

Preparation, Structure, and Mössbauer Spectra of Tin Tungsten Bronzes

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Received July 6, 1970

Preparation and properties of some new tungsten bronzes Sn_xWO_3 are reported with compositions in the range $x = 0.4-0.01$. Details of the structure types as elucidated by single crystal methods are described which relate some of these bronzes to known alkali bronzes while a number of hitherto unknown orthorhombic and hexagonal types are described. Tin Mössbauer spectral parameters indicate a loss of electrons from every tin atom to produce Sn(II) in several crystallographic sites but do not support the view that inclusion metal atom clusters exist in the tungsten bronze structures.

Introduction

Tungsten bronzes with orthorhombic, tetragonal, and hexagonal structures have been known for a number of elements for some time (1-3). These have recently been the subject of a review which revealed the very sparse data in some areas (4). This paper presents data on the hitherto unknown tin tungsten bronzes which exhibit all three main structure types.

Superstructures of both the hexagonal and tetragonal forms have occasionally been reported but there is some speculation about such superlattice phases. The literature is most detailed on the cubic tungsten bronzes of sodium which are discussed as classical examples of nonstoichiometric oxides (1, 5). In these cubic bronzes the ReO_3 structure is continuously transformed into the perovskite structure by interpolation of ions within the correct size range into cubic positions. This simple picture as Wadsley points out (5) may not be the final one when the details of the oxygen atom positions are determined but so far such studies have not been forthcoming.

All the bronze structures have been described as containing ions interpolated in tunnel-like continuous cavities enclosed by the framework of WO_6 octahedra. These structures have only been determined in any detail for the sodium, and to a lesser

extent, the heavier alkali metal bronzes (2, 4). For the sodium system the full phase diagram has been described by Ribnick et al. (1). Some general points have been abstracted from this earlier work which suggests that as x in M_xWO_3 decreases so too does the symmetry of the structure, that the structure adopted is controlled largely by the ionic radius of the inclusion metal ions, and that the limiting compositions are determined by the concentration of the electrons that must be present in a delocalized conduction band.

The sites in the WO_6 octahedral network that are available for occupation by the inclusion metal in the various known or assumed structures have the following sizes: cubic 0.96 Å, tetragonal 0.96 and 1.29 Å, hexagonal 1.63 Å. The bronzes with the small Na^+ cations adopt the cubic structure, and as the concentration of sodium decreases the symmetry of the lattice is lowered while the structure changes through two tetragonal phases. At very low sodium contents ($x < 0.05$) an orthorhombic structure has been observed. The tetragonal structure can be regarded as being built up of three-, four-, and five-membered rings of WO_6 octahedra in which each unit cell contains interstitial sites of two types. The largest of these sites, of which there are eight per unit cell is bounded by 10 tungsten ions in the

form of a pentagonal prism. These large holes are available for occupancy by larger ions like K^+ (1.33 Å) and the limiting stoichiometry for this structure would be $K_{0.6}WO_3$.

It might be assumed that for a composition of say $Na_{0.5}WO_3$ where Na^+ could occupy both types of site a certain degree of disorder with respect to Na^+ would exist in the structure. A neutron diffraction study of the $Na_{0.75}WO_3$ bronze indicated that the sodium atoms were at the lattice sites assumed for the cubic structure and formed an ordered, rather than a random, sublattice (6). This example highlights the lack of detailed structural work since the systems mainly examined contain light atoms and the X-ray methods employed are insensitive to most inclusion metal and oxygen atom positions since the scattering process is dominated by the tungsten. This raises the question as to whether the inclusion metal atoms are responsible for the weak superlattice reflections sometimes found in studies involving these materials or whether they arise as a result of slight distortions in the tungsten-oxygen positions in the WO_6 octahedra.

