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The Oxidation State of Europium in Niobates and Tantalates Having the Tetragonal Tungsten–Bronze Structure

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Europium-151 Mössbauer spectroscopy has been used to study the oxidation states and magnetic properties of europium in 15 mixed metal niobates and tantalates having the tetragonal tungsten–bronze structure. All the compounds featured substantial concentrations of Eu(III) in addition to the expected Eu(II) and this was shown to account for the low magnetic susceptibilities of the compounds. There was no evidence of electron charge hopping, at least on the Mössbauer timescale (~10 nsec) and no evidence of magnetic ordering of Eu(II) down to 4.2°K. The significance of these results is briefly discussed.

Introduction

Ternary and more complex oxide phases of niobium and tantalum have been extensively studied in recent years because of their interesting structural relationships, their ferroelectric properties, and their possible applications in electro-optic devices. In these phases, the presence of a large divalent cation M^{II} such as Sr, Ba, or Pb tends to produce a tetragonal tungsten–bronze structure (*1–3*), whereas tervalent rare-earth cations M^{III} produce perovskite phases (*4, 5*). Europium, with its two oxidation states Eu^{II} and Eu^{III}, is thus a particularly interesting substituent. Compounds of general formula $M^{I}_{2}M^{II}_{2}Eu_2Nb_{10}O_{30}$ and $M^{I}_{2}M^{II}_{2}Eu_2Ta_{10}O_{30}$ have been shown (*6, 7*) to have the tetragonal tungsten–bronze structure when M^{I} = Na, K and M^{II} = Ca, Sr, Ba, Eu. They are black (Nb) or dark brown (Ta) in color and are semiconductors or insulators. At first sight it would seem that these compounds should contain only Eu^{II} but the observed magnetic moments were always significantly below the expected value of 7.94 B.M. (*7*). We therefore undertook a Mössbauer spectroscopic study to determine the oxidation state(s) and magnetic properties of the europium at 4.2°K. The isotope ^{151}Eu is particularly convenient for such a study since it has a natural abundance of 47.8%, a transition energy E_γ of 21.53 keV, a natural experimental linewidth of 1.31 mm sec^{-1}, a very large chemical isomer shift from Eu^{II} to Eu^{III} of ~13 mm sec^{-1}, and a well-resolved magnetic hyperfine interaction (*8*).

The tetragonal tungsten–bronze structure can formally be derived from that of perovskite by rotation of fourfold groups of chains of MO_6 octahedra through 45° about the *c*

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axis $[00\bar{1}]$ so that four-fifths of the square perovskite tunnels are replaced alternately by triangular and pentagonal tunnels (*9*). The structure is shown in Fig. 1: each unit cell contains 10 MO_6 octahedra (M = Nb, Ta, W, etc.) which means that there are 4 triangular, 4 pentagonal, and 2 square tunnel sites available. The M–O–M angle along the c axis deviates from 180° and this leads to a slight pleating of the chains in this direction. The triangular sites are either empty or occupied by small cations such as $\mathrm{Li^{I}}$, $\mathrm{Be^{II}}$, or $\mathrm{Mg^{II}}$ as in $\mathrm{Li_4K_6Nb_{10}O_{30}}$ (*10, 11*). Cations occupying the square perovskite-type tunnel sites are coordinated by 12 oxygens and have 10 other cations within 400 pm, whereas those occupying the pentagonal tunnel are coordinated by 9 or 10 oxygens and have 9 other cations within 400 pm (excluding any cations in the triangular tunnel sites since these are not occupied in the compounds studied in the present work). For $M^{\mathrm{I}}_2M^{\mathrm{II}}_2\mathrm{Eu_2Nb_{10}O_{30}}$ and $M^{\mathrm{I}}_2M^{\mathrm{II}}_2\mathrm{Eu_2Ta_{10}O_{30}}$ all the square and pentagonal tunnel sites are occupied by Na, K, Sr, Ba, and Eu, apparently randomly, as previously found (*12*) for $A_2B_2C_2\mathrm{Nb_{10}O_{30}}$ with A = Na or K, B = Ca or Sr, C = Ca, Sr, or Ba. This indicates that the square tunnel sites are sufficiently large to accommodate the large potassium and barium ions, r(12 coord) = 164 pm and 161 pm, respectively (*13*). Likewise, for the compound $\mathrm{Eu_6Nb_{10}O_{30}}$ (i.e., $\mathrm{Eu_{0.6}NbO_3}$) all six square and pentagonal tunnel sites are occupied, whereas for $\mathrm{Eu}M_2\mathrm{O_6}$ (i.e., $\mathrm{Eu_5Nb_{10}O_{30}}$ and $\mathrm{Eu_5Ta_{10}O_{30}}$) only five of the six available sites are filled.

