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A Study of Vanadium Antimonate by Antimony-121 Mössbauer Spectroscopy and Magnetic Susceptibility

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Abstract

Two non-stoicheiometric modifications of vanadium antimonate have been examined by antimony-121 Mössbauer spectroscopy and magnetic susceptibility. The oxidised variation prepared by calcination of antimony(III) oxide and vanadium(V) oxide in air contains vanadium(IV) and antimony(V) and the data are consistent with a formulation $V(IV)_{0.89}Sb(V)_{0.89}O_4$. A monophasic antimony deficient vanadium antimonate prepared in oxygen-free nitrogen contains vanadium(III), vanadium(V) and antimony(V) and may be formulated as $V(III)_{0.72}V(V)_{0.28}Sb(V)_{0.72}O_{3.58}$.

Introduction

Although the compositions of rutile-related vanadium antimonate have been the subject of some confusion in the past [1–5] recent work [6] has shown that a single phase oxidised vanadium antimonate can be formed from the reaction between antimony(III) oxide and vanadium(V) oxide in air whilst a monophasic antimony-deficient modification is formed from the reaction performed in oxygen-free nitrogen.

Although the oxidised vanadium antimonate has been shown to contain vanadium(IV) [7] and antimony(V) [5] the more recent work [6–8] has also shown that the chemical and structural properties of the rutile-related vanadium antimonates are more complex than previously supposed and that the nature of all the cationic oxidation states in the different non-stoicheiometric phases is unclear. Given that an early magnetic susceptibility study [4] was unable to differentiate between the presence of vanadium(IV) and vanadium(III) and in view of the limited Mössbauer data available on the vanadium antimonates [5], we have examined two non-stoicheiometric vanadium antimonates by computer interpreted magnetic susceptibility measurements and by antimony-121 Mössbauer spectroscopy to identify the nature of the cationic species which exist in these materials.

Experimental

The oxidised- and antimony-deficient-vanadium antimonates were prepared by solid state reactions between antimony(III) oxide and vanadium(V) oxide as previously described [6].

The magnetic measurements were performed with a Faraday-type balance in fields up to 10 kOe and at temperatures between 77 and 300 K. The data were computer fitted.

The antimony-121 Mössbauer spectra were recorded with a Cryophysics microprocessor controlled Mössbauer spectrometer using a $Ca^{121m}SnO_3$ source with both source and absorber at 77 K. The drive velocity was calibrated with a $^{57}Co/Rh$ source and a natural iron foil absorber. All spectra were computer fitted.

Results and Discussion

Both the monophasic antimony-deficient vanadium antimonate prepared under strictly anaerobic conditions and the oxidised modification of vanadium antimonate formed in air gave single peak ^{121}Sb Mössbauer spectra characteristic of antimony(V) (Fig. 1).

The temperature dependence of the reciprocal of the corrected molar susceptibilities, χ_M^{-1}, for the two modifications of vanadium antimonate are shown in the least squares computer fitted plots of χ_M^{-1} *vs.* T which are depicted in Figs. 2 and 3.