In the hexagonal structure the WO_6 octahedra are formed into six-membered rings with cavities of 1.63 Å. These are available for occupation by larger ions leading to a limiting composition of $M_{0.3}WO_3$. Potassium ions, radius = (1.33 Å), Rb^+ (1.48 Å), and Cs^+ (1.69 Å) form hexagonal bronzes, and, largely on the basis of the hexagonal symmetry of the indium bronze, In_xWO_3 ($x = 0.26 - 0.33$), it was concluded that indium was present essentially as In^+ (3). The great stability of the indium bronze in contrast to the instability of compounds known to contain In^+ makes this conclusion interesting and leads one to consider possible descriptions of the bonding in these materials. The bonding may be more important than the ionic size in determining the structural type. One way of considering this point is to study the structure types existing in the bronzes containing inclusion metals which can exhibit more than one stable valency state and hence a range of ion size. So far such studies have been limited, and, as in the case of indium, the oxidation state of the inclusion metal has been inferred from the symmetry of the bronze structure. Thus one aim of this study has been to determine directly the oxidation state of the inclusion element where relatively stable states exist, and so bronzes have been prepared which contain the Mössbauer active elements tin, iron and europium. This paper reports early results from the work in the tin system which is to date farther advanced than the work in the other systems. By using the Mössbauer technique it

was hoped to probe the nature of the bonding in the system and so to provide more data by which the controversy might be resolved concerning which atomic orbitals are the constituents of the conduction band (7-10). Mackintosh (7) and Fuchs (8) consider the conduction band to be composed of overlapping inclusion metal orbitals while Sienko and Goodenough suppose that it is mainly the tungsten orbitals which are involved, and electrons are donated from the inclusion atoms into the $W5d(t_{2g})$ band. Mackintosh assumes that the energy band formed by the overlap of inclusion metal atomic orbitals lies below that formed by the tungsten $5d(t_{2g})$ orbitals. This model can explain the increasing symmetry of the bronze lattice with increasing metal content since a cubic structure would provide maximum mutual overlap of the metal p orbitals. The changeover from metallic to semiconduction behaviour at low inclusion metal content is also anticipated. Fuchs has suggested a model for the sodium bronzes in which the sodium atoms occur in clusters and for which the local conduction electron density is independent of inclusion metal concentration. This model has been raised to give a quantitative account of observed magnetic susceptibility and electronic specific heat data because the local electron density for the clusters is then independent of the overall composition. There is no direct experimental evidence for the existence of clusters in any tungsten bronze systems, and it was felt that an examination of the Mössbauer effect in the new materials prepared here might provide some evidence on this point.

The radii of Sn^0 (1.62 Å), Sn^{2+} (1.12 Å), and Sn^{4+} (0.71 Å), along with the fact that all three states are relatively stable suggests an interesting system with respect to potential occupancy of the sites in the cubic, hexagonal, and tetragonal bronze structures for high Sn content materials. Preparations have been attempted using SnO_2 , SnO , and Sn as the starting materials. In all cases there is direct evidence that no Sn^{4+} exists in these systems. A complex series of hexagonal, tetragonal, and orthorhombic bronzes has been identified for bronzes in the composition range Sn_xWO_3 , $x = 0.01 - 0.4$. All of these contain Sn^{2+} and possibly Sn^0 which might indicate clusters of Sn atoms in the structure but most likely reflect some inhomogeneity in the system. Different crystal forms have been identified under the microscope but all preparations contain some long needle crystals growing from the compacted pellet which suggests a form of vapour growth. These needles have been found to be bundles of extremely thin whisker crystals which because of

