reported by Evans (6) appear to be in error, probably because of the poor quality of the spectra obtained. To attribute the high catalytic activity of the U–Sb–O phases relative to the pure Sb–O phases to considerably increased Sb–O covalency in the former is therefore not correct. The increased catalytic activity is undoubtedly caused by the variety of possible oxidation states and the ease of electron transfer between them. The difference in catalytic activity between $USbO_5$ and USb_3O_{10} (14) may well be related to the increased ionic character of the Sb–O bonds in the latter as evidenced by the more positive isomer shift, that is, +0.57 mm/sec for USb_3O_{10} compared to +0.28 mm/sec for $USbO_5$. The more ionic system would allow a more facile electron transfer between antimony and uranium ions and would lead to enhanced activity.

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