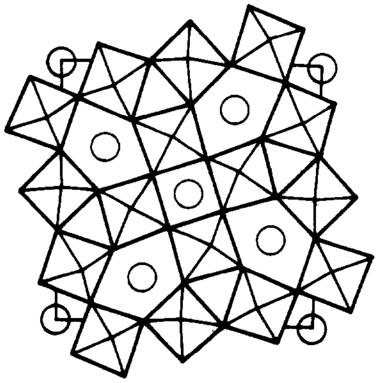

FIG. 1. The tetragonal tungsten–bronze structure projected along $[00\bar{1}]$; the square and pentagonal tunnel sites are occupied and the triangular sites are empty.

Experimental

The 15 compounds were prepared in Caen as previously described (*6*) and the Mössbauer spectra were obtained in Leeds using powdered samples containing approximately 25 mg Eu/cm^2. Transmission geometry was used with both the source and absorber immersed in liquid helium at 4.2°K in an Elscint cryostat MHC-3. The source was obtained from the Radiochemical Centre, Amersham and contained a nominal 300 mCi $^{151}\mathrm{SmF_3}$ ($t_{1/2}$ 90 years) mounted in a specially designed holder to withstand repeated thermal cycling. The spectrometer incorporated an Elscint MVT-3 transducer coupled to a MFG-3 waveform generator and a NaI(Tl) detector. The data were accumulated in two halves of a 512-channel Elscint (MEDA) multichannel analyzer and were folded to give $\sim 5 \times 10^5$ counts per channel in the resulting 256-channel spectra; they were computed using programs originally written by Dr T. C. Gibb. Isomer shift values are quoted relative to $\mathrm{EuF_3}$ taken as zero. Percentage resonance effects were of the order of 10 to12%.

Results and Discussion

Typical spectra are shown in Fig. 2, from which it is at once apparent that (a) there is a substantial concentration of Eu(III) in addition to the expected Eu(II); (b) there is no charge hopping or averaging of oxidation states of europium on the Mössbauer timescale (9.7×10^{-9} sec); and (c) there is no magnetic ordering of Eu(II) at least down to 4.2°K, despite the systematically greater

