

EUROPIUM—¹⁵¹MOSSBAUER EFFECT STUDY OF EUROPIUM ORTHOVANADITE

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¹⁵¹Eu Mössbauer spectroscopy on EuVO₃ in the temperature range of 9 - 293 K indicated that there is a large increase of $eV_{zz}Q_g$ when temperature goes from 293K down to 9K.

1. INTRODUCTION

Europium perovskite series EuMO₃ (M = a metal element) belongs to the orthorhombic space group P₁ma(D_{2h}¹⁶). Several ¹⁵¹Eu-Mössbauer works concerning this series have been reported. An early work for M=Al, Cr, Fe, and Co showed single lines with unusually large linewidths in the range of 3.5~4.0 mm/s at room temperature /1/. The values are to be compared to the natural width of 1.31 mm/s and typical experimental values of roughly 2.5 mm/s for ordinary europium compounds against a source of ¹⁵¹SmF₃. The authors fitted the spectra with a single Lorentzian line not considering a quadrupole interaction. Later, Stadnik and de Boer measured spectra of EuMO₃ (M=Co, Cr, Mn, Fe and Sc) at room and liquid-nitrogen temperatures and observed broad, asymmetric single lines /2/. They fitted the spectra by the transmission integral method taking the existence of a quadrupole interaction into account. Gibb also made a research on EuMO₃ with M=Cr, Mn, Fe, and Co /3/. The observed quadrupole coupling constant $eV_{zz}Q_g$ was in good agreement with the predicted value for EuFeO₃ from a crystal-field calculation, and, for the solid solution EuFe_{0.8}Cr_{0.2}O₃, induced magnetic exchange interactions were discussed. It seems that nobody has yet made a Mössbauer research on EuVO₃. We intended to explore the hyperfine interactions in EuVO₃ using the 21.6 keV transition between the 7/2 and 5/2 nuclear levels of ¹⁵¹Eu.

2. EXPERIMENTAL

EuVO₄ was prepared from stoichiometric amounts of Eu₂O₃ and V₂O₅ powders of both 99.99 % purity. The materials were ground, thoroughly mixed, and fired at 900 °C for 4h, then at 1100 °C for 2 h, and slowly cooled down to room temperature. The procedure was carried out in air. The EuVO₄ sample obtained in this way was heated in flowing H₂ at 1000 °C for 2h and then slowly cooled down to room temperature so as to yield EuVO₃. The EuVO₃ sample was characterized by X-ray diffraction as pure single-phase EuVO₃ with the known orthorhombic

structure. The ^{151}Eu Mössbauer measurement was performed on a powdered absorber with a thickness of 15 mg Eu/cm^2 . The source was $^{151}\text{SmF}_3$. The 21.6 keV γ -rays were detected with a thin NaI detector. The spectra were measured in the temperature range of $9 - 293 \text{ K}$. The isomer shift is given with respect to EuF_3 . The magnetization of the sample was measured in the temperature range of $77 - 600 \text{ K}$ using a vibrating-sample magnetometer in the external magnetic field of 6 and 16 kOe .

3. RESULTS AND DISCUSSION

Although the observed magnetization was not proportional to the applied magnetic field H in the temperature region measured, we defined a formal magnetic susceptibility as magnetization divided by magnetic field, M/H . The temperature dependence of the reciprocal of the formal gram susceptibility χ of our EuVO_3 sample is shown in Fig. 1. At high temperatures europium orthovanadate has paramagnetic properties, but the reciprocal of the formal gram susceptibility deviates from linearity against temperature due to the anomalous behavior of Eu^{3+} ions /4/. The

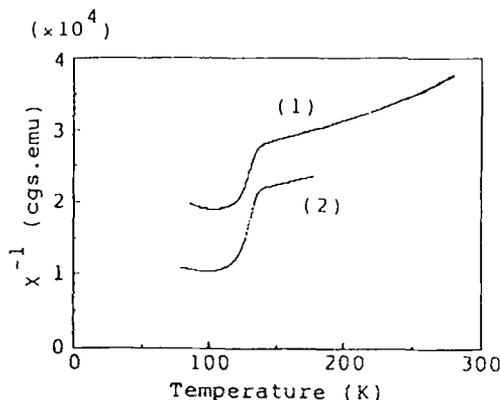


Fig. 1 Temperature dependence of the reciprocal of formal gram susceptibility χ of EuVO_3 in the magnetic field $H=16 \text{ kOe}$ (1) and 6 kOe (2).

magnetic susceptibility of europium orthovanadate rises strongly below about 130 K . This temperature is the point of transition from the paramagnetic to a magnetically ordered state. The lattice state corresponds to an antiferromagnetic distribution of the magnetic moments of the V^{3+} ions with a slight noncollinearity below the transition temperature /5/.

