DIRECT EVIDENCE FOR ENERGY TRANSFER BETWEEN RARE EARTH IONS IN TERBIUM-EUROPIUM TUNGSTATES*

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We have directly observed the transfer of excitation energy from one species of rare earth ion to another in terbium-europium tungstates of the general formula $(Tb_{1-x}Eu_x)_2(WO_4)_3$.[1] The primary experiment consisted of the absorption of monochromatic light in a terbium absorption line (20.2×10^3 cm^{-1}) with a resulting emission of the red europium fluorescence (16.2×10^3 cm^{-1}). In this note we describe the details of this and other confirmatory experiments.

Powdered samples of the rare earth tungstates were prepared by combining appropriate amounts of the rare earth oxides and tungstic acid, grinding in an agate mortar, and firing at 1000°C in platinum vessels in an oxygen atmosphere. The samples were fired for 12 hours, cooled, remixed, and fired again. The mixed rare earth materials were prepared either by premixing the rare earth oxides and reacting with tungstic acid, or by reacting mixtures of the component rare earth tungstates. The results were equivalent for both methods.

The intense red fluorescence at 6150 Å of Eu^{3+} in rare earth tungstates has been previously observed.[2,3] In our initial work, samples of both $(Gd_{1-x}Eu_x)_2(WO_4)_3$ and $(Tb_{1-x}Eu_x)_2(WO_4)_3$ were prepared with $x \cong 0.2$. Polychromatic uv excitation of these two materials indicated a Eu^{3+} ion fluorescence yield which appeared to be at least an order of magnitude larger for the Tb compound. This suggested that the most pronounced energy transfer effect occurred with terbium. For this reason, this system was most extensively examined.

Monochromatic excitation radiation was obtained from a Bausch and Lomb high-intensity grating monochromator using a tungsten source. In addition, appropriate Optics Technology, Inc. interference filters and a Corning 3-75 filter were used to eliminate second-order radiation and scattered light from the monochromator output. The fluorescence spectra were photographed with a Jarrell-Ash $f/6.3$ grating spectrograph. Because of the low level of fluorescence intensity produced by this method of selective excitation, it was necessary to use a relatively wide slit width and exposure times of the order of hours. The samples were at room temperature. The mercury spectrum was recorded on each spectrogram for easy wavelength comparison and identification.

The principal experiment consisted of exciting the $^5D_4$ level of the Tb^{3+} ion in $(Tb_{0.8}Eu_{0.2})_2(WO_4)_3$ powder samples with 4950Å (20.2×10^3 cm^{-1}) radiation and photographing the fluorescence spectra. The result of this experiment is shown in Fig. 1(a). By comparison with the fluorescence spectra of the Eu^{3+} ion in $(Gd_{0.8}Eu_{0.2})_2(WO_4)_3$ [Fig. 1(b)] and Tb^{3+} ion fluorescence in $(Gd_{0.8}Tb_{0.2})_2(WO_4)_3$ [Fig. 1(c)], it is clear that the major component in the fluorescence spectra of the terbium-europium compound is fluorescence from the Eu^{3+} ion. In Fig. 2, the energy-level diagrams of Eu^{3+} and Tb^{3+} ions (following Thomas et al.[4,5]) are shown. The $^5D_2$ and $^5D_1$ levels of the Eu^{3+} ion are separated from the $^5D_4$ level of the Tb^{3+} ion by roughly 1200 cm^{-1} and 1300 cm^{-1}, respectively. Under our conditions of excitation there was therefore no ambiguity in determining that the primary absorption process occurred in the terbium ion. However, as further confirmation of this point we have also utilized the same conditions of exci-

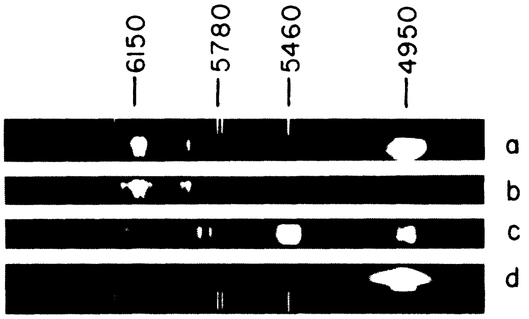

FIG. 1. Fluorescence spectra of (a) $(Tb_{0.8}Eu_{0.2})_2(WO_4)_3$ excited by 4950Å radiation (terbium absorption), (b) $(Gd_{0.8}Eu_{0.2})_2(WO_4)_3$ excited by polychromatic ultraviolet, (c) $(Gd_{0.8}Tb_{0.2})_2(WO_4)_3$ excited by polychromatic ultraviolet, (d) $(Gd_{0.8}Eu_{0.2})_2(WO_4)_3$ excited by 4950Å radiation. Comparison of spectra (b) and (c) with (a) shows that the main component of the fluorescence (at 6150 Å) in the Tb-Eu compound (a) is due to Eu. Spectra (a) and (d) were obtained under identical exposure conditions. The absence of the 6150Å Eu fluorescence in (d) is to be noted. The mercury spectrum is shown above spectrum (a) and below (d) for calibration.