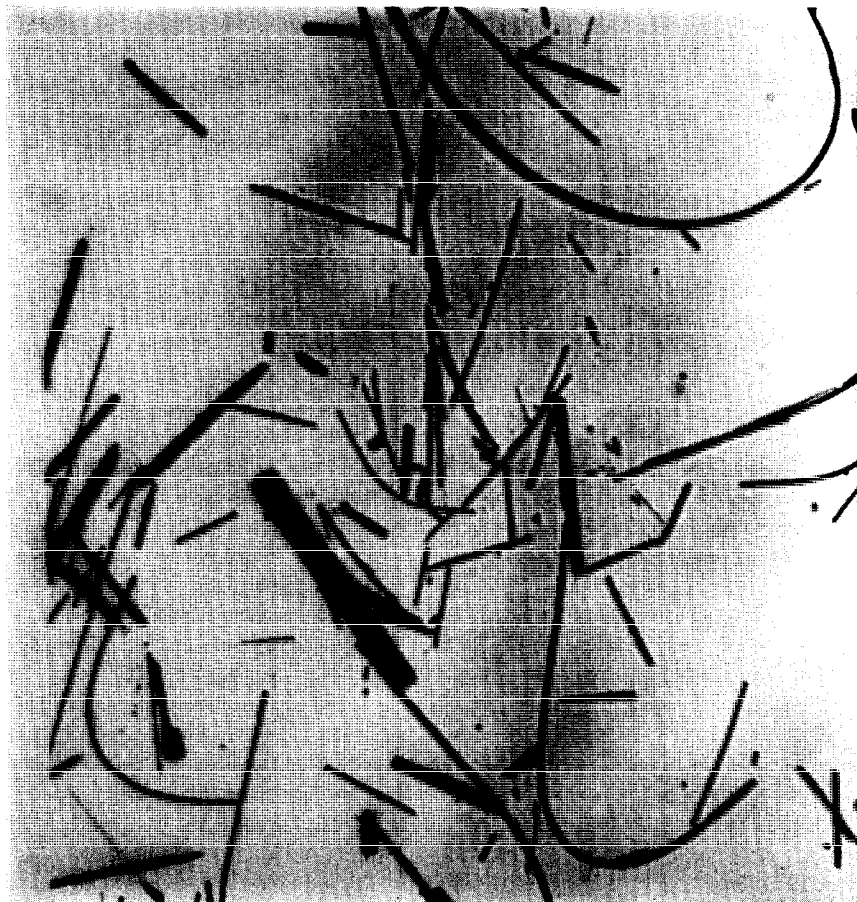
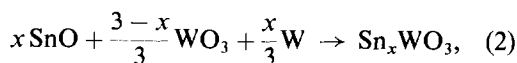
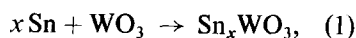


FIG. 1. Micrograph of a part of an $\text{Sn}_{0.2}\text{WO}_3$ preparation $\times 920$ showing some thin whisker bundles. The radius of curvature of some of the whiskers can be used to estimate the tensile strength of the material.

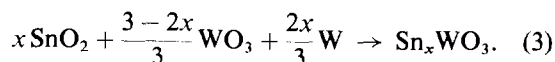
their size and crystal type present great difficulty with respect to X-ray analysis; some of these are shown in Fig. 1.

Experimental

AnalaR grade tin and SnO_2 were used along with Sn and WO_3 of high purity supplied by Kodak Chemicals Limited. The weights of materials required for the reactions summarized by Eqs (1)–(3) for a range of x values 0.01–0.4 were calculated and weighed out.



and



Pellets about 0.5 g were pressed from the well mixed reagents and sealed in silica tubes at pressures $< 10^{-6}$ mm Hg. The volume of each tube was approximately 2 ccs and the length 6 cms. The tubes were heated at temperatures in the range 950–1150°C for 1–3 weeks. Most samples were cooled normally while a few were quenched in cold water. All preparations were washed on sintered glass crucibles with 10% HF, HCl, distilled H_2O , NaOH, H_2O , and acetone consecutively. None of these reagents had any noticeable effect on the products.

A large number of crystals from each preparation were examined by single crystal techniques and occasionally by powder methods. The bronze preparations which have been examined have compositions Sn_xWO_3 with x having the value 0.01, 0.1, 0.2, 0.3, and 0.4. From each prepared sample, individual crystals were selected as being suitable for single crystal X-ray diffraction techniques; the dimensions of each crystal were never greater than

0.1 mm. Lattice parameters of the crystals were determined by measurement of single crystal and Weissenberg photographs.

Mössbauer spectra were obtained on a spectrometer and using the techniques described in detail elsewhere (11). A 5 mc BaSnO_3 source was used and SnO_2 at room temperature was taken as zero velocity. The quantity of Sn which could be used for resonant absorption was limited to approximately 1 mgm/cm² by the presence of the heavy tungsten atoms in the samples, and counting proceeded for several days, giving 1–10 million counts/channel.

Results and Discussion

The visual examination of the products of these reactions strongly suggested that new bronzes had been produced from the bulk materials, ranging in colour from blue to deep purple as the tin composition increased. A rough determination of the electrical resistivity of one compact with composition $\text{Sn}_{0.3}\text{WO}_3$ showed a metallic-type behaviour with a value $10^{-3} \Omega \text{ cm}$ at 25°C. Single crystal determinations of specific resistance of $\text{Na}_{0.49}\text{WO}_3$ are reported in (4) as $1.05 \times 10^{-4} \Omega \text{ cm}$ at 25°C. The materials from all preparations have been shown to be chemically inert with respect to a wide range of acids and alkalis but did reduce ammoniacal AgNO_3 , producing a deposit of silver. All these properties are associated with those of a tungsten bronze. The X-ray powder patterns from all the products were extremely complex but showed no lines that could have arisen from the starting materials. The high tin content materials had patterns that were almost completely indexed on the tetragonal or hexagonal structures that were later found from the single crystal work. All of the above leads to the view that the hitherto unknown tin tungsten bronzes had been prepared. More positive proof for this can be seen from the more detailed crystallographic examination of the preparations.