In Fig. 2 are shown the ^{151}Eu Mössbauer spectra of EuVO_3 taken at 293K , 77K , and 9K . The values of the isomer shift confirm that the Eu ions are in the trivalent oxidation state and increase with a decrease in temperature due to the second-order Doppler effect. The spectrum at 9K displays a considerably broadened asymmetric peak. We fitted the spectrum at 9 K with twelve lines taking a quadrupole interaction with variable η into account. Consideration of a quadrupole interaction led to a much smaller χ^2 value and an excellent fit, which indicates that the broadening

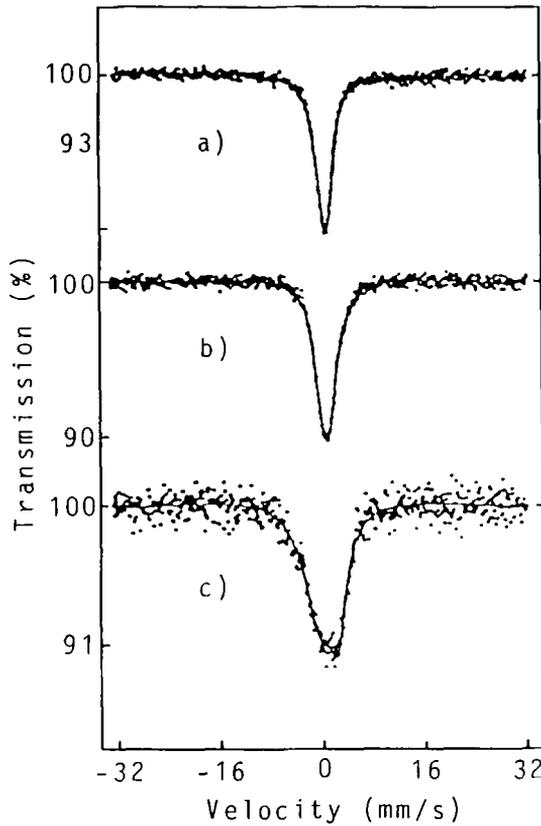


Fig. 2 ¹⁵¹Eu Mössbauer spectra of EuVO₃ at a) 293K , b) 77K and c) 9K.

is not due to absorber thickness effects but to a quadrupole interaction. The spectra at 77 K and 293 K were analyzed also assuming a quadrupole interaction with the same value of η as that obtained at 9 K. The Mössbauer parameters derived from the spectra are presented in Table 1. For the sake of comparison, those of Eu₂O₃ are also included.

The absolute values of the quadrupole coupling constant increase with a decrease in temperature. Let us consider the origin of the electric field gradient (e.f.g.) at Eu³⁺. The ⁷F₀ ground state for Eu³⁺ (4f⁶) is diamagnetic and does not give rise to an electric field gradient. However, there are low-lying excited states, ⁷F₁ at approximately 520K and ⁷F₂ at 1540 K [3,6]. The resulting admixture of the excited states into the ground state can produce a finite e.f.g. which is temperature dependent [2]. This contribution is considered to be smaller than the lattice contribution due to the charge distribution of the surrounding ions in the crystal lattice. However, the latter does not depend on temperature, if the lattice expansion is negligible. The e.f.g. tensor can be written as

$$eq_{lm} = (1-R)eq_{lm}^{(val)} + (1-\gamma_{\infty})eq_{lm}^{(lat)}, \quad (1)$$

where $l,m=x,y,z$. The first term derives from the electrons in the partially filled 4f shell which

also produce a secondary effect on the closed inner shells expressed by the 'atomic' Sternheimer factor R . The second term arises from the ions surrounding Eu^{3+} , but is affected by the distortion of the closed inner shells which is expressed by the 'lattice' Sternheimer factor γ_{∞} .

The valence contribution to e.f.g. tensor at a temperature T is obtained by a Boltzmann summation as

$$eq_{lm}(\text{val}) = \frac{\sum_i [eq_{lm}^i \exp(-E_i/kT)]}{\sum_i \exp(-E_i/kT)}. \quad (2)$$

E_i ($i=1,2,3,\dots,9$) is the nine energy levels for Eu^{3+} ($L=3, S=3$) corresponding to the states, 7F_0 , 7F_1 , and 7F_2 . The equation (2) indicates the effect of temperature on the quadrupole interaction. The results of calculation on $eV_{zz}Q_g$ according to equations (1) and (2) for EuMO_3 were basically in agreement with experimental values /2,3/. It is to be noted that from room temperature down to 77K, the maximum increase of $eV_{zz}Q_g$ so far reported is about 30 % (for EuScO_3 /2/). But, for EuVO_3 , the observed increase is much more pronounced and does not seem to be explained satisfactorily on the basis of the above equations (1) and (2).

In conclusion, the present experiment reveals an interesting property of EuVO_3 , that is, a large change in quadrupole coupling constant with temperature. It will be necessary to make further research to clarify the origin of the change.

Table 1 Mössbauer parameters of EuVO_3 and Eu_2O_3

Compound	Temperature	Isomer Shift ^a	Quadrupole Coupling Constant	Asymmetric Parameter
	T(K)	δ (mm/s)	$eV_{zz}Q_g$ (mm/s)	η
EuVO_3	293	0.83	4	0.7 ^b
	77	0.90	8	0.7 ^b
	9	0.91	18	0.7
Eu_2O_3	293	1.03	0	

a With respect to EuF_3 . b Fixed at this value in fitting.

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