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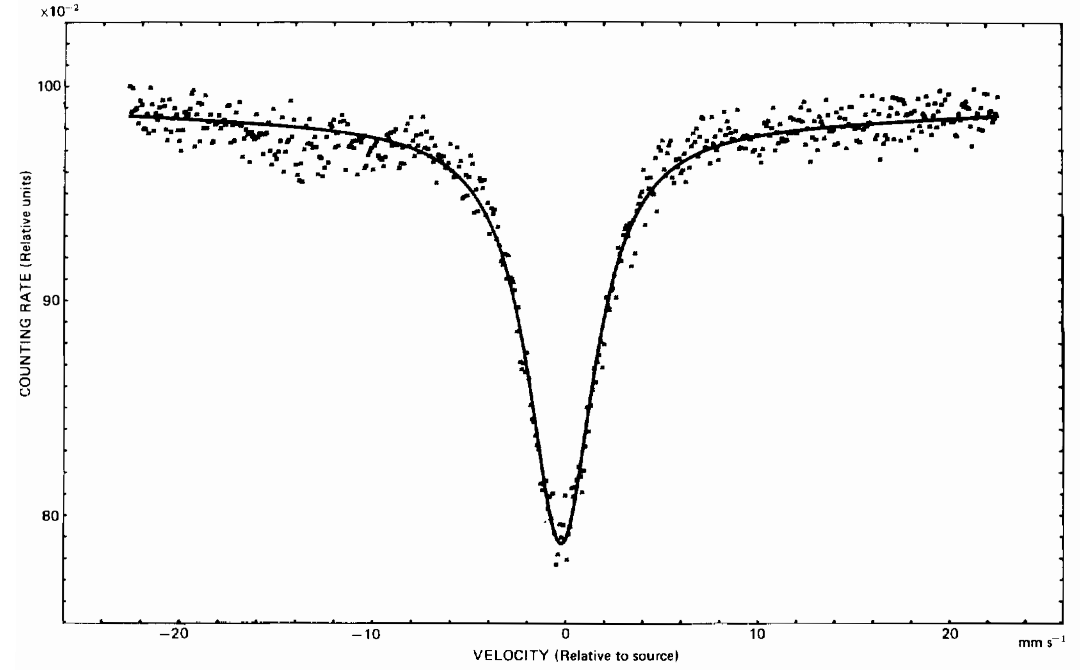

Fig. 1. Antimony-121 Mössbauer spectrum recorded from oxidised vanadium antimonate.

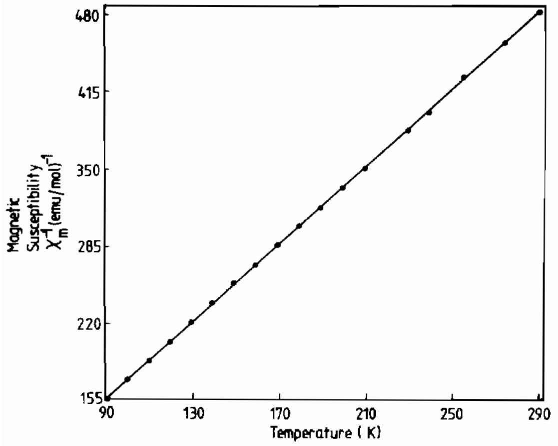

Fig. 2. Temperature dependence of the magnetic susceptibility of monophasic antimony-deficient vanadium antimonate.

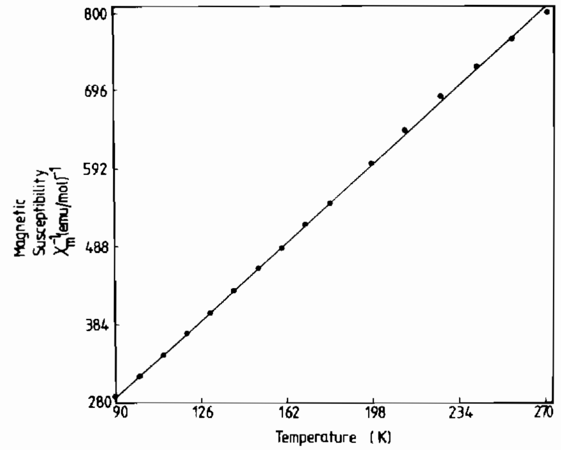

Fig. 3. Temperature dependence of the magnetic susceptibility of oxidised vanadium antimonate.

The molar susceptibilities are field independent for fields varying between 1 kOe and 10 kOe and Figs. 2 and 3 show that the two compounds obey Curie–Weiss Laws over the temperature range 77–300 K. The values of the paramagnetic Curie Temperatures, θ_C, and Curie Constants, c, are given in Table 1. The negative values of θ_c for both phases, which are related to the interactions producing the spontaneous magnetisation, may indicate that some antiferromagnetic interaction occurs at very low temperatures. However, the magnetic ordering may not be complete until temperatures less than 4 K are reached.

