Europium-151 Mössbauer Spectroscopic Studies of Europic Oxide

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^{151}Eu Mössbauer spectra of europic oxide show a single absorption peak which is both broad and asymmetric as a result of unresolved quadrupole splitting. Attempts to fit such spectra to a single Lorentzian peak have been found to be unsatisfactory. A more satisfactory analysis has been obtained by taking quadrupole splitting into account. The effects of prior heat treatment of europic oxide on the Mössbauer spectra have been investigated, and it is concluded that observed variations in isomer shift are not attributable to the cubic-monoclinic phase transition.

In the course of a study of the isomer shift of europic oxide with respect to europic fluoride[1] it was observed that the isomer shift varied from sample to sample by as much as 0·2 mm s^{-1}, the largest deviation from the average value occurring with an Eu_2O_3 sample isotopically enriched in ^{151}Eu (99·15% ^{151}Eu). Variations of a similar magnitude have been reported by Gerth *et al.*[2] for the isomer shift at room temperature of cubic europic oxide relative to monoclinic europic oxide. Deeney *et al.*[3] observed a variation of 0·25 mm s^{-1} in

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[1] N. R. Large, R. J. Bullock, P. Glentworth, and D. A. Newton, *Phys. Letters*, 1969, **29***A*, 352.

[2] G. Gerth, P. Kienle, and K. Luchner, *Phys. Letters*, 1968, **27***A*, 557.

[3] F. A. Deeney, J. A. Delaney, and V. P. Ruddy, *Phys. Letters*, 1968, **27***A*, 571.

the isomer shift when the oxide was heated over the range of 100—1000 K, and attributed this variation to the formation of non-stoicheiometric oxides (pseudophases). However, in their study of mixed oxide systems, Dulaney *et al.*[4] found the isomer shift of cubic europic oxide to be +1·037 (±0·014) mm s^{-1}, compared with a value of +1·030 (±0·007) mm s^{-1} for the monoclinic phase, both relative to europic fluoride; this is in direct conflict with the results of Gerth *et al.*[2] It is important to establish the reasons for the variations in isomer shift if europic oxide is to be used as a standard absorber in the study of europium compounds.

The apparent line width of the single Eu^{III} resonance in a europic oxide spectrum is at least a factor of 2 greater than the natural line width of 1·36 mm s^{-1}.[5] Goodman *et al.*[6] have suggested that this line broadening is due to unresolved quadrupole splitting arising from the 7/2 to 5/2 nuclear transition of ^{151}Eu, and that under these circumstances the isomer shift derived from fitting a single Lorentzian peak to the observed peak may deviate from the true isomer shift. However, it has been shown that for high values of the asymmetry parameter a symmetrical spectrum is obtained,[7] and under these circumstances the true and apparent isomer shifts coincide.

There has so far been no satisfactory explanation for either the observed variations in isomer shift, or the broad line widths of the Eu^{III} resonance in europic oxide. This paper attempts to correlate these parameters with the various known crystalline phases of europic oxide.

Anomalous behaviour of europic oxide has also been reported in magnetic susceptibility studies.[8-10] Direct experimental measurements of magnetic susceptibility do not agree with values calculated from spectroscopic data. Since the calculated and measured magnetic susceptibilities for ionic europic fluoride are in agreement, it has been suggested by Kern *et al.*[8] that the discrepancy in the oxide results may be connected with increased covalency of the oxide. The positive isomer shift of europic oxide relative to europic fluoride[1] is also an indication of the greater covalent character of the oxide relative to the fluoride.

Between room temperature and its melting point europic oxide is believed to be capable of existing in at least five phase modifications.[11-15] The phases identifiable above 2100 °C are not observed when the oxide is rapidly cooled to room temperature. However, the monoclinic form is metastable at room temperature and can be obtained by rapid cooling from temperatures above the cubic–monoclinic transition temperature to room temperature. Thus, the cubic and monoclinic forms, and mixtures of the two, may be prepared by controlled heating and cooling of the oxide.

$$\underset{\text{cubic}}{\mathrm{C}} \xrightleftharpoons{1075\ ^{\circ}\mathrm{C}} \underset{\text{monoclinic}}{\mathrm{B}} \xrightleftharpoons{2100\ ^{\circ}\mathrm{C}} \mathrm{A,H,X} \xrightleftharpoons{2330\ ^{\circ}\mathrm{C}} \text{melt}$$

In the cubic phase each europium atom has six nearest neighbour oxygen atoms.[16] These oxygen atoms are arranged in the form of a cube, two corners of which are vacant. For half the europium atoms these vacancies are at the face diagonal. In the monoclinic phase there are three non-equivalent europium sites, all of which are seven-co-ordinate.