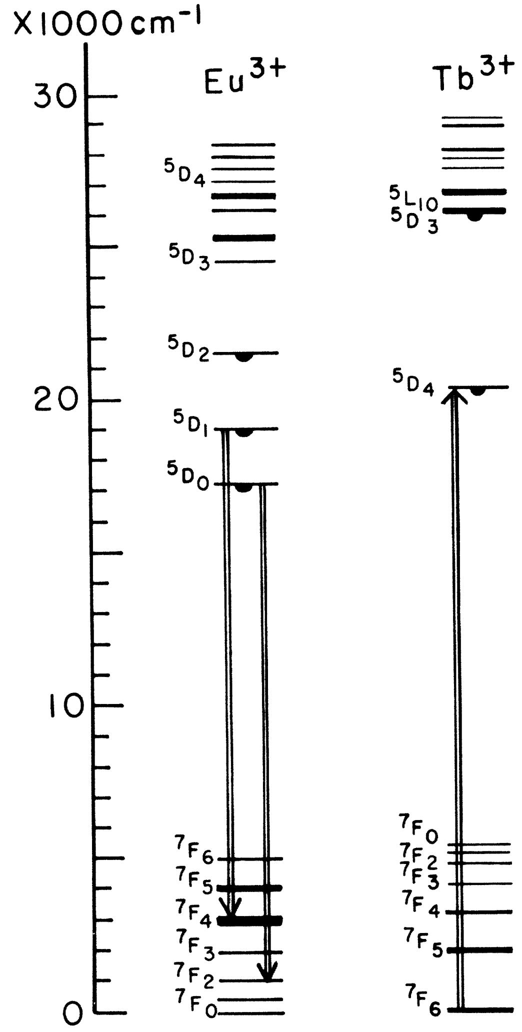

FIG. 2. Energy-level diagrams of the Tb^{3+} ion and the Eu^{3+} ion [following Thomas et al. (references 4 and 5)]. The excitation of the Tb and the fluorescence of the Eu in $(Tb_{0.8}Eu_{0.2})_2(WO_4)_3$ in the present experiment are indicated by the arrows.

tation (i.e., 4950 Å for 3 hours) with $Gd_{0.8}Eu_{0.2}(WO_4)_3$ [Fig. 1(d)] as was employed with the $(Tb_{0.8}Eu_{0.2})_2(WO_4)_3$. For the gadolinium-europium compound, we find no observable fluorescent effect. The ratio of the intensity of the europium fluorescence in the terbium-europium compound to that in the gadolinium-europium compound is estimated from this experiment to be in excess of 1000. This indicates conclusively that we are not simply observing an effect due to some weak and unobserved europium or tungstate ion absorption.

It is our belief that the energy transfer between the terbium and europium ions proceeds via a nonradiative process. There are, for example, no allowed europium absorption lines which overlap the principal terbium fluorescence. As further evidence on this point a study was made of a series of terbium-europium tungstates in which the atom fraction of europium varied from 10^{-4} to 10^{-1}. In this study, it was found that the fluorescence intensity of the terbium under polychromatic uv excitation was only slightly decreased (about 40%) with increasing Eu concentration. However, the intensity of Eu fluorescence exceeded that of the Tb for all Eu concentrations greater than about 10^{-3} atom fraction. As an extreme example, the integrated intensity of the Eu fluorescence in $(Tb_{0.9}Eu_{0.1})_2(WO_4)_3$ was in excess of 100 times the intensity of the terbium fluorescence in $(Tb_{0.9999}Eu_{0.0001})_2(WO_4)_3$. There are no terbium absorptions which could trap the terbium fluorescence "resonantly" with eventual degradation. Therefore, it seems clear that the large ratio of the europium fluorescence intensity to that of terbium cannot arise from a simple terbium emission-europium absorption process.

Comparison of the terbium fluorescence intensities in $(Tb)_2(WO_4)_3$ and $(Gd_{0.8}Tb_{0.2})_2(WO_4)_3$ indicates a strong nonradiative de-excitation process in concentrated terbium tungstate systems. The europium ion appears to serve as an additional path for the de-excitation of the terbium ions. The mechanism for this energy transfer is, however, still undetermined. We expect that more quantitative studies employing single-crystal samples will be most instructive in this regard.