The structures, or the unit cells and superlattice cells of the structures, which have been found in these bronzes will be described in turn without attempting to classify them according to their Sn content. Most of the structures described below were found in bronze specimens over the range of Sn contents described, and several structures were found in each bronze specimen; none of the bronze preparations which are available at the moment produced crystals of one structure only. However, the powder work that was done indicates that for a given composition one type greatly predominates.

Tetragonal Structure. The existence of this struc-

ture among these tin bronze preparations is particularly important because it corresponds exactly to the tetragonal I structure of the sodium and potassium bronzes, and the analogy between the tin bronzes and the other known bronzes is therefore firmly established.

For a crystal of composition $\text{Sn}_{0.4}\text{WO}_3$, all reflections were indexed in terms of a body-centred tetragonal unit cell with dimensions, $a = 17.19 \text{ \AA}$ and $c = 7.57 \text{ \AA}$. The corresponding cell for a sodium tungsten bronze reported by Magneli (12) has dimensions, $a = 17.10 \text{ \AA}$ and $c = 7.50 \text{ \AA}$. However, in the case of both the sodium and the tin tungsten bronzes, all reflections with odd l values were consistently fainter than the rest, and the above unit cells might be regarded as the unit cells of a superlattice, and the basic structural unit would have a primitive tetragonal cell with $A = a/2$ and $C = c/2$.

To help establish the identity of the tin bronzes, the $hk0$ reflections were compared directly with those of a prepared sodium bronze using zero-layer Weissenberg photographs of crystals of composition $\text{Sn}_{0.4}\text{WO}_3$ and $\text{Na}_{0.298}\text{WO}_3$; relative intensities were very closely comparable over the whole range of reflections up to $h = k = 24$. The comparability of the two structures in this projection along [001] confirm that the tin bronze, like the sodium, has a structure penetrated by pentagonal and triangular tunnels parallel to [001].

The superlattice referred to above and probably caused by ordering of Sn atoms within the tunnels, is not an essential feature of this tetragonal structure either in the tin tungsten bronzes or other bronzes. A crystal of composition $\text{Sn}_{0.3}\text{WO}_3$ showed no evidence of the superlattice. The sodium bronze crystal showed only extremely weak superlattice reflections, and potassium tungsten bronzes with no superlattice have been reported (2).

Hexagonal Structure. Like the tetragonal structure, this was found only in bronzes with a high tin content, $\text{Sn}_{0.4}\text{WO}_3$ and $\text{Sn}_{0.3}\text{WO}_3$, and it too has its counterpart in the known potassium, rubidium and cesium tungsten bronzes.

Crystals of this type, which are almost always of a hexagonal platy habit, give diffraction patterns which can be indexed in terms of a hexagonal unit cell with dimensions approximately $a = 7.30 \text{ \AA}$ and $c = 3.76 \text{ \AA}$, which may be compared with those of a hexagonal potassium tungsten bronze (12), $a = 7.40 \text{ \AA}$ and $c = 7.56 \text{ \AA}$. Several features of the diffraction patterns given by the tin bronzes show, however, that the structure exhibits complexities which cannot be interpreted in terms of this fundamental hexagonal cell. One of these is that, as in all the tin bronze

structures so far examined, superstructures are formed with unit cells which in this case have dimensions $a' = 2a$ or $4a$ and $c' = 2c$.

Another complicating feature is revealed by the fact that all the crystals appear to be twins which show by the separation of corresponding reflections that the c axis is not perpendicular to (001) and the departure from this is $0^\circ 50'$. The structure would correctly be described in terms of a monoclinic cell with dimensions $A = a\sqrt{3}$, $B = b$, $C = c$ and $B = 90^\circ 50'$. While all the strong reflections and almost all the faint reflections are accounted for by this cell, there remain some very faint and diffuse reflections which always occur on these diffraction patterns and which cannot be indexed on this cell.