EXPERIMENTAL

Preparation and Heat Treatment of Eu_2O_3 *Samples*.—Europic oxides samples composed of cubic and monoclinic phases in varying proportions were obtained by controlled heating and cooling of commercial europic oxide (99·9% Eu_2O_3 supplied by Koch–Light Ltd.) in a platinum crucible. The samples were heated for varying periods either above or below 1075 °C, the transition temperature between the two phases. Some of the samples were rapidly cooled at room temperature by removal from the furnace, others were left inside the furnace to cool slowly to room temperature. In no case was a weight loss of more than 1% observed. By varying the temperature of the sample, the period of heating, and the method of cooling, the cubic to monoclinic ratio was varied to cover the whole composition range, and the cubic to monoclinic ratio obtained was in each case determined by analysis of *X*-ray powder diffraction data. The $^{151}Eu_2O_3$ (99·15% ^{151}Eu) used as a reference absorber in this and our previous work was examined by *X*-ray powder diffraction techniques and shown to be a poorly crystalline cubic form. This $^{151}Eu_2O_3$ was prepared by the Electromagnetic Separator Group, Harwell, in the following way. After mass separation of europic chloride volatilized at 1100 °C, the ^{151}Eu ions were collected as europium metal on a cooled copper target which was subsequently dissolved in nitric acid. Following adjustment of the pH of the solution, europic oxalate was precipitated, centrifuged off, and ignited at 800 °C to give $^{151}Eu_2O_3$.

Mössbauer Spectrometry.—The Mössbauer spectrometer used in this investigation was based on that described by Cranshaw.[17] A Si(Li) detector and single channel pulse amplitude selector were used to detect and isolate the 21·7 keV γ-peak, and the counts were accumulated in 256 channels of a Laben multi-channel analyser. A stationary source and moving absorber arrangement was employed, with both source and absorber at room temperature. Velocity calibration was carried out by means of a sodium

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[17] T. E. Cranshaw, *Nuclear Inst. Methods*, 1964, **30**, 101.

nitroprusside absorber and a ^{57}Co source, and the reference velocity position was determined from the enriched $^{151}Eu_2O_3$ absorber with a $^{151}SmF_3,2H_2O$ source. Europic oxide absorbers containing approximately 12 mg cm^{-2} of Eu were mounted with an acetone–Zapon glue in a 20 mm diam. hole in a Perspex plate backed by a thin aluminium foil.

RESULTS AND DISCUSSION

Single Lorentzian Peak Analysis.—The Mössbauer parameters obtained by fitting the spectral data to a single Lorentzian distribution are shown in Table 1. This simple model assumes first, that all the europium atoms are equivalent and in one specific environment, and secondly, that there is no quadrupole splitting. On comparing the results for 100% cubic Eu_2O_3 with those for 100% monoclinic Eu_2O_3, it is clear that the isomer shift values for the two phases are virtually identical.

TABLE 1

Phase composition and Mössbauer parameters of Eu_2O_3: single Lorentzian peak analysis

Source and heat treatment of Eu_2O_3 samples	% Phase composition (±2%) Cubic	Monoclinic	Isomer shift relative to $EuF_3,2H_2O$ mm s^{-1} (±0·02)	Line width mm s^{-1} (±0·02)	% Resonant effect (±0·2)
$^{151}Eu_2O_3$ (isotopically enriched)	100		+0·85	3·30	16·4
Eu_2O_3 (as supplied by Koch-Light)	100		+0·98	2·76	11·5
800 °C for 6 h slow cool to R.T.	100		+1·07	2·99	9·2
900 °C for 6 h slow cool to R.T.	100		+1·07	3·00	11·9
1000 °C for 6 h slow cool to R.T.	100		+1·07	3·00	9·7
800 °C for 6 h rapid cool to R.T.	100		+1·08	2·92	10·8
1000 °C for 6 h rapid cool to R.T.	100		+1·09	3·62	9·6
1180 °C for 6 h slow cool to R.T.	95	5	+1·09	3·13	8·5
1190 °C for 6 h rapid cool to R.T.	50	50	+1·10	2·97	7·9
1190 °C for 8 h rapid cool to R.T.	25	75	+1·10	3·00	7·8
1190 °C for 9 h rapid cool to R.T.	20	80	+1·12	3·31	10·2
1195 °C for 6 h rapid cool to R.T.	5	95	+1·09	3·04	6·6
1200 °C for 9 h rapid cool to R.T.	—	100	+1·09	3·51	6·2

TABLE 2

Phase composition and Mössbauer parameters of Eu_2O_3: eight line quadrupole splitting analysis

