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Effect of Temperature on the Luminescence from Eu_2O_3*,†

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An effect of temperature on the shift of the Eu^{3+} ion luminescence from the $^5D_0 \rightarrow {}^7F_0$ transition has been studied experimentally for powdered C-type (bcc) and B-type (monoclinic) Eu_2O_3. Knowledge of both the temperature and the pressure dependencies enabled us to separate the temperature-derived and the volume-derived contributions to $d\nu/dT$. Details of the temperature effect and a mechanism for the shift in luminescence are discussed. © 1993 Academic Press, Inc.

Introduction

The temperature dependence of the position and width of the optical emission lines from transition metal and rare earth ions in crystals has been studied by several workers (*1–5*). Attempts have been made with moderate success to explain theoretically the observed shifts by the interaction of the *d* or *f* electrons with lattice vibrations (*4, 5*). However, changes in temperature affect not only the interaction between ions and lattice vibrations but also, because of thermal expansion, the interatomic spacing in the crystal. The shift with temperature of an energy level of a metal ion in a crystal is due to two effects: one arises from the electron–phonon coupling, and the second comes from a change of the crystal field interaction via thermal lattice expansion. The previous workers did not separate these two different contributions and only considered the effect of electron–phonon coupling. Hill and Hