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The Preparation, Phase Relationships, and Eu-151 Mössbauer Spectroscopy of Europium Tungsten Bronzes and Related Phases

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Crystal chemistry and phase relations for the bronze-forming region of the Eu–W–O system have been investigated. A bronze Eu_xWO_3 is stable up to 1000°C when $x \leqslant 0.125$ and in the region $0.085 \leqslant x \leqslant 0.125$ the symmetry is cubic. A tetragonal bronze exists at $x = 0.05$, and an orthorhombic bronze with a structure closely related to the orthorhombic form of WO_3 exists below $x = 0.01$. Mössbauer spectra at room temperature and at 80 K indicate that in all these phases the europium is highly ionized as Eu(III) with no electron localization to give (EuII) even at low values for x. The decomposition products of the bronzes have been established, and the Mössbauer parameters for the highly nonstoichiometric tungstates Eu_xWO_4 were determined. Both Eu(II) and Eu(III) resonances were obtained, and a cation vacancy model for Eu_xWO_4 was found to fit the data best. In conformity with the foregoing data, a sample of composition "$Eu_2W_2O_7$" was found not be be a pyrochlore but to comprise a mixture of Eu_6WO_{12}, Eu_xWO_4, and W. The phase relationships for the europium bronze system Eu_xWO_3 are compared with those of other ionic bronzes Na_xWO_3, Li_xWO_3, and Al_xWO_3.

Introduction

Current researches on mixed tungsten bronze systems have highlighted the paucity of data on europium tungsten bronzes. A recent study of phase relations and crystal chemistry in the Eu–W–O system (*1*) has confirmed the existence of a cubic bronze Eu_xWO_3 with x in the range 0.07–0.15 but gave no detailed information on the bronze region. Earlier, Ostertag (*2*) reported the preparation of the cubic bronze with $0.085 < x < 0.16$. Both reports noted a slight splitting of several reflections and broadening of high-angle reflections in X-ray powder patterns of $Eu_{0.15}WO_3$ that suggested a phase change to lower symmetry at the upper limit of europium content. If this were the case then the europium bronze would be unusual compared to other bronze systems where the highest symmetry is obtained at the highest guest metal concentration. There exists a passing mention to a lower symmetry europium bronze with composition $Eu_{0.015}WO_3$ in a communication dealing with the Al_xWO_3 system (*3*).

From the cubic symmetry and magnetic susceptibility measurements of Ostertag it has been inferred that europium exists as Eu(III) in the bronze. This makes these bronzes intrinsically interesting since in general guest elements in bronzes are found to exhibit their lowest oxidation state, for example, In^+ in In_xWO_3 (*4*), Sn^{2+} in Sn_xWO_3 (*5*), and Cu^+ in Cu_xWO_3 (*6*). Thus, it was thought desirable to use the Mössbauer effect to determine directly the europium oxidation state. Another reason for using this technique was to see if the europium valency changed on lowering the symmetry of the bronze at lower europium contents. It was

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soon found that in fact the Mössbauer technique is a valuable aid in phase identification studies when mixtures of low-symmetry phases result from preparations or decompositions.

Experimental

Materials used in this study were Eu_2O_3 (99.99% Rare Earth Products Ltd), WO_3 (Specpure grade Johnson and Matthey), W metal (99.99% Johnson and Matthey), and Eu metal (>99.9% Rare Earth Products Ltd). Samples were prepared by dry-mixing the appropriate weights of Eu_2O_3–WO_3–W or WO_3–Eu in closed weighing bottles in a tumble mixer for 24 hours and then sealing 2–3 g in silica ampules at vacuum $<10^{-5}$ mm Hg. These tubes were heated for 240 hours at 1000°C. Only specimens that showed no visual evidence of attack on the silica tube were used in the subsequent study. Several preparations were remixed after the initial examination and heated for a further 10 days to check that equilibrium had been achieved. Periodically analyses were performed by gravimetric oxidation to the Eu_2O_3–WO_3 join in a procedure similar to that of McCarthy (*7*) using a Stanton thermal balance. X-ray powder data were obtained using an 11.49 cm Debye–Scherrer camera and a Guinier focusing camera using nickel filtered $CuK\alpha$ radiation ($\lambda = 1.54178$ Å). Because of the many colored phases, red, orange, blue, purple, golden, and yellow, microscopy with both transmitted and reflected light was extensively used throughout the phase analyses in conjunction with the X-ray analyses. The Mössbauer spectrometer used to obtain the europium-151 spectra in this work has been described previously (*8*). A source of 10 Ci of samarium-151 as samarium fluoride with a recoil-free fraction of 0.15 at 300 K and 0.45 at 80 K was used. This has been shown to give a linewidth close to the natural linewidth expected for an unsplit absorber. Eu_xWO_3 samples with $x > 0.05$ provided no experimental problems and although count rates were rather low at 300 counts per channel per hour, acceptable spectra could usually be obtained in 40 hours counting. By cooling the source to 80 K a threefold improvement in f factor was achieved. The geometry was also improved by halving the source to detector distance; this resulted in an observable base line curvature, but the triangular wave form enabled this to be removed by folding the two symmetric halves of a spectrum onto each other before computing. Using this arrangement it became possible to obtain the Eu-151 spectrum of two samples containing very low concentrations of europium, namely, $x = 0.02$ and $x = 0.01$ in Eu_xWo_3. Chemical isomer shifts δ' are quoted relative to EuF_3 at room temperature and are uncorrected for the small error introduced by computing the resonance as an undistorted Lorentzian (*9*). A few specimens were examined on a variable-temperature Gouy magnetic susceptibility balance down to 80 K.

Results and Discussion

The Upper Limit of Eu_xWO_3 and its Decomposition Products

A series of samples of composition Eu_xWO_3 ($x = 0.5$, 0.4, 0.3, 0.2, and 0.1) were prepared from the oxides and tungsten metal; these were blue-black in color at $x = 0.1$, changing to a dull rust color at $x = 0.5$. Microscopy, X-ray analysis, and Mössbauer spectroscopy all confirmed that the $x = 0.1$ specimen was a single-phase cubic bronze. The other samples consisted of a mixture of deep blue crystals, relatively large flakes of orange crystal, and golden metallic crystals. Mössbauer spectroscopy showed an increasing percentage of Eu(II) in the mixtures (Table I) as x increased and the X-ray patterns for these samples showed many more lines than those of the cubic bronze. A specimen of $EuWO_4$ was synthesised from WO_3, Eu_2O_3, and W metal in a sealed evacuated tube and examined. Its Mössbauer parameters ($\delta' = -12.8$ mm sec^{-1}, $\Gamma = 3.57$ mm sec^{-1}) were in agreement with those of the Eu(II) phase in these preparations (see data in Table IV to be discussed later) and its appearance was like that of the orange-red crystals. It was found to have the expected tetragonal scheelite structure $a = 5.411$ Å, $c = 11.93$ Å which gave an x-ray diffraction

TABLE I

MÖSSBAUER DATA ON EUROPIUM-TUNGSTEN BRONZES AT 80 K

	Eu(II)			Eu(III)		
x in Eu_xWO_3	%	δ'[a] (mm sec^{-1})	Γ[b] (mm sec^{-1})	%	δ' (mm sec^{-1})	Γ (mm sec^{-1})
0.5	90	−12.89(4)[c]	4.2(3)	10	0.00(2)	2.5(1)
0.4	84	−12.60(8)	4.1(3)	16	−0.05(8)	1.4(3)
0.3	67	−12.76(7)	3.6(2)	33	−0.07(2)	2.0(1)
0.2	trace	—	—	100	+0.03(4)	2.1(2)
0.1	0	—	—	100	0.00(2)	2.1(2)
0.08	0	—	—	100	0.00(4)	2.5(2)
0.07	0	—	—	100	−0.07(4)	2.33(7)
0.06	0	—	—	100	−0.04(7)	2.5(1)
0.05	0	—	—	100	−0.05(3)	2.34(7)
0.04	0	—	—	100	−0.17(1)	3.34(9)
0.02	trace	—	—	100	+0.14(9)	2.5(4)
0.01	0	—	—	100	+0.24(6)	3.8(6)

[a] δ' relative to EuF_3 at room temperature.

[b] Γ full width at half-maximum resonance.

[c] Figures in parentheses are standard deviation in last significant figure.

pattern which, when added to that of WO_2, accounted for the extra lines in the samples examined above $x = 0.1$. Thus the bronze above a limiting europium content is unstable and decomposes to a cubic bronze of lower x value, plus $EuWO_4$ and WO_2.

A more detailed examination involving the preparation of closely related compositions in the region $x = 0.1$ to 0.2 enabled an upper limit of 0.125 ± 0.005 to be established for the composition of the cubic europium bronze. This is somewhat lower than either of the previously reported values and might be a result of the lower preparation temperature in this work 1000°C as against 1050°C in earlier work or the much longer time given for the reaction here. There is no evidence in this work to suggest a lower symmetry bronze above $x = 0.125$, thus indicating that the europium bronze system behaves like other tungsten bronzes in this respect.

An attempt was made to see if the method of preparation affects the upper limit of europium content. A series of specimens with $x = 0.32, 0.2, 0.11$, and 0.08 were prepared from WO_3 and europium metal at 1050°C. Large single crystals of WO_3 were used in an attempt to obtain single crystals of bronze for subsequent studies. Only one of these samples $x = 0.2$ gave a good Eu(III) Mössbauer resonance, and even in this case it was only a fraction of the observed effect for the 0.2 sample prepared from Eu_2O_3. This sample contained a much higher percentage of the Eu(II) phase than expected. All the remaining samples contained WO_2 and $EuWO_4$ thought to arise because europium vapor produced a concentration of europium on the surface of the WO_3 crystals that then decomposed to $EuWO_4$ and WO_2. This suggests that the diffusion of europium is slow at this temperature.

The Cubic Region $Eu_{0.125}WO_3$–$Eu_{0.085}WO_3$

Preparations in the range $x = 0.125$ down to 0.085 were all deep blue-black in color, and single-phase by X-ray diffraction, optical microscopy, and Mössbauer spectroscopy. The lattice parameter of the cubic phase can be expressed as a linear relationship $a_0 = 3.787 + 0.200x$ from 3.812 Å at $x = 0.125$

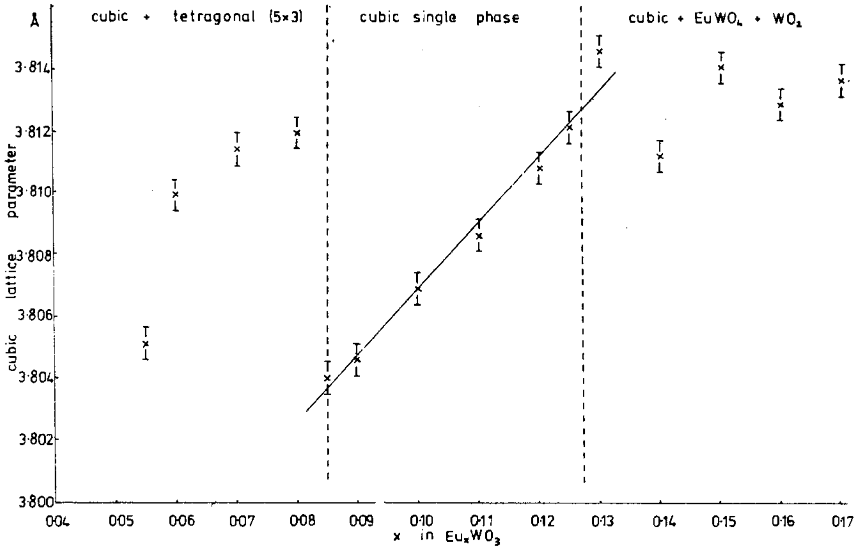

FIG. 1. Lattice parameter versus composition curves for europium–tungsten bronzes.

to 3.804 Å at $x = 0.085$ (see Fig. 1). The intercept of 3.787 Å for $x = 0.0$ represents the parameter of a theoretical cubic WO_3 lattice. Similar values for the intercept have been obtained in another study (*10*) and are shown in Table II. Mössbauer parameters throughout this region show no change (Table I) in that the europium always exists as Eu^{3+} ions. The observed shift indicates that ionisation is as complete as that in EuF_3 with no sign of a negative shift that would occur due to shielding if the 6*p* orbitals were occupied as required by the Mackintosh–Fuchs theory (*11*). Hence it can be concluded that the Sienko–Goodenough model (*12*) is more in accord with the cubic bronze.

TABLE II

CONSTANTS FOR LATTICE PARAMETER VERSUS COMPOSITION PLOTS FOR SOME CUBIC BRONZE SYSTEMS

M_xWO_3 System	Slope	Intercept (Å)	Reference
$Eu_{0.085-0.125}$	0.200	3.787	This work
$Na_{0.45-0.97}$	0.082	3.785	(*10*)
Li	−0.134	3.782	(*10*)
Gd	0.230	3.785	(*10*)
U	0.278	3.785	(*10*)

The temperature at which aerial oxidation began and the temperature at which the maximum rate of oxidation occurred were only slightly influenced by the europium content, with the most stable composition being $Eu_{0.1}WO_3$ where oxidation began at 625°C and reaching a maximum rate at 775°C. A D.T.A. examination of a cubic bronze $Eu_{0.12}WO_3$ showed no phase changes or decomposition up to 1050°C.

Bronzes with Low Europium Content

A number of preparations in the region $0.058 < x < 0.085$ were observed to be two phase by X-ray diffraction and optical microscopy. The Mössbauer technique was not able to distinguish between the two phases. Figure 1 shows that the lattice parameter of the cubic bronze in equilibrium with a phase of tetragonal symmetry varies systematically. No variations in the lattice parameters of the tetragonal phase $a = 5.295$ Å, $c = 3.871$ Å could be detected throughout this region. A preparation of stoichiometry $Eu_{0.06}WO_3$ was estimated from x-ray diffraction intensities to contain 19 mole% of the cubic bronze $Eu_{0.115}WO_3$ $a_0 = 3.810$ Å and 81% of the tetragonal phase, which puts the composition of the tetragonal phase at $Eu_{0.048}WO_3$. Similarly, preparations with $x = 0.08$, 0.07, and 0.055 were found to contain 42, 29, and 10% of cubic bronze with compositions $Eu_{0.125}WO_3$, $Eu_{0.122}WO_3$, and $Eu_{0.09}WO_3$, respectively. All this suggests that the composition of the tetragonal bronze is 0.048–0.050 Eu. The Mössbauer spectra of specimens with x in the region 0.085–0.05 showed 100% Eu(III) and since from 58–91% is the tetragonal phase then the Eu in this structure is ionised as completely as in EuF_3 with no detectable difference from Eu(III) in the cubic bronze. Table I shows this to be true down to $x = 0.05$. The preparation of $Eu_{0.05}WO_3$ was found to be single phase and tetragonal $a = 5.295$ Å, $c = 3.871$ Å.

This tetragonal phase has a very narrow range of composition because when $x < 0.048$ x-ray diffraction and microscopic examination revealed a second noncubic phase. Only when the mix composition was $Eu_{0.05}WO_3$ was a microscopic and X-ray single phase product obtained. The Mössbauer parameters of this tetragonal phase were identical to that of the cubic bronze phase which leads one to expect that the local environment of the Eu(III) is identical in both structures. However, experiments with Eu(III) coordination compounds (*13*) have shown that Mössbauer spectroscopy is not a very sensitive probe of environment. Magnetic susceptibility measurements on cubic $Eu_{0.08}WO_3$ and tetragonal $Eu_{0.05}WO_3$ gave coincident results, and one can infer from the two types of experiment that in both structures the Eu(III) ions occupy virtually unaltered 12-coordinate cubic sites. Furthermore, in the tetragonal phase complete ionisation of Eu(III) must still occur, and since the measurements were made at 80 K the electrons must still be completely delocalised leading to metallic conduction in the bronze $Eu_{0.05}WO_3$ even though on an electronic basis of 0.15 electrons per WO_3 this bronze is well below the point at which transition to a semiconductor should have occurred.

In the range $0.015 < x < 0.05$ the phase analysis by x-ray diffraction was complicated by the low symmetry and large lattice parameters of the phases. Only Guinier films were useful. A personal communication from Professor Pouchard (*3*) was of assistance in the interpretation, for he had obtained earlier a single crystal from a preparation of overall composition $Eu_{0.015}WO_3$ in which he observed a weak superlattice for the orthorhombic unit cell. Thus $a \approx 2a$, where a has the value close to that for the orthorhombic form of WO_3, $b \approx 2b$, and $c \approx 2c$. Table III shows that calculated and experimental $\sin^2\theta$ values for a preparation of $Eu_{0.02}WO_3$, which show it to be a two-phase mixture of the $Eu_{0.05}WO_3$ tetragonal phase and an orthorhombic phase with $a = 14.43$ Å, $b = 15.703$ Å, $c = 7.671$ Å. This two-phase region extends down to $x = 0.01$ where a single phase region of the orthorhombic bronze can be identified down to values of x very close to zero.

