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Mössbauer-Effect Study of Europium in Glass

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Mössbauer spectra have been obtained for ^{151}Eu in some silicate and phosphate glasses. In the silicate glasses Eu^{3+} behaves very much as it does in Eu_2O_3. The isomer shift relative to Eu_2O_3 is ~ 0.1 mm/sec. Some broadening of the line can be attributed to unresolved quadrupole splitting and to disorder in the glass structure. The recoilless fraction is 0.33. Measurements made at elevated temperatures indicate a complicated dependence of isomer shift on temperature cycling. In europium phosphate glass the isomer shift is ~ -0.3 mm/sec, and the linewidth is approximately the same as for the silicate glasses.

INTRODUCTION

Approximately ten papers have been published[1] about the Mössbauer effect of iron in various alkali silicate, borosilicate, borate, and phosphate glasses. There have also been a number of studies[2] of tin in glass. Thus far, however, only two papers have dealt with the Mössbauer effect of rare-earth ions in glass, and both of these[3] were about Tm^{3+}. Because of the technological importance of glasses doped with rare-earth ions, it is worthwhile to exploit any experimental technique which yields information about their structure. It is well known that Mössbauer spectra yield information about the ionization or valence state of the Mössbauer ion, the site symmetry, and the local electric and magnetic fields. Still other information can sometimes be obtained, for example, by varying the temperature of the specimen. This paper deals with the Mössbauer spectra of several silicate glasses which contain different amounts of Eu_2O_3, and with europium phosphate glass.

SAMPLES

All of our samples were obtained from Cleek of the Inorganic Glass Section of the National Bureau of Standards. The analysis of the silicate glasses is given in Table I. The phosphate glass was made by mixing stoichiometric amounts of europium oxide and ammonium phosphate and heating. The resulting glass presumably has the composition $Eu(PO_3)_3$.

The absorbers were prepared by grinding the

TABLE I. Composition of samples.

	L-21		*L*-11		*L*-20	
	Mol %	Wt %	Mol %	Wt %	Mol %	Wt %
SiO_2	72	57.8	74	64.4	74.95	67.2
Na_2O	15	12.4	15	13.5	15	13.9
BaO	5	10.3	5	11.1	5	11.5
ZnO	5	5.4	5	5.9	5	6.1
Eu_2O_3	3	14.1	1	5.1	0.25	1.3

glass samples to powder with mortar and pestle. The powder was placed between two Mylar windows in an aluminum holder. Absorbers with a number of different "resonant" thicknesses were made in order to determine experimentally the Mössbauer fraction for the glass specimens.

EXPERIMENTAL DETAILS

The Mössbauer spectra were obtained by using a spectrometer of more or less standard design. The drive is patterned after those described by DeVoe[4] and Cohen.[5] The pulse-height analyzer was usually operated in the multichannel scaling mode. In this mode a square wave which has the same frequency and phase as the channel sweep can be taken out of the analyzer. The square wave is improved a bit and then integrated to produce a triangular wave. This wave passes into an error signal amplifier and then a power amplifier which also follow Cohen's designs.

Our Mössbauer drive is double ended so that two spectra can be obtained simultaneously by mounting a source on each end. The γ rays are detected by using two identical systems, one for each source. The pulses from the single-channel analyzer are routed into (two inputs of) a four-input multichannel scaler and then into the pulse-height analyzer. Each spectrum is stored in one-half of the memory.

The great advantage of the double-ended drive is that one can run simultaneously an "unknown" specimen and a calibration standard. We used the spectrum of ^{57}Fe in powdered sodium nitroprusside as our standard. We assumed that the isomer shift (relative to a cobalt in copper source) is -0.48 mm/sec and that the quadrupole splitting is 1.726 mm/sec for this material. These figures are the ones given for a single crystal of sodium nitroprusside by Spijkerman *et al.*[6]

The source material for the ^{151}Eu γ rays was powdered and encapsulated $^{151}Sm_2O_3$ which was obtained from a commercial supplier.