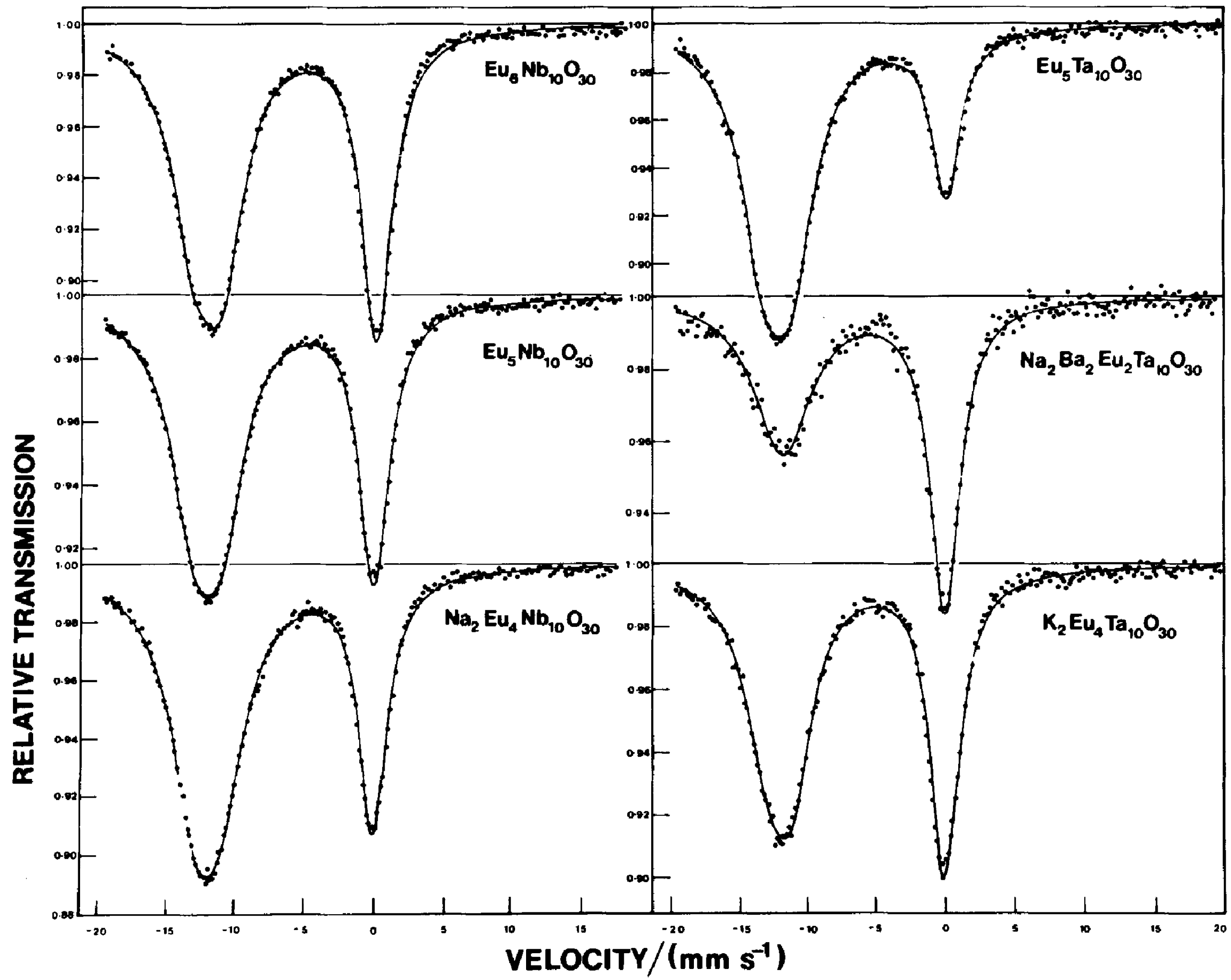

FIG. 2. Some typical europium-151 Mössbauer spectra for the mixed europium niobates and tantalates at 4.2°K.

linewidth of the Eu(II) resonance. Detailed information on isomer shifts, linewidths, and χ^2 values for the 15 compounds studied are given in Table I, from which it can be seen that the linewidths for the Eu(II) components of the spectra are invariably greater than those for Eu(III), frequently by a factor of 2 or more. Indeed, appreciably better least-squares fits to the spectra were often obtained by allowing for two components within the Eu(II) resonance (and occasionally also for Eu(III)) as shown in Table I. However, this probably merely reflects the distortions in the oxide sublattice and the variable occupancy of neighboring cation sites with the several cation species present rather than the existence of chemically or crystallographically distinguishable species. Quadrupole effects are rarely resolvable in europium spectra (*8*) though they can lead to non-Lorentzian lineshapes (*14*); in the presence of several electric field gradients arising from the statistical distribution of the various cations, such effects might well lead to a broadening that would be better fitted as a sum of Lorentzians.