Orthorhombic Structures. The tin tungsten bronzes not only form structures which, like the ones described above, are common to other types of tungsten bronze, but they crystallize in structures not previously reported as being found among the bronzes. These new structures occur predominantly at the lower tin concentrations ($x = 0.01-0.2$). The most interesting of these are a group of three orthorhombic structures which will be described together since while their unit cells and their superlattices differ from one another, they show clearly by the distribution of intensities in their diffraction patterns that they can be regarded as belonging to one family of structures. There appears to be every reason for thinking that further members of the family may yet be discovered. The three structures will be referred to as 5-type, 6-type and 8-type, and unit cells for these have the following dimensions:

5-type	$a = 16.54 \text{ \AA}$	$b = 3.78 \text{ \AA}$	$c = 7.40 \text{ \AA}$
6-type	$a = 20.42 \text{ \AA}$	$b = 3.78 \text{ \AA}$	$c = 7.44 \text{ \AA}$
8-type	$a = 28.62 \text{ \AA}$	$b = 3.89 \text{ \AA}$	$c = 7.35 \text{ \AA}$

Diffraction patterns of all three structures contain reflections which are considerably fainter than the rest of the pattern but which are nevertheless sharp and clear. Assuming that these reflections are caused by superlattices, the following are the dimensions of the superlattice unit cells:

5-type	$A = a \times 2$ $= 33.1 \text{ \AA}$	$B = b \times 14$ $= 53.0 \text{ \AA}$	$C = c$
6-type	$A = a$	$B = b \times 12$ $= 45.4 \text{ \AA}$	$C = c$
8-type	$A = a \times 2$ $= 57.3 \text{ \AA}$	$B = b \times 10$ $= 38.9 \text{ \AA}$	$C = c$

In the case of the 5-type and the 6-type, it would be possible to regard the c -dimension of the basic

unit as being half that stated above, and then take $C = 2c$. This doubt as to whether a reflection is to be regarded as being caused by a superlattice is unavoidable until crystals can be produced which do not give these reflections. At present reflections are assumed to belong to a superlattice because of their faintness and also because some variability of the overall intensity of these reflections occurs from one crystal to another.

A marked peculiarity common to all these three orthorhombic structures is a regular periodic variation of intensity with the h index. Along any row of points hkl of the weighted reciprocal lattice, as h increases the intensity rises to a maximum at every fifth, sixth, and eighth point in the case of 5-type, the 6-type, and the 8-type, respectively; the reciprocal lattice points which are roughly halfway between these maxima have very low intensities. Clearly, while each of these structures has a large repeat distance corresponding to the large a -dimension, a subunit of each structure exists, and the a dimensions of these subunits are as follows:

5-type	subunit $a' = 1/5a = 3.31 \text{ \AA}$,
6-type	subunit $a' = 1/6a = 3.40 \text{ \AA}$,
8-type	subunit $a' = 1/8a = 3.58 \text{ \AA}$.

The closely similar values of a' for the 5-type and the 6-type, as well as similarities in the distribution of intensities among the reflections, shows that the relation between these two is closer than between either of them and the 8-type. A detailed structure determination is being undertaken in order that the nature of the subunits and their relation to the complete structures can be understood.

To complete the catalogue of orthorhombic structures which have been discovered, one which was found in a specimen of composition $\text{Sn}_{0.3}\text{WO}_3$ must be mentioned, in order chiefly to illustrate further the variety of structures which these tin bronzes may assume. It has unit cell dimensions which are approximately $a = 3.72 \text{ \AA}$, $b = 3.69 \text{ \AA}$, $c = 6.42 \text{ \AA}$, but it shows similar complexities to those exhibited by the hexagonal structures described earlier in that the c axis is not at precisely 90° to (001), and superlattice reflections are obtained which, while almost all can be indexed in terms of a unit cell which has dimensions of $A = 2a$, $B = 2b$, and $C = 2c$, cannot all be accounted for.

Other Structures. Crystals from specimens with composition $\text{Sn}_{0.01}\text{WO}_3$ were orthorhombic and had the following approximate unit cell dimensions: $a = 3.85 \text{ \AA}$, $b = 3.60 \text{ \AA}$, $c = 7.34 \text{ \AA}$.

At this very low tin concentration the crystals

were invariably imperfect, each selected crystal, however small, evidently containing regions with a variety of b -dimensions in the range 3.4–3.85 Å.