In order to obtain Mössbauer spectra at elevated temperatures, a simple oven was constructed. The oven body is a short length of aluminum pipe. The heating element is a piece of carbon cloth. This cloth can be in the path of the γ rays since it has a very small γ-ray absorption coefficient. The powdered glass samples are held between two sheets of mica which are separated by a mica spacer. The ends of the pipe are covered with aluminum plates which have aluminum foil windows. A temperature of 500 °C can be reached in a few minutes. At 500 °C the power consumption is only about 15 W. The source-to-detector distance is less than 3 in. Therefore, high count rates can be maintained.

RESULTS FOR SILICATE GLASSES

A typical spectrum for one of the silicate glasses which contains europium is shown in Fig. 1. Usually we collected about 10^4 counts in each of 256 channels. The Mössbauer spectra appear to be single Lorentzian curves which are, however, rather broad in comparison with the natural linewidth for ^{151}Eu. The room-temperature isomer shifts, relative to Eu_2O_3, are given in Table II and are $\sim +0.1$ mm/sec.

The smallest isomer shift of a Eu^{2+} compound relative to Eu_2O_3 is about -10 mm/sec.[7] It follows that europium is present in these glasses as Eu^{3+}. There is no evidence for the occurrence of Eu^{2+}. Moreover, since the observed isomer shifts are small even in comparison with those for most europic compounds, it appears that the surroundings of Eu^{3+} in the glasses are very similar to the surroundings of Eu^{3+} in the oxide. This similarity in structure of the oxide and the glass has recently been affirmed by Rice and DeShazer.[8] They studied the absorption and fluoresence spectra of Eu^{3+} in a borosilicate glass. They concluded that the Eu^{3+} ions locate in two or possibly three average environment sites in the glass which are very much like the three sites occupied by Eu^{3+} ions in the monoclinic form of crystalline Eu_2O_3. A similar conclusion with regard to Tm^{3+} in soda-silica glasses and in Tm_2O_3 was reached by Uhrich and Barnes.[3]

In any study of the structure of a glass, one would like to find out whether the metal ions present are glass formers or glass modifiers. For example,

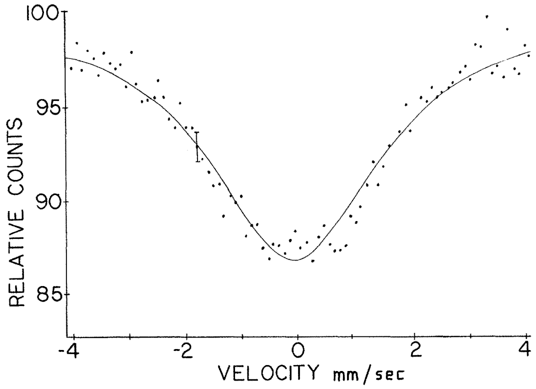

FIG. 1. Typical Mössbauer spectrum for ^{151}Eu in a europium silicate glass.

TABLE II. Room-temperature isomer shifts, relative to Eu_2O_3, of the europium glasses, and linewidths.

Sample	Eu_2O_3 (wt %)	Isomer shift (mm/sec)	Linewidth (cm/sec)
L-21	14.1	0.10 ± 0.02	0.39
L-11	5.1	0.07 ± 0.03	0.39
L-20	1.3	0.11 ± 0.05	0.39

in a simple alkali silicate glass such as $Na_2O \cdot 3SiO_2$, Si^{4+} is the glass former and Na^+ is the modifier. The sodium ions presumably are located in the interstices of the network formed by linked (SiO_4) tetrahedra. Our data indicate that Eu^{3+} ions do not simply replace Si^{4+} ions in such structural units as, for example, Fe^{3+} can. The coordination of Eu^{3+} to approximately six oxygen atoms seems to be preserved in the glasses, and also Eu^{3+} may be too large an ion to fit comfortably inside a regular tetrahedron of oxygen atoms. Probably the Eu^{3+} ions find a congenial environment by entering the glass network as modifiers. However, we cannot completely exclude the possible existence of linked structures resembling distorted (EuO_6) octahedra. In the latter case Eu^{3+} could be regarded as a glass former.