The relative concentration of Eu(III) in these compounds can be estimated from the Mössbauer resonance areas on the assumption (which is reasonable for oxide phases at 4.2°K) that Eu(III) and Eu(II) have the same recoil-free fraction. The results are listed in Table II, from which it is clear that a substantial fraction of europium is present as Eu(III). This, at first sight, is surprising for a group of compounds whose stoichiometry and magnetic properties have previously been interpreted on the basis of Eu(II) only (*7*, *15*), but this merely emphasizes the insensitivity of magnetic moments of Eu(II)-containing compounds to the presence of Eu(III). In fact, the present results are entirely consistent with the previous magnetic data, as can be seen from the calculations summarized in Table II: these estimate the magnetic susceptibility χ on the assumption that there are no supernumerary oxide ions in the structure and that the

TABLE I

COMPUTED ^{151}Eu MÖSSBAUER PARAMETERS AT 4.2°K[a]

Compound (formula per unit cell)	Isomer shifts, $\delta/(\mathrm{mm\ sec}^{-1})$		Line widths, $\Gamma/(\mathrm{mm\ sec}^{-1})$		
	Eu(II)	Eu(III)	Eu(II)	Eu(III)	χ^2
$Eu_6Nb_{10}O_{30}$	−13.15, −11.09	−0.01	4.24, 3.73	2.77	813
$Eu_5Nb_{10}O_{30}$	−13.03, −11.01	−0.04	4.48, 3.93	2.71	505
$Na_2Sr_2Eu_2Nb_{10}O_{30}$	−12.19	−0.35, +0.77	6.83	2.27, 1.58	322
$K_2Sr_2Eu_2Nb_{10}O_{30}$	−11.83	−0.11	5.36	2.58	504
$Na_2Ba_2Eu_2Nb_{10}O_{30}$	−11.90	−0.09	5.62	2.81	415
$K_2Ba_2Eu_2Nb_{10}O_{30}$	−12.12, −11.12	−0.69, +0.55	4.22, 3.17	2.36, 1.93	272
$Na_2Eu_2Eu_2Nb_{10}O_{30}$	−12.90, −11.03	−0.05	4.71, 4.40	2.54	432
$K_2Eu_2Eu_2Nb_{10}O_{30}$	−12.85, −11.09	−0.23	4.47, 3.72	2.57	363
$Eu_5Ta_{10}O_{30}$	−13.55, −11.31	−0.01	3.98, 4.25	2.58	426
$Na_2Sr_2Eu_2Ta_{10}O_{30}$	−12.17	−0.04	6.29	2.55	309
$K_2Sr_2Eu_2Ta_{10}O_{30}$	−12.07	−0.33	5.78	2.68	229
$Na_2Ba_2Eu_2Ta_{10}O_{30}$	−11.95	−0.11	5.17	2.63	293
$K_2Br_2Eu_2Ta_{10}O_{30}$	−12.82, −11.23	−0.12	4.19, 3.27	2.63	254
$Na_2Eu_2Eu_2Ta_{10}O_{30}$	−12.82, −10.94	+0.02	4.89, 3.65	2.77	566
$K_2Eu_2Eu_2Ta_{10}O_{30}$	−12.93, −11.21	−0.09	4.44, 3.35	2.63	308

[a] Approximately 235 degrees of freedom. Isomer shift δ (± 0.05 mm sec^{-1}) relative to EuF_3 at 4.2°K.

TABLE II

AMOUNTS OF Eu(II) AND Eu(III) PER UNIT CELL BASED ON RESONANCE AREAS, AND DERIVED MAGNETIC MOMENTS[a]

