QUADRUPOLE INTERACTIONS AT EUROPIUM SITES IN $Eu_3V_2O_7$ AND Eu_2VO_4

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The electric-quadrupole interactions at the Eu sites in $Eu_3V_2O_7$ and Eu_2VO_4 oxides have been studied at room temperature with ^{151}Eu Mössbauer spectroscopy. Both divalent and trivalent Eu ions were found in the oxides. The fraction of Eu^{2+} is 17.1(8) % in $Eu_3V_2O_7$ and 39.0(1.6) % in Eu_2VO_4. The values of the quadrupole coupling constant, $eV_{zz}Q_g$, obtained from the fits using a full Hamiltonian method are -6.594(50) and -8.043(65) mm/s for Eu^{3+}, and -13.168(402) and -18.032(134) mm/s for Eu^{2+}, respectively in $Eu_3V_2O_7$ and Eu_2VO_4. The magnitude of $eV_{zz}Q_g$ in Eu_2VO_4 is the largest ever reported for Eu^{2+} in any Eu oxide system.

1. INTRODUCTION

Studies of electric-quadrupole interactions with zero-field ^{151}Eu Mössbauer spectroscopy (MS) are very useful since, in contrast to zero-field ^{57}Fe MS, information on both the magnitude and the sign of V_{zz} can be obtained. This is very important since the knowledge of the experimental value of V_{zz} is essential for testing /1/ different theoretical models used to calculate V_{zz}.

For most Eu oxides, Eu ions occur either as Eu^{3+} or Eu^{2+}. However, for some oxides both Eu^{2+} and Eu^{3+} ions are expected to be present simultaneously. This seems to be the case for Eu_2VO_4 and $Eu_3V_2O_7$ oxides in which Eu ions are thought /2/ to occur simultaneously as Eu^{2+} and Eu^{3+}. There is, however, no direct experimental evidence to support this conjecture. It is the large difference between the isomer shift, δ, values corresponding to Eu^{2+} and Eu^{3+} ions which makes ^{151}Eu MS an ideal tool to resolve such problems.

The purpose of this work is twofold. First, it aims at determining the oxidation state of Eu ions in $Eu_3V_2O_7$ and Eu_2VO_4 oxides. Second, since the symmetry of the Eu sites in these oxides /2/ implies the existence of the electric field gradient (EFG) tensor, this paper aims at determining the values of $eV_{zz}Q_g$. The results of this study are compared with other published data, and some general characteristics of the hyperfine parameters in oxides as well as the importance of various contributions to the EFG tensor are discussed.

2. EXPERIMENTAL

The polycrystalline oxides Eu_2VO_4 and $Eu_3V_2O_7$ were synthesized according to the standard procedure /2/. X-ray diffraction measurements showed that they are single phase and have a tetragonal crystal structure.

The Mössbauer spectra were recorded at room temperature using a Wissel II spectrometer, which was calibrated with an iron foil. A sinusoidal reference signal was used and the resulting mirror-image spectra were folded. A 100 mCi $^{151}Sm(SmF_3)$ source was used.

The surface densities of the Mössbauer absorbers corresponding to Eu_2VO_4 and $Eu_3V_2O_7$ were 19.6 and 11.0 mg Eu/cm^2, respectively; the absorbers can therefore be regarded as thin ones. The Mössbauer spectra were fitted with a full Hamiltonian method.

3.   RESULTS AND DISCUSSION

It is evident from Fig. 1 that Eu ions in $Eu_3V_2O_7$ occur concurrently in divalent and trivalent oxidation state. Assuming the same Debye-Waller factor for Eu^{2+} and Eu^{3+} in this oxide, the fraction of the divalent Eu ions obtained from the surface ratio of the Eu^{2+} and Eu^{3+} components of the spectrum is 17.1(8) %.