Although the Mössbauer spectra of the europium glasses appear to be single Lorentizan curves, it is quite likely that there is unresolved hyperfine structure. Magnetic hyperfine structure can be ruled out because these glasses are not magnetically ordered at room temperature and because the spin relaxation time is short compared with the lifetime of the nuclear state. There remains the possibility of quadrupole splitting.

Since the ground state of Eu^{3+} is $^7F_0$, there is (in a zeroth-order approximation) no electric field gradient at the nucleus due to the electrons in the partially filled $4f$ shell. However, coupling of the ground state to the low-lying excited states can give rise to a field gradient. In crystalline Eu_2O_3 the europium ions are at sites of low symmetry.[9] The situation is undoubtedly the same for Eu^{3+} in the glasses. Therefore, there should also be an electric field gradient at the Eu^{3+} nuclei due to the crystal field of the oxygen ligands and more distant ions. There are, moreover, antishielding corrections which may be large and temperature dependent.

The nuclear spin of the ground state of ^{151}Eu is $\frac{5}{2}$ and that of the excited 21.7 keV state is $\frac{7}{2}$. The spin degeneracy of these states is (partially) removed by the interaction of the nuclear quadrupole moment with the asymmetric electric field discussed above. The quadrupole interaction Hamiltonian cannot be diagonalized exactly unless the asymmetry parameter η is zero or diagonalized numerically unless η is known. Since we cannot extract a value for η from the unresolved spectrum, we shall for convenience take η to be zero. If $\eta \neq 0$, no major revisions are required in the physical aspects of the following discussion.

The ratio of the quadrupole moment of the excited state to that of the ground state[10] is 1.28. With this value for Q_{ex}/Q_{gnd} and with $\eta = 0$, the changes in the transition energies due to perturbation of the nuclear states by the quadrupole interaction are as given in Table III. The splitting of the resonance line by the quadrupole interaction is $\sim e^2qQ/4$, or somewhat more if the weak $\frac{5}{2} \to \frac{3}{2}$ transition is considered. Clearly the quadrupole interaction can give rise to considerable broadening of the Mössbauer spectrum.

The recoilless fraction for the absorber f' is a quantity of some interest because of its connection with the binding of the Mössbauer nuclei in the solid. For identical single-line source and absorber, f' can be determined by measuring the dip in the spectrum as a function of absorber thickness. When source and absorber are not identical, the problem of determining f' is more complicated. Shirley, Kaplan, and Axel[11] give the following formula:

$$P_{\text{expt}} = (\Gamma_a / \Gamma_{\text{expt}}) f [1 - e^{-t/2} I_0(t/2)], \qquad (1)$$

where P_{expt} is the fractional change in absorption at the center of the resonance line, f is the Mössbauer fraction for the source, $I_0(t/2) = J_0(it/2)$ is a zeroth-order Bessel function, and $t = n\sigma_m' f'$. n is the number of resonant nuclei per unit area and σ_m' is the effective maximum absorption cross section;

$$\sigma_m' = \frac{\lambda^2}{2\pi} \frac{(2I_{ex}+1)}{(2I_g+1)} \frac{1}{(1+\alpha)} .$$

α is the internal conversion coefficient. Also in Eq. (1), Γ_a is the width one would measure if source and absorber were identical, and Γ_{expt} is the width actually measured.

We obtained Mössbauer spectra for nine glass specimens with different absorption length. Equation (1) fits our data (see Fig. 2) if we make the

TABLE III. Changes in the γ-ray energies for ^{151}Eu due to the quadrupole interaction. It is assumed that $Q_{ex}/Q_{gnd} = 1.28$ and $\eta = 0$. The energies are given in units of $e^2qQ_{gnd}/4$.