Compound	Percentage Eu(III)[b]	Amount per unit cell Eu(II)	Eu(III)	M(IV)	$\chi \times 10^6$ (cgs)	$(\mu_M)_{calc}$ (B.M.)	μ_{exp} (B.M.)
$Eu_6Nb_{10}O_{30}$	36.3	3.82	2.18	4.18	19,260	6.78	6.95
$Eu_5Nb_{10}O_{30}$	32.8	3.36	1.64	1.64	19,570	6.87	7.19
$Na_2Sr_2Eu_2Nb_{10}O_{30}$	55.7	0.89	1.11	1.11	14,990	5.98	6.36
$K_2Sr_2Eu_2Nb_{10}O_{30}$	46.0	1.08	0.92	0.92	16,910	6.35	7.05
$Na_2Ba_2Eu_2Nb_{10}O_{30}$	36.4	1.27	0.73	0.73	18,830	6.70	7.30
$K_2Ba_2Eu_2Nb_{10}O_{30}$	41.9	1.16	0.84	0.84	17,720	6.50	6.48
$Na_2Eu_2Eu_2Nb_{10}O_{30}$	28.6	2.86	1.14	1.14	20,440	6.98	6.79
$K_2Eu_2Eu_2Nb_{10}O_{30}$	19.6	3.22	0.78	0.78	22,260	7.28	7.41
$Eu_5Ta_{10}O_{30}$	21.2	3.94	1.06	1.06	21,920	7.23	7.56
$Na_2Sr_2Eu_2Ta_{10}O_{30}$	30.9	1.38	0.62	0.62	19,940	6.90	7.27
$K_2Sr_2Eu_2Ta_{10}O_{30}$	32.3	1.35	0.65	0.65	19,640	6.84	7.37
$Na_2Ba_2Eu_2Ta_{10}O_{30}$	50.7	0.99	1.01	1.01	16,000	6.18	7.01
$K_2Ba_2Eu_2Ta_{10}O_{30}$	45.9	1.08	0.92	0.92	15,910	6.16	6.97
$Na_2Eu_2Eu_2Ta_{10}O_{30}$	38.5	2.46	1.54	1.54	18,420	6.63	7.01
$K_2Eu_2Eu_2Ta_{10}O_{30}$	38.7	2.45	1.55	1.55	18,370	6.62	7.14

[a] Calculated, as described in text, using $\chi(Eu^{II})$, $26{,}200 \times 10^{-6}$; $\chi(Eu^{III})$, 4800×10^{-6}; $\chi(Nb^{IV})$, 1200×10^{-6}; $\chi(Ta^{IV})$, 1200×10^{-6}.

[b] Based on computed area ratios; the third significant figure is retained solely for the purpose of calculation.

presence of Eu(III) is compensated for by the presence of Nb(IV) or Ta(IV). The corresponding magnetic moments based on the Mössbauer data $(\mu_M)_{calc}$ were then calculated using the Curie expression $\mu_M = 2.8278(\chi \cdot T)^{1/2}$ B.M. and the values so obtained are compared with the experimental values μ_{exp} in the last two columns of Table II. The agreement is seen to be very satisfactory. Similar agreement is obtained if the very small contributions from the presumed Nb(IV) and Ta(IV) are ignored. Likewise, the use of a Curie–Weiss relation $\mu_M = 2.8278\{\chi(T+\theta)\}^{1/2}$ B.M. made little difference because of the small θ values reported for these compounds (*15*).

No proof of the presence of Nb(IV) or Ta(IV) in these phases has yet been obtained despite preliminary studies by electron spin resonance and X-ray photoelectron spectroscopy (of the surface layers). However, the semiconducting or insulating properties of the compounds (*7*) imply that the supernumerary electrons introduced by the presence of Eu(III) must be localized somewhere, and the most feasible place is the valence band of the octahedral cations Nb and Ta. Analytical data rule out the possibility of substantial loss of europium on the scale required to produce the observed concentrations of Eu(III) according to the equation $3Eu(II) \rightarrow 2Eu(III) + Eu_{vap}$. Likewise, X-ray diffraction data preclude the presence of impurity phases in the required concentrations. The conclusion seems inescapable that the air-stable compounds $M^I_2M^{II}_2Eu_2Nb_{10}O_{30}$ and $M^I_2M^{II}_2Eu_2Ta_{10}O_{30}$ contain substantial concentrations of Eu(III) which vary from compound to compound but which appear to be constant on repeated preparation of any given compound (*15*).