Whisker Crystals. This type of crystal was found in almost every bronze preparation, sometimes as a small proportion of the crystalline sample, the rest of which consisted of more massive crystals, and sometimes comprising almost the whole of the prepared sample. Figure 1 shows the form of these crystals. It was impossible, because of the small size of the individual whiskers, to obtain diffraction patterns from which a unit cell could be determined unambiguously, but in two cases a clear indication of the unit cell was obtained.

The first of these was a small bundle of whiskers from a specimen of composition $\text{Sn}_{0.1}\text{WO}_3$. The diffraction patterns showed that the structure of the individual whiskers was similar to the last type described above with variable a and b dimensions. The c dimension was approximately 3.7 Å, and a superlattice was clearly evident with a unit cell for which $C = 8c$.

An attempt was made to obtain diffraction patterns from individual whiskers selected from a specimen of composition $\text{Sn}_{0.4}\text{WO}_3$. The evidence obtained was sufficient to show that the structure was almost certainly orthorhombic and of the 5-type or the 6-type already described; the pronounced difference between the a and b dimensions produces a characteristic diffraction pattern which cannot be confused with the other structures found among these bronzes.

This crystallographic survey has clearly shown the analogy with the known alkali bronzes but it has also highlighted the new structures that exist in these systems. The broad picture of increasing symmetry with increasing inclusion metal content is shown. Experiments are under way to prepare homogeneous specimens by annealing for exceedingly long times, and preliminary results show that this can be achieved for specimens above $x = 0.2$, the final specimens being entirely composed of massive rather than whisker crystals. However, it does seem at this stage that in this system structural homogeneity may be extremely difficult to achieve. Differences in the free energy of these structures are probably so small that even slight changes in conditions during the long preparation result in inhomogeneities within the crystal. This aspect is at present being investigated by high resolution electron microscopy.

Mössbauer Spectra. Where possible, the Mössbauer samples were obtained as crystals of uniform appearance by separation under the microscope. In

this way bunches of whisker material were removed from the high tin content specimens. X-ray photographs of representative portions of the samples showed the orthorhombic form in $\text{Sn}_{0.01}\text{WO}_3$, which gave way through the tetragonal form to a great predominance of the hexagonal form in $\text{Sn}_{0.40}\text{WO}_3$.

Typical spectra are shown in Fig. 2. All samples showed the same basic spectrum which was in the region characteristic of quadrupole-split Sn(II) compounds. The chemical isomer shifts (δ) ranged about a value of 3.4 mm/sec, with a quadrupole splitting (Δ) of 1.2–1.6 mm/sec. There was no evidence of a Sn(IV) species in any of the samples, which is in accord with the fact that no cubic phases were found in the X-ray work. An upper limit of 10% can be placed on the proportion of Sn(0) in the metallic state, which, if present, would produce an additional resonance in the region of the low-velocity Sn(II) component.

The absence of Sn(0) is significant and shows that an extended overlapping of the orbitals of the tin atoms to form a metallic band system does not occur, as might be the case if the tin occupied adjacent substitutional sites in clustered arrays as proposed by Mackintosh (7) and Fuchs (8) for the case of the sodium bronzes.

The presence of Sn(II) indicates that electrons have been withdrawn from the tin atoms. Comparison of the observed chemical isomer shift with the electronic configuration scale recently established by Goldanskii and co-workers (13), suggests that p electrons have been withdrawn rather than s . According to this scale, the increase in the chemical isomer shift from the values characteristic of Sn(0) phases ($5s^1 5p^3$) indicates a valence-electron configuration of $5s^{1.1} 5p^{2.7}$, where the s electron density at the nucleus and hence the chemical isomer shift have been increased due to the higher s character of the orbitals and the reduction in shielding from the $5p$ electrons. Donation of the $5p$ electrons into the WO_3 conduction system assumed by the Goode-nough–Sienko model (9–10) accounts for the metallic conductivity in the same way that donation of Na $3s$ electrons does in the sodium bronzes.

The absence of Sn(0) in the spectrum of $\text{Sn}_{0.40}\text{WO}_3$ even at 4.2°K sets an upper limit of 0.002 kcal/mole on the ionisation energy of Sn(0) to Sn(II) in the bronze lattice, and implies that the Sn(II) do not act as trapping centres for the conduction electrons. This is in accord with the nonactivated electrical conductivity found in high-sodium bronzes Na_xWO_3 down to 4.2°K (14).