Ground state	Excited state	Energy change	Relative intensity
$\frac{1}{2}$	$\frac{3}{2}$	0.25	0.48
$\frac{1}{2}$	$\frac{1}{2}$	-0.12	0.58
$\frac{1}{2}$	$-\frac{1}{2}$	-0.12	0.28
$\frac{3}{2}$	$\frac{5}{2}$	0.38	0.71
$\frac{3}{2}$	$\frac{3}{2}$	-0.35	0.48
$\frac{3}{2}$	$\frac{1}{2}$	-0.72	0.14
$\frac{5}{2}$	$\frac{7}{2}$	0.28	1.00
$\frac{5}{2}$	$\frac{5}{2}$	-0.82	0.28
$\frac{5}{2}$	$\frac{3}{2}$	-1.54	0.04

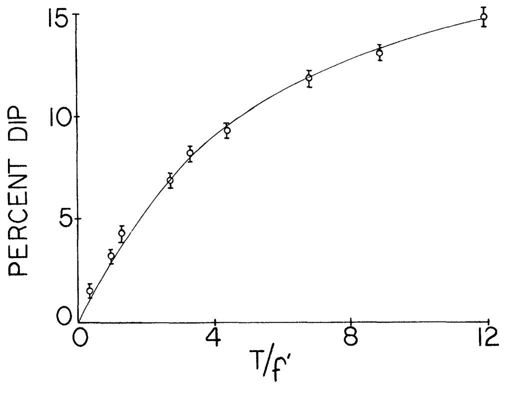

FIG. 2. Fractional dip versus thickness for ^{151}Eu in a silicate glass. The solid curve satisfies the equation dip$=f\,[1-e^{-t/2}I_0(t/2)]$ with $f=0.214$, $f'=0.327$.

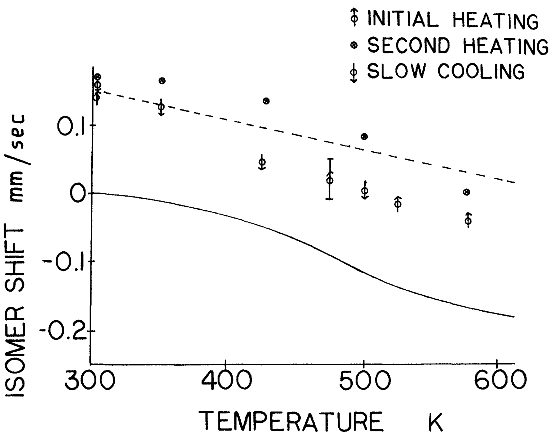

FIG. 3. Isomer shift versus temperature for ^{151}Eu in a silicate glass. The results of Deeney, Delaney, and Ruddy on Eu_2O_3 are shown as a solid curve. The dashed line is the expected second-order Doppler shift.

reasonable assumption that $\Gamma_a/\Gamma_{\mathrm{expt}}$ is independent of thickness. A least-squares fitting procedure yielded $f'=0.327$ and $(\Gamma_a/\Gamma_{\mathrm{expt}})f=0.214$.

Our value for f' is close to the value 0.36 given by Shirley *et al.*[12] for Eu_2O_3 at room temperature. The linewidth measured by Shirley *et al.*[12] was 0.23 cm/sec, or 0.20 when corrected for absorber thickness. If we take this to be the appropriate number to use for Γ_a and if we take Γ_{expt} to be the linewidth we measured for the europium glasses extrapolated to zero thickness (0.32 cm/sec), then we find that $f=0.34$, in good agreement with Shirley *et al.* The smaller value for the recoilless fraction in the glasses than in the oxide indicates that Eu^{3+} is less tightly bound in the glass. Additional quadrupole splitting and disorder in the glasses contribute about 0.12 cm/sec to the linewidth.

A study was made of the variation of the isomer shift with temperature. Some variation due to the second-order Doppler shift is to be expected. This variation was calculated by using a Debye model for the glass. Although it is not likely that this model is appropriate, no more realistic model has been proposed. The observed and calculated changes in the isomer shift are shown in Fig. 3. There is a greater decrease than one expects from the second-order Doppler shift and a hysteresis effect associated with heating and cooling the sample. The results are similar to those of Deeney *et al.*[13] on Eu_2O_3 which are also shown in Fig. 3. As noted by Deeney *et al.*, the hysteresis effect is rather complex. It depends on the rate of heating, the maximum temperature reached, and possibly other factors.