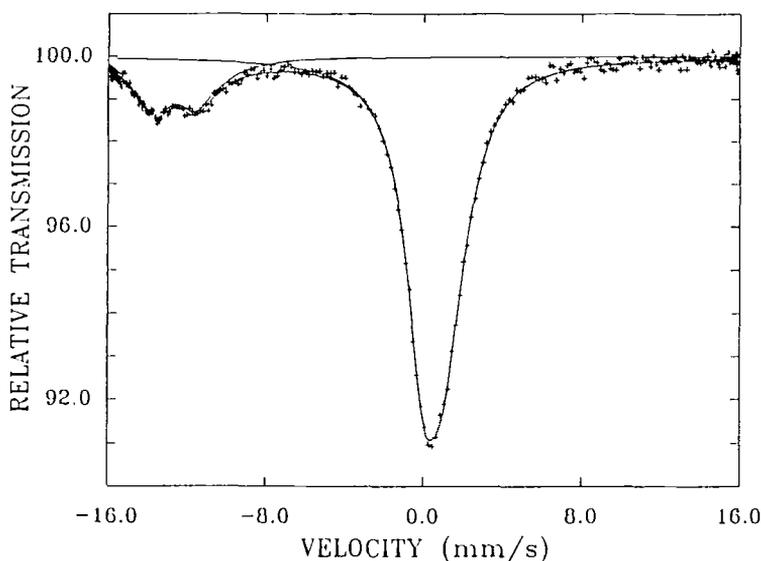Fig. 1. ^{151}Eu Mössbauer spectrum of $Eu_3V_2O_7$ at room temperature. The solid line is a least-squares fit with two quadrupole subspectra, which are also shown, corresponding to divalent and trivalent Eu ions.

The values of the parameters δ (relative to the source), $eV_{zz}Q_g$, η (the asymmetry parameter), and Γ (the full linewidth at half maximum) obtained from the fit shown in Fig. 1 are respectively -12.533(44) mm/s, -13.168(402) mm/s, 0.81(8), and 2.080(101) mm/s for Eu^{2+} ions. The corresponding parameters for Eu^{3+} ions are 0.635(5) mm/s, -6.594(50) mm/s, 0.60(6), and 2.256(32) mm/s.

The ^{151}Eu Mössbauer spectrum of Eu_2VO_4 (Fig. 2) clearly demonstrates the presence of both divalent and trivalent Eu ions. The fraction of Eu^{2+} ions in this oxide is 39.0(1.6) %. The values of δ, $eV_{zz}Q_g$, η, and Γ obtained from the fit shown in Fig. 2 are respectively -11.855(13) mm/s, -18.032(134) mm/s, 0.25(2), and 2.173(28) mm/s for Eu^{2+} ions. The corresponding parameters for Eu^{3+} ions are 0.536(5) mm/s, -8.043(65) mm/s, 0.49(2), and 2.445(22) mm/s.

Eu intermetallic compounds which contain Eu atoms in two oxidation states on crystallographically equivalent sites usually are in an intermediate valence state /3/. Their

[151]Eu Mössbauer spectra at low temperature show Eu^{2+} and Eu^{3+} lines. At room temperature, however, these lines collapse to a single line whose value of δ is the weighted average of the δ values of Eu^{2+} and Eu^{3+} lines /3/. The fact that at room temperature two distinct Eu^{2+} and Eu^{3+} subspectra are observed (Figs. 1 and 2) with δ values characteristic for ionic Eu^{2+} and Eu^{3+} proves that these subspectra cannot be associated with a mixed valence phenomenon, which would be most unlikely to occur in oxides. The individual integrity of Eu^{2+} and Eu^{3+} ions in $Eu_3V_2O_7$ and Eu_2VO_4 is thus puzzling. Its origin is unknown and should be investigated theoretically. The only other Eu oxide system in which a similar integrity of the Eu^{2+} and Eu^{3+} ionic states was observed is the system of mixed metal niobates and tantalates /4,5/.
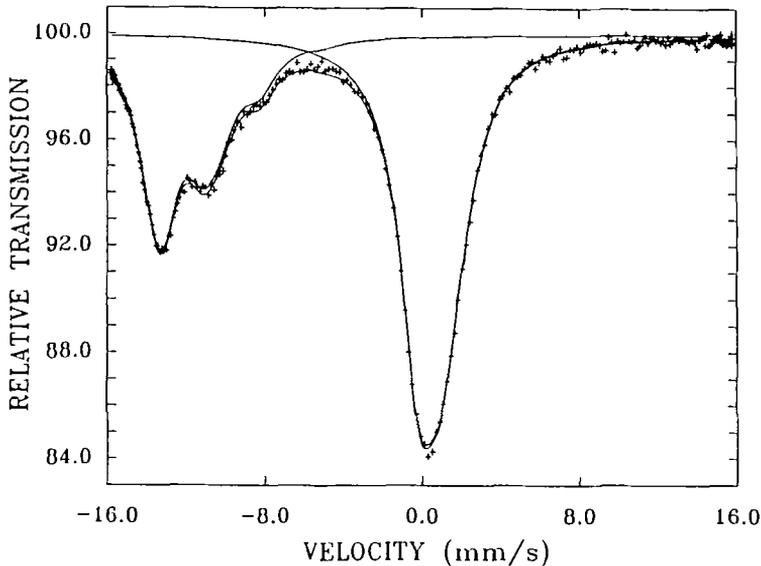