It was eventually possible to obtain Mössbauer data for two very low europium content preparations, namely, $Eu_{0.02}WO_3$ and $Eu_{0.01}WO_3$. It can be seen in Table I that there is a small but definite change to negative values of δ' and to a wider line width Γ for the orthorhombic compound compared to the tetragonal (5 × 3) phase but the europium is still present as Eu(III).

Nonstoichiometric Tungstates

Table I shows that a trace of Eu(II) was present in the $x = 0.02$ bronze preparation but not in the $x = 0.01$ sample. This anomaly may have been due to a slight local inhomogeneity producing some $EuWO_4$, which although too small an amount to be detected by X-rays could just be found by Mössbauer spectroscopy because of its high europium content. It is also possible that errors could have led to this sample being in a two-phase region not explored by McCarthy (*1*) consisting of orthorhombic Eu_xWO_3 and $Eu_2W_3O_{12}$. The latter proposition was felt to be unlikely since the structure of $Eu_2W_3O_{12}$ has been described as $(Eu_{0.67}\square_{0.33})WO_4$ in which all the europium is present as Eu(III) in nearly regular eightfold coordination by oxygen (*14*). Such a compound with ordered vacancies and some similarities to the bronzes was felt to be interesting with respect to its Mössbauer parameters, and therefore it was prepared in a sealed evacuated tube from $Eu_2O_3 + WO_3$ at 1040°C. Its parameters are given in Table IV which show it to be 100% Eu(III) and to be

TABLE III

X-RAY POWDER DATA FOR $Eu_{0.02}WO_3$

		$10^4 \sin^2\theta$(calc)			
Intensity[a]	$10^4 \sin^2\theta$ (obs)	Orthorhombic	($h\,k\,l$)	Tetragonal (5 × 3)	($h\,k\,l$)
VS	398	—	—	399	0 0 1
W	408	404	0 0 2	—	—
S diffuse	422	414	1 4 0	430	1 1 0
S diffuse	455	457	1 1 2	—	—
VW	503	499 500	5 0 1 5 0 3	—	—
W	531	529	5 3 1	—	—
S	613	614	2 2 2	614	1 0 1
VVW	620	621	0 3 2	—	—
VVW	642	638	3 4 0	—	—
S	820	818	1 4 2	—	—
M	835	838	5 1 1	829	1 1 1
VS	860	861	4 0 2	860	2 0 0
W	930	931	5 3 0	—	—
VVW	939	934	0 1 3	—	—
VVW	1007	1007 1006	0 5 2 0 2 3	—	—
VVW	1226	1224	6 2 1	—	—
VS	1258	—	—	1259	2 0 1
W	1410	1410	2 4 3	—	—
VVW	1434	1432	6 0 2	—	—
M diffuse	1464	1464	4 5 2	1474	2 1 1
M diffuse	1488	1488	7 2 0	—	—
S	1596	—	—	1596	0 0 2
W	1641	1646	5 1 3	—	—
VS	1811	—	—	1811	1 0 2

[a] VVW, very very weak; VW, very weak; W, weak: M, medium; S, strong; VS, very strong.

TABLE IV

MÖSSBAUER DATA FOR NONSTOICHIOMETRIC EUROPIUM TUNGSTATES AT 80 K

Compound Eu_xWO_4	x calc. from resonance areas	Eu(II)		Eu(III)	
		δ'^a (mm sec^{-1})	Γ^b (mm sec^{-1})	δ' (mm sec^{-1})	Γ (mm sec^{-1})
$EuWO_4$	1.00	−12.8	3.57	—	—
$Eu_{0.90}WO_4$	0.88	−12.64(6)[c]	3.84(16)	0.38(6)	2.29(19)
$Eu_{0.85}WO_4$	0.84	−12.76(7)	3.94(18)	0.38(4)	2.27(12)
$Eu_{0.80}WO_4$	0.79	−12.77(12)	5.23(39)	0.40(3)	2.27(10)
$Eu_{0.66}WO_4$	0.66	—	—	0.48(3)	2.19(10)

[a] δ' relative to EuF_3 at room temperature.