Figure 4 is a plot of the linewidth as a function of the temperature. The linewidth, unlike the isomer shift, does not depend on whether the sample is being heated or cooled. The decrease in the linewidth from 300 to 425 °K is probably due to a decrease in the unresolved quadrupole splitting, which decrease is due in turn to a decrease in the contribution of the 4*f* electrons to the electric field gradient at the nucleus. For some rare-earth compounds,[14] the quadrupole splitting falls by an order of magnitude when the temperature is raised about 300 °K. However, for Eu^{3+} the change in the field gradient is due to the change with temperature in the occupation of states with different *J* values rather than states within an approximately degenerate ground manifold. The decrease in the linewidth is therefore small for Eu^{3+}.

Several mechanisms might be responsible for the increase in the linewidth for temperatures greater than 425 °K. The increase might be due to increasing distortion of the glass structure which results in a different isomer shift for each nucleus. The broadening might also be due to diffusion.[15] In this case the increase in the linewidth is

$$\Delta\Gamma_{\mathrm{diff}}=2h/\tau_0\,,$$

where τ_0 is the mean time an atom stays at one site.

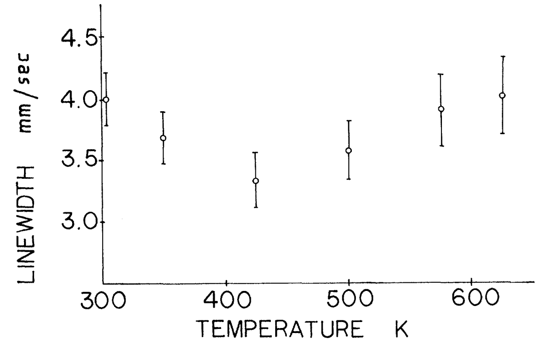

FIG. 4. Linewidth versus temperature for ^{151}Eu in a silicate glass.

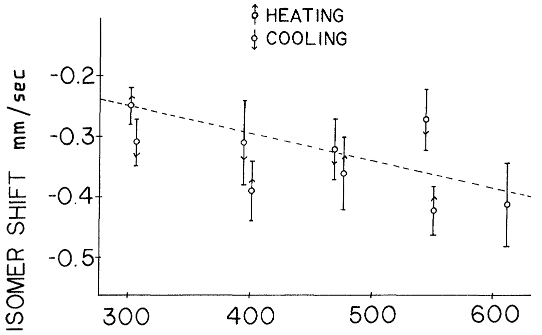

FIG. 5. Isomer shift versus temperature for ^{151}Eu in a europium phosphate glass. The dashed line is the expected second-order Doppler shift.

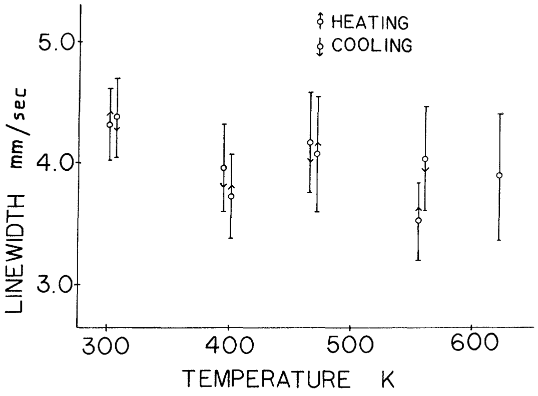

FIG. 6. Linewidth versus temperature for ^{151}Eu in a phosphate glass.

The diffusion coefficient is given by

$$D = l^2/6\tau_0 ,$$

where l is the jump distance. If we take 1 mm/sec to be the increase in the linewidth at 750 °K, and take l to be 4.8 Å, we find that D is 3×10^{-9} cm^2/sec. No direct measurement of the diffusion coefficient of Eu^{3+} ions in glass value has been made, but this value is not unreasonable.[16]

RESULTS FOR PHOSPHATE GLASS

Figures 5 and 6 show, respectively, the isomer shift and the linewidth as a function of temperature for europium phosphate glass. The dashed line in Fig. 5 is the isomer shift due to the second-order Doppler effect. The experimental points follow this line to within the estimated error of measurement. The change in the linewidth with temperature between 300 and 450 °K is appreciably smaller than for the europium silicate glass. It follows from these two results that the unresolved quadrupole splitting is smaller in the phosphate glass.

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