Source and heat treatment of Eu_2O_3 samples	% Phase composition Cubic	Monoclinic	Isomer shift relative to $EuF_3,2H_2O$ mm s^{-1} (±0·01)	Component line width mm s^{-1} (±0·02)	Quadrupole splitting term mm s^{-1} (±0·05)	% Resonant effect (±0·02)
$^{151}Eu_2O_3$ (isotopically enriched)	100		+0·88	2·90	−1·30	17·8
Eu_2O_3 (as supplied by Koch–Light)	100		+1·02	2·40	−1·19	12·7
1200 °C for 9 h rapid cool to R.T.		100	+1·09	3·29	−1·00	6·4

Eight-fold Quadrupole Splitting Analysis.—The Mössbauer γ ray in ^{151}Eu is emitted from a nuclear spin state of +7/2 to the ground state of +5/2. The Hamiltonian corresponding to the interaction between the Eu nucleus and its environment is:

$$\mathscr{H}_q = \frac{eQ}{4I(2I-1)} \cdot V_{zz}[3\hat{I}_z^{2} - \hat{I}^{2} + \tfrac{1}{2}\eta(\hat{I}_+^{2} + \hat{I}_-^{2})]$$

where V_{zz} (the major component of the electric field gradient at the nucleus) is equivalent to $-4(1-\gamma_\infty)A_2^{0}$, as defined by Ofer *et al.*[18]

If it is assumed that the asymmetry parameter is close to zero, the spin quantum number selection rules permit eight transitions between the sub-levels, and the relative intensities of these lines can be derived from the squares of the Clebsch–Gordan coefficients.[19]

The unresolved nature of the quadrupole splitting in europic oxide makes it difficult to determine the sign of the quadrupole splitting term, defined here as $\frac{1}{4}eQ \,.\, V_{zz}$. However, both the 100% cubic phase and 100% monoclinic phase spectral data give more satisfactory fits with a negative quadrupole splitting term. The resultant Mössbauer parameters for the two distinct phases and the $^{151}Eu_2O_3$ sample are given in Table 2. Despite the allowance for incipient quadrupole splitting, the component width still greatly exceeds the natural line width of 1·36 mm s^{-1}, varying from 2·40 mm s^{-1} for the cubic phase to 3·29 mm s^{-1} for the monoclinic phase.

An analysis of the variation of spectral shape with the asymmetry parameter has been reported.[7] The spectral data obtained here for the 100% cubic and 100% monoclinic Eu_2O_3 samples have been analysed assuming a non-zero asymmetry parameter. This procedure gave isomer shifts and component line widths which were essentially the same as those given in Tables 1 and 2. However, the sign of the quadrupole splitting term was found to be dependent on the asymmetry parameter. The most satisfactory fits of the data were obtained, for the 100% cubic phase, with an asymmetry parameter of 0·6 and a negative quadrupole splitting term, and for the 100% monoclinic phase, with an asymmetry parameter of 0·4 and a positive quadrupole splitting term.

The apparent large line widths result from analysis of the spectra in terms of quadrupole splitting for a single europium environment, whereas it is probable that there are a number of non-equivalent europium sites.[2]

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[18] Ref. 5, p. 444.

[19] P. Glentworth, D. A. Newton, A. L. Nichols, N. R. Large, and R. J. Bullock, *J.C.S. Dalton*, 1973, 546.

The analysis should, therefore, in principle, be carried out in terms of a number of different europium environments each of which could involve quadrupole splitting, but giving rise to similar isomer shifts. Such an analysis would, however, be very uncertain in view of the unresolved nature of the spectra.

The $^{151}Eu_2O_3$ sample gave a peculiarly low isomer shift, approximately 0·2 mm s^{-1} less positive than all the other heated oxide samples. A similar value was obtained for this sample after reheating to 800 °C for 2 h. The untreated Eu_2O_3 sample, as supplied by Koch–Light Ltd., also showed an abnormally low isomer shift. An unenriched oxide sample, prepared by ashing europic oxalate at 800 °C, in imitation of the $^{151}Eu_2O_3$ preparation, gave a spectrum similar to heat treated oxides of natural isotopic abundance.

We have shown that the discrepancies observed by ourselves and others [1-3] in the isomer shift values obtained for europic oxide samples, cannot be explained in terms of differences between the cubic and monoclinic forms of the oxide. Moreover, since we have observed no significant variation in isomer shift in the cubic form when heated to temperatures in the range 800—1200 °C, it is difficult to formulate an explanation on the basis of the existence of pseudophases as proposed by Deeney *et al.*[3] It is clear that Eu_2O_3 is not a satisfactory standard for ^{151}Eu Mössbauer spectrometry.

The authors would like to thank Dr. P. T. Moseley, A.E.R.E., for the *X*-ray powder diffraction measurements. We acknowledge financial support by the S.R.C.

[2/2455 *Received, 31st October,* 1972]