TABLE I. Curie Temperatures and Curie Constants for Vanadium Antimonate Phases.

Phase	Curie temperature (K)	Curie constant ($\times 10^{-3}$ emu g^{-1} K^{-1})
Monophasic antimony deficient vanadium antimonate	−7.7 ± 5.0	2.62 ± 0.06
Oxidised vanadium antimonate	−11.4 ± 6.8	1.47 ± 0.06

The results of the Mössbauer and magnetic susceptibility measurements may be used to improve the accuracy of the general chemical formulations which have been used to describe these phases. The monophasic antimony deficient vanadium antimonate has been described [6] as $VSb_{1-y}O_{4-3/2y}$ and, given the ^{121}Sb Mössbauer spectrum (*vide supra*) and ESR data [7], would appear to contain antimony(V) and vanadium(III). However, the magnetic measurements described here cannot be interpreted in terms of a model in which the only paramagnetic cation present is vanadium(III) with a dipolar magnetic moment μ of 2.83 β [9]. However, a formulation $V(III)_{1-y}V(V)_y\,Sb(V)_{1-y}O_{4-3/2y}$, which satisfies the analytical and ESR data reported earlier [6, 7] and the Mössbauer results described above, allows the effective dipolar magnetic moment to be related to the Curie constants derived from the magnetic measurements and permits a satisfactory fit of the magnetic data. Hence the effective dipolar magnetic moment can be expressed:

$$\mu^2_{\mathrm{eff}} = [2.83(1-y)]^2 = \frac{8c}{\mathrm{PM}}\,[\mathrm{Pa(V)} + (1-y)\mathrm{Pa(Sb)} + (4-3/2y)\mathrm{Pa(0)}] \tag{1}$$

where PM is the molecular weight of the stoicheiometric vanadium antimonate; Pa(V), Pa(Sb) and Pa(0) are the atomic weights of V, Sb and O respectively; and c is the Curie Constant for the monophasic antimony deficient vanadium antimonate obtained from the plot of the corrected molar susceptibilities χ_M^{-1} against T (Fig. 2). From eqn. (1) a value for y of 0.28 is obtained and enables the monophasic vanadium antimonate to be formulated as $V(III)_{0.72}V(V)_{0.28}Sb(V)_{0.72}O_{3.58}$.

Given that the oxidised vanadium antimonate has been shown by Mössbauer spectroscopy to contain antimony(V) (*vide supra*) and by ESR to contain vanadium(IV) [7], the material is amenable to description by the general formulation [5, 7] $V(III)_{1-9y}V(IV)_{8y}Sb(V)_{1-y}O_4$. Hence the effective dipolar magnetic moment can be expressed:

$$\mu^2_{\mathrm{eff}} = [\mu\mathrm{V(III)}(1-9y) + \mu\mathrm{V(IV)}8y]^2 = \frac{8c}{\mathrm{PM}}\,[(1-y)\mathrm{Pa(V)} + (1-y)\mathrm{Pa(Sb)} + 4\mathrm{Pa(0)}] \tag{2}$$

where μV(III) = 2.83 β and μV(IV) = 1.73β [9] are the dipolar magnetic moments of vanadium(III) and vanadium(IV); and c is the Curie Constant for oxidised vanadium antimonate derived from the data depicted in Fig. 3. From the expression (eqn. 2) a value for y of 0.11 is obtained which permits the oxidised vanadium antimonate to be formulated as $V(III)_{0.01}V(IV)_{0.88}Sb(V)_{0.89}O_4$. Hence the concentration of vanadium(III) in this phase is insignificant and the oxidised vanadium antimonate formed by calcination in air may be best formulated as $V(VI)_{0.89}Sb(V)_{0.89}O_4$.

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