Phases which contain an element in two oxidation states on crystallographically equivalent sites usually show "charge hopping" phenomena (*16*) and an "averaged" oxidation state in their Mössbauer spectra (*17*). The individual integrity of Eu(II) and Eu(III) when distributed with other cations on the square and pentagonal sites of the tetragonal tungsten–bronze structure is thus most unusual and can probably be related to the fact that a change in occupancy of the well-shielded 4*f* orbitals is involved rather than a change in the more exposed outer *p* or *d* orbitals. A similar charge localization has been observed in the Mössbauer spectrum of Eu_3S_4, which shows two well-resolved peaks with relative intensities 2 : 1 at low temperatures; however, even in this compound, electron hopping becomes discernible above 200°K and above 250°K the spectrum collapses to a broadened single absorption which progressively narrows to a sharp single resonance with a chemical shift which is the weighted average of the two previous lines (*18*). The room temperature spectra of the present compounds shows no such collapse, indicating an even higher energy barrier to fast-electron interchange on the Mössbauer timescale.

The third striking feature of the results is the absence of any magnetic ordering of the Eu(II) moments at 4.2°K. In these tetragonal tungsten–bronze phases the nearest-neighbor cation distances are ~380 to 390 pm, which are comparable with the Eu(II)–Eu(II) distances in the ferromagnetically ordered compounds EuO (363 pm, T_C 77°K), EuS (421 pm, T_C 16°K), and EuSe (437 pm, T_C 8°K), and substantially less than in the weak antiferromagnetic EuTe (467 pm, T_N 11°K). However, in the rock-salt structure adopted by the europium chalcogenides the ferromagnetic interaction between nearest-neighbor Eu(II) ions is along ⟨110⟩, whereas for perovskites and related structures this vector involves an indirect Eu–O–Eu interaction between next-nearest neighbors. The direct Eu–Eu interaction in perovskite-like structures is along ⟨100⟩ (*19*). Since little overlap can be expected between the 4*f* orbitals on adjacent Eu(II) the only possible ferromagnetic coupling would be from the overlap of the 5*d* orbitals on one Eu(II) with the 4*f* orbitals on its neighbor. In the perovskite structure the crystal field stabilizes the e_g state relative to the t_{2g} state and so the interaction will be with the oxygens located on the edges of the coordination polyhedra. The observed paramagnetic behavior of the present compounds down to at least 4.2°K implies that any ferromagnetic exchange via the e_g orbitals is extremely weak and comparable in strength with the 180° antiferromagnetic exchange. The possibility of such antiferromagnetism at temperatures below 2.8°K has been considered for the perovskite-like compound $Eu_2^{II}(Eu^{III}Ta)O_6$ since its measured magnetic susceptibility below this temperature is lower than the theoretical value (*20*). It should also be remembered that the large amounts of Eu(III) and other cations in the present tetragonal bronze phases greatly reduces the probability that a given Eu(II) ion has another Eu(II) as nearest neighbor. However, this factor by itself need not obliterate magnetic ordering since it it known that EuO remains ordered with little, if any, diminution in the hyperfine field when up to 30% of the Eu(II) is replaced by Eu(III) or another lanthanide ion as in $[(EuO)_{1-x}(\mathit{Ln}N)_x]$. (*21*). Any tendency for the larger Eu(II) ions to be preferentially located in the (larger) pentagonal tunnel sites and for the smaller Eu(III) ions to occupy the (smaller) square tunnel sites preferentially would, of course, diminish the statistical probability of long-range magnetic ordering of the Eu(II) ions still further. Recent results (*15*) suggest that such preferential occupancy may indeed occur in these tetragonal tungsten–bronze phases.

In summary, the use of ^{151}Eu Mössbauer spectroscopy has shown that a suite of 15 mixed metal niobates and tantalates with the tetragonal tungsten–bronze structure which had previously been thought to contain only Eu(II) in fact contain 20 to 55% of the europium as Eu(III). There is no charge-hopping between these two oxidation states and, although the Eu(II) resonance is somewhat broadened, there is no indication of magnetic ordering at 4.2°K.

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