Fig. 2. [151]Eu Mössbauer spectrum of Eu_2VO_4 at room temperature. The solid line is a least-squares fit with two quadrupole subspectra, which are also shown, corresponding to divalent and trivalent Eu ions.

The magnitude of the quadrupole coupling constant found for Eu^{2+} in Eu_2VO_4 is the largest reported to date for a divalent Eu ion in any oxide. A larger magnitude of this constant [-19.289(289) mm/s] was found for trivalent Eu ions in $Eu_3Ti_2O_7$ /6/. This can be compared with the value of this constant in the range 44-48 mm/s reported for divalent Eu ions in stoichiometric and nonstoichiometric $Eu_xRh_3B_3$ /7,8/, which is the largest ever reported for any Eu system.

From a perusal of the literature on the measured values of $eV_{zz}Q_g$ in Eu oxides /9/, two characteristics become evident. First, in most oxides $eV_{zz}Q_g$ is negative both for Eu^{2+} and Eu^{3+} ions. Our results confirm this general feature. Second, the temperature change of the magnitude of $eV_{zz}Q_g$ is small and negative for temperatures below 300 K.

Any component V_{ij} of the EFG tensor at an Eu site in an oxide can be written as /10/ $V_{ij} = V_{ij}^{(1)} + V_{ij}^{latt} + V_{ij}^{(2)}$, where $V_{ij}^{(k)}$ is due to the 4f configuration in k-th order perturbation theory, and V_{ij}^{latt} is the lattice contribution which does not depend on temperature if lattice expansion is negligible. For Eu^{3+} ions with the $^7F_0$ ground state, there is no first-order 4f

contribution. However, since the excited states $^7F_1$ and $^7F_2$ are not very far above the ground state, there is a significant second-order 4f contribution to the EFG tensor, which is weakly temperature dependent. For Eu^{2+} ions with the $^8S_{7/2}$ ground state, the lattice term is the only appreciable contribution.

A survey of calculations in the literature /9/, which are based on a point-charge model, shows that the lattice contribution to $eV_{zz}Q_g$ for Eu^{2+} and Eu^{3+} ions is negative, independent of the crystal structure of a given oxide. Thus, the lattice contribution accounts for the negative sign of $eV_{zz}Q_g$ observed here and in the other works /9/. The point-charge model calculations for divalent Eu ions account reasonably well for the order of magnitude of the experimental $eV_{zz}Q_g$ /9/, in spite of limitations inherent to such calculations /1,11/. For trivalent Eu ions, apart from the lattice contribution, one also has to calculate the second-order 4f contribution. Calculations of the latter require information on the crystal field parameters for a given oxide, which are often not available. Such calculations show /9/ that $eV_{zz}^{(2)}Q_g$ is positive and equal in magnitude to about half of $eV_{zz}^{latt}Q_g$. It may be thus concluded that for most Eu oxides, the experimentally determined negative sign of $eV_{zz}Q_g$ for trivalent Eu ions reflects the expected larger lattice contribution to the EFG tensor than the second-order 4f contribution.

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