A more detailed consideration of the quadrupole

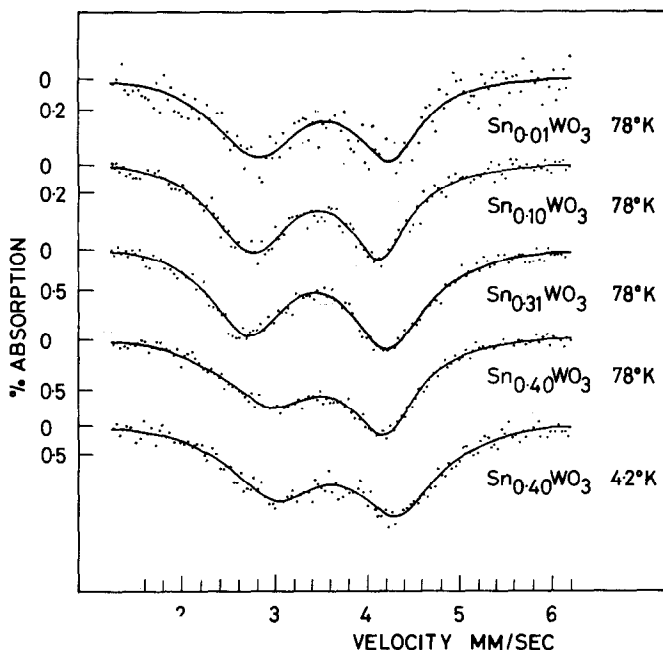


FIG. 2. The Mössbauer spectra of Sn_xWO_3 and the computed sum of two Lorentzian peaks (lines), showing the quadrupole doublet of Sn(II). The spectrum of $\text{Sn}_{0.40}\text{WO}_3$ at 78°K shows the most pronounced asymmetry.

doublet spectra shows that the two components do not have equal intensities, the asymmetry being most pronounced for $\text{Sn}_{0.40}\text{WO}_3$. A similar asymmetry found in the spectra of SnS and SnSe has recently been shown to arise from vibrational anisotropy of the modes of the tin atoms (15) which is favoured by the relative ease of vibration in the direction perpendicular to the layers of which the structure is composed. Such an effect, first predicted by Karyagin (16), increases with temperature, which was also found to be the case for the spectra of the tin bronzes over the temperature range used (4.2 – 295°K in some cases). Such a resonance would be expected from Sn(II) in the tunnel sites in the bronze lattice, since vibration in the tunnel direction will be less constrained than that in the perpendicular direction. The increase in the asymmetry from $\text{Sn}_{0.01}\text{WO}_3$ to $\text{Sn}_{0.40}\text{WO}_3$ would indicate an increasing proportion of occupied tunnel sites.

Alternatively, the asymmetry could arise from the asymmetrical overlap of two or more sets of quadrupole doublets, each arising from a slightly different Sn(II) environment, which may indicate a range of sites in each structure, but which would more likely arise from the presence of a mixture of forms in the Mössbauer samples. It is unlikely, however, that these effects would combine to produce the observed marked temperature dependence of the asymmetry. Possible asymmetry arising from

a net orientation of the crystallites in the sample was shown to be absent since it persisted when the samples were intimately ground with a tenfold excess of alumina, and did not change when one of the samples was rotated through $22\frac{1}{2}^\circ$ and 45° relative to the incident γ -ray beam.

Investigations aimed at isolating the possible origins of asymmetry are proceeding.

In both the X-ray and Mössbauer work no difference could be detected in specimens of a given x value made by all three preparative methods. In all cases reaction seems to proceed by inclusion of Sn in the WO_3 structure by vapour phase reaction in such a way that the very thin whisker crystals occur. These continue to take up tin when available which when a critical concentration has been reached, undergoes an ordering process leading to the orthorhombic and higher symmetry phases. Thus it might not be surprising to find that small conditional changes can have very marked structural effects.

Further Mössbauer experiments are envisaged on very well-annealed specimens, on new iron bronzes recently prepared, and on a range of bronzes containing both Sn and Fe, Sn and Eu.

Some of the tin bronzes are also to be the subject of more detailed X-ray work and in particular it is hoped to determine the structures of some of these interesting materials.

Acknowledgments

We wish to thank Professor N. N. Greenwood for Mössbauer facilities at Newcastle University.

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