[b] Γ full width at half-maximum resonance.

[c] Figures in parentheses are standard deviation in last significant figure.

even more ionic than europium in the bronzes.

The monoclinic structure of $Eu_2W_3O_{12}$ is related to the scheelite structure found for $EuWO_4$. A region of solid solution between these two phases has been described from $x =$ 0.82–1.00 in Eu_xWO_4, and two defect models which could account for the solid solution have been suggested, viz., an interstitial anion model $[Eu_{x(1-2y)}{}^{2+}Eu_{2xy}{}^{3+}]\ WO_4(O_{xy})_i$, or a cation vacancy model $[Eu_{1-3y}{}^{2+}Eu_{2y}{}^{3+}\square_y]WO_4$. Samples of Eu_xWO_4 with $x = 1.0$, 0.90, 0.85, 0.80, and 0.66 were prepared from Eu_2O_3, WO_3, and W at 1000°C in order to test which model was the more appropriate and to establish data enabling this phase to be recognized in these bronze studies. This preparative route was chosen rather than the alternative one from Eu_2O_3, Eu metal, and WO_3 because the earlier work on the bronzes had shown that the reaction between europium and WO_3 leads to inhomogeneities in the mix with resultant difficulties in achieving equilibrium.

Data in Table IV show a gradual change of the ratio Eu(II): Eu(III) in the range $x =$ 0.66–1.00 for Eu_xWO_4. The ratio of Eu(II): Eu(III) was calculated from the ratio of the resonance areas assuming that the oxidation state had the same recoil-free fraction; the ratio changes in the manner expected for the cation vacancy model, i.e., $(1 - 3y)/2y$ but the interstitial anion model is not rigorously excluded. A spectrum is shown in Fig. 2. There is a slight change in the chemical isomer shift of Eu(II) and Eu(III) between the extremes of $EuWO_4$ and $Eu_2W_3O_{12}$ (i.e., $Eu_{0.66}WO_4$). These specimens were prepared in sealed ampules from reagents calculated to give Eu_xWO_4 and so obtain interstitial oxygens in the numbers required some WO_4^{2-} units must be eliminated with the appearance of a tungsten oxide phase most likely to be WO_2. These were never any evidence of this in the x-ray or microscopic examinations, which does lend strength to the proposed cation vacancy model.

In a concurrent investigation still to be completed and reported in detail on mixed europium–tin–tungsten–bronze systems a cubic phase with composition $M_2W_2O_7$ was suspected which could have been a europium pyrochlore $Eu_2{}^{3+}W_2{}^{4+}O_7{}^{2}{}_{-}$. According to the current phase diagram, however, such a phase would break down to give $EuWO_4$, Eu_6WO_{12}, and W metal. Accordingly a sample of composition $Eu_2W_2O_7$ was prepared and examined by X-ray diffraction and Mössbauer spectroscopy. It was in fact found to be a mixture containing two europium-bearing phases: 32.8 (7%) of the total resonance area at 80°K had $\delta' = 0.90(5)$ mm sec^{-1} and $\Gamma = 5.0(6)$ mm sec^{-1}, and the remaining 67.2 (7%) of the resonance had $\delta' = 13.48(4)$ mm sec^{-1}, and $\Gamma = 5.3(1)$ mm sec^{-1}. Thus one-third of the sample of "$Eu_2W_2O_7$" consisted of a Eu(III) compound having a chemical isomer shift unlike any other found in these systems and which is presumably Eu_6WO_{12}, whereas two-thirds of the sample consisted of a Eu(II) compound the isomer shift of which was not that of the $EuWO_4$ end member. It could be that $EuWO_4$ can be reduced by free