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Note added in proof.—Results similar to these have been reported recently.[6]

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[1] On the basis of fluorescence quenching and enhancement, indirect evidence is available for energy transfer between rare earth ions: see L. G. Van Uitert et al., J. Chem. Phys. 36, 1793, 1797 (1962); 37, 986 (1962); G. E. Peterson and P. M. Bridenbaugh, J. Opt. Soc. Am. 53, 301, 494 (1963).

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MÖSSBAUER EFFECT IN LIQUIDS: INFLUENCE OF DIFFUSION BROADENING*

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Measurements of the Mössbauer effect can yield information relating to phonon spectra in solids.[1] Under appropriate circumstances the resonance can also be observed in liquids,[2] and such measurements yield information relating to diffusion effects during the nuclear state lifetime. We report here measurements on cobalt-57 chloride in glycerol and on Co^{57} embedded in the organic molecules porphyrin and hemoglobin, from which effective sizes for the diffusing objects are deduced. A further result relates to the Mössbauer recoil process and shows that in the presence of large diffusion effects the massive molecules do not recoil independently in the fluid, but rather the recoil momentum is transmitted to the entire fluid mass.

Diffusion broadening in neutron scattering from liquids has been discussed by Vineyard.[3] His analysis has been explicitly applied to Mössbauer scattering by Singwi and Sjölander.[4] They find the probability for recoil-free emission of a photon in the presence of diffusion to be proportional to

$$\exp[-R/4k_BT]\int\exp[i(\vec{k}\cdot\vec{r}-\omega t)-(\Gamma/2\hbar)|t|]\times F_s^{\,c}(\vec{r},t)d\vec{r}dt, \tag{1}$$

where $R=E_\gamma^2/2mc^2$ is the classical recoil energy of a diffusing body of mass m following the emission of a photon of energy $E_\gamma=\hbar kc$. The state lifetime is $\tau=\hbar/\Gamma$ and $E-E_\gamma=\hbar\omega$. $F_s^{\,c}(\vec{r},t)$ in Eq. (1) denotes the classical self-diffusion function, which in the case of a simple diffusive type of motion is given by the solution to the classical self-diffusion equation with diffusion constant D:

$$F_s^{\,c}(\vec{r},t)=(4\pi D|t|)^{-3/2}\exp(-r^2/4D|t|). \tag{2}$$

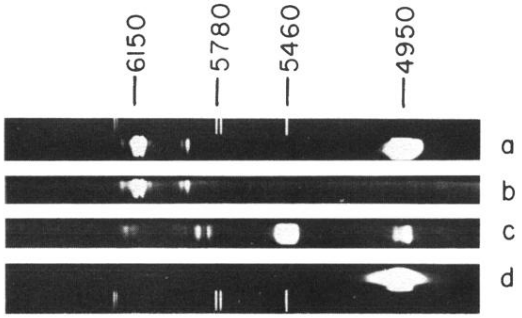
The intensity of the recoil-free emission of a photon of energy E is then

$$I(E)=\frac{(I_0/2\pi)(\Gamma+2\hbar k^2D)}{(E-E_\gamma)^2+\frac{1}{4}(\Gamma+2\hbar k^2D)^2}, \tag{3}$$

a Lorentzian spectrum centered at E_γ with width $\Delta\epsilon=\Gamma+2\hbar k^2D$.

We have observed experimentally the broadening $\Delta\epsilon$ of the recoil-free emission line as the diffusion constant increases. The 100-nsec 14-keV gamma level in Fe^{57} was used, and because of the small effects expected with broad lines, the experiments were performed using liquid sources containing the parent nuclide (270-day Co^{57}) rather than liquid absorbers. The procedure circumvents difficulties encountered in absorber experiments arising from gamma-ray attenuation in the nonresonant atoms comprising the host molecules. In order to obtain diffusion constants of the requisite magnitude (10^{-10} to 10^{-8} cm^2/sec), glycerol was used as a solvent. By variation of the temperature, the viscosity η and hence T/η could be varied over several orders of magnitude. The efficacy of glycerol for this purpose and the applicability of macroscopic viscosity measurements to atomic processes has been demonstrated by Bloembergen.[5] Neutron studies of diffusion in glycerol have been made by Larsson and Singwi.[6]

Sources of cobalt-57 chloride in glycerol were prepared by adding nominally carrier-free cobalt-57 chloride in HCl to glycerol. A $(99.5\pm0.5)\%$ glycerol sample was prepared by pumping on the solution for about one week. The glycerol concentration was determined by direct measurement at 27°C of the viscosity of a similarly prepared but nonradioactive solution. Values for the viscosity of water-glycerol solutions in the temperature range of interest (-50°C to 0°C) were obtained by normalizing the extrapolated measurements of Tammann and Hesse[7] to the



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