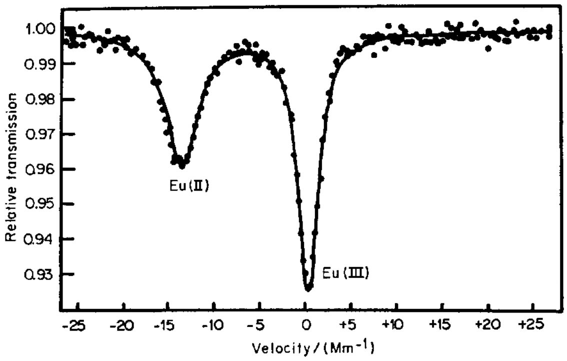

FIG. 2. Mössbauer spectrum for $Eu_{0.8}WO_4$ at liquid nitrogen temperature.

tungsten to produce $Eu_{1-x}WO_{4-x}$ or that "$Eu_2W_2O_7$" decomposes into Eu_xWO_4, and Eu_6WO_{12} and not to the stoichiometric end member.

The X-ray examination of this preparation showed that Eu_6WO_{12} as identified by McCarthy together with "$EuWO_4$" and a trace of W were present. However, each of the tungstate lines was split in the manner expected for a sample that contained two phases with close related lattice parameters. Taking the isomer shift value for the Eu(II) phase into account it seems most likely that some $EuWO_4$ is being reduced by free tungsten.

A subsequent experiment showed that after 3 days the phase assemblage was $Eu_6WO_{12} + EuWO_4 + W$, but after 12 days at 1000°C the intensity of the W pattern decreased and the $EuWO_4$ lines became doublets, thus supporting the view that the assemblage needs considerable time to reach equilibrium as free W reduces the stoichiometric tungstate.

General Discussion

The work provides further direct evidence for the simple model of tungsten bronzes in which guest metals are incorporated as ions and donate electrons to a band based on tungsten and oxide orbitals. Following from this simple model one has come to expect considerable similarity in the phase behavior of tungsten bronze systems, but even allowing for the variability of the available data the great variety of the reported behavior is noticeable. Some of the variations can be rationalized if one focuses on the relative behavior of the guest ions, a point which tends to be overlooked in the approach which ascribes the chemistry and physics of the bronzes primarily to the behavior of the WO_3 host lattice. For example, the preference for tin bronzes at high tin content to exhibit tetragonal (12 × 3)* symmetry (*5*) and not the hexagonal symmetry expected both from size considerations and comparisons with K_xWO_3. This can be ascribed to the availability of pentagonal sites in the (12 × 3) structure, which provide space for an asymmetric site (*16*) and allows the lone pair of electrons on tin to be accommodated more easily. It is then not surprising to find that the bronzes of later transition elements, Cu, Ag (*6*), Fe (*17*), Co, and Ni (*18*) form an anomalous group being characterized by very low symmetry even at high metal concentrations and having unusual magnetic and electrical properties. This narrows down the area of search for valid comparisons for the results of this work; comparisons should be sought among bronze systems of metals whose chemistry is essentially ionic. Even then we are presented with some facts which indicate some underlying tendencies related to size differences. Figure 3 shows the phase sequence for Na_xWO_3, Li_xWO_3, Eu_xWO_3, and Al_xWO_3 as a function of the number of electrons per tungsten atom donated to the conduction band. Taking the sodium case as "normal" (mainly because the phase sequence is well established and changes gradually to lower symmetry as the number of band electrons per tungsten atom through well-defined single- and two-phase regions), we can see that by increasing the guest metal ion valency and by decreasing its size the (12 × 3) phase is not formed, the upper limit of stability of the phase of highest symmetry decreases, and the change over ratios are at markedly different points. For high charge and small size it can be seen from the Al_xWO_3 case that the symmetry of the phases is always low and the phase order unique. Comparing Eu_xWO_3 and Al_xWO_3 where the ions are 3+ the decrease in symmetry can probably only be accounted for in terms of ionic radii ($Al^{3+} = 0.50$ Å, $Eu^{3+} = 1.03$ Å) even though these ions are located in almost identically sized 12-coordinate sites. The Li_xWO_3 and Eu_xWO_3 results show that, as the size decreases or ionic charge increases, the upper limit of stability of the phases decreases while the lower limit goes to lower values of band-electron concentration. For example, the upper limit of cubic phase stability at $Eu_{0.125}WO_3$ does not overlap with the lowest composition for the cubic phase in the Na_xWO_3, case at $Na_{0.45}WO_3$, whereas for Li_xWO_3 and Eu_xWO_3 the lower limit of the cubic phase

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* This notation is felt to be less confusing than the use of tetragonal I or tetragonal II, it represents the tetragonal I phase in the original work by Magneli (*15*).

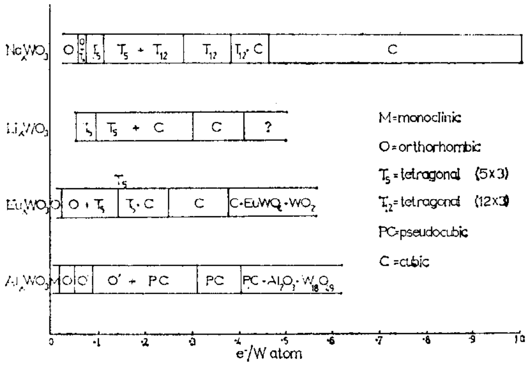

FIG. 3. Comparison of phases present in M_xWO_3 at increasing electron concentration per tungsten atom.

goes down to 0.3 and 0.255 electrons per tungsten atom, respectively. Thus, within this comparable group, the variation in phase stability and phase boundaries with charge and size suggests that, when data are available, a model involving coulombic forces as the major factor in stability might be useful if consideration is limited to M^{n+}–O^{2-} attractions and M^{n+}–W^{6+} repulsions.

An interesting feature of the present work is the constant oxidation state of Eu^{3+} in the bronzes. This feature is more intriguing when the behavior of europium in mixed europium–tin–tungsten bronzes is considered for in this system a tetragonal (3 × 12) phase does exist which contains both europium and tin in their divalent forms. Thus it seems that the tetragonal (12 × 3) structure requires low valent ions. This work will be described and discussed in a later publication.

Another interesting feature revealed by this work is that when the critical x value is exceeded in Eu_xWO_3 the europium precipitated from the structure appears as Eu^{2+} in $EuWO_4$ and not as Eu^{3+} in $Eu_2W_3O_{12}$ which might have been expected from the presence of Eu^{3+} in the bronze.

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References

1. G. J. McCarthy, R. D. Fischer, and J. Sanzgiri, *J. Solid State Chem.* **5**, 200 (1972).
2. W. Ostertag, *Inorg. Chem.* **5**, 758 (1966).
3. M. Pouchard, F. Berdoulay, and D. Vandeven, *C.R. Acad. Sci.*, **266C**, 1066 (1968).
4. J. S. Anderson and A. Swanson, *Mat. Res. Bull.* **3**, 149 (1968).
5. I. J. McColm, R. Steadman, and A. Howe, *J. Solid State Chem.* **2**, 555 (1970).
6. L. E. Conroy and M. J. Sienko, *J. Amer. Chem. Soc.* **79**, 4048 (1957).
7. G. J. McCarthy, W. B. White, and R. Roy, *J. Amer. Ceramic Soc.* **52**, 463 (1969).
8. I. Colquhoun, N. N. Greenwood, I. J. McColm, G. E. Turner, *J. Chem. Soc.* (*Dalton*) 1337 (1972).
9. B. A. Goodman, N. N. Greenwood, and G. E. Turner, *Chem. Phys. Letters* **5**, 181 (1970).
10. M. A. Wechter, H. R. Shanks, and A. F. Voigt, *Inorg. Chem.* **7**, 845 (1968).
11. R. Fuchs, *J. Chem. Phys.* **42**, 3718 (1965).
12. M. J. Sienko, *in* "Nonstoichiometric Compounds," Advances in Chemistry Series No 39, (R. F. Gould, Ed.) Amer. Chem. Soc. (1963).
13. G. E. Turner, Ph.D. Thesis, University of Newcastle-upon-Tyne (1972).
14. D. H. Templeton and A. Zalkin, *Acta Crystallogr.* **16**, 762 (1963).
15. A. Magneli and B. Blomberg, *Acta Chem. Scand.* **5**, 372 (1951).
16. R. Steadman, *Mat. Res. Bull.* **7**, 1143 (1972).
17. I. J. McColm, to be published.
18. M. Pouchard, J. P. Chaminade, J. P. Doumerc, J. C. Launay, and P. Hagenmuller, *Mat. Res. Bull.* **7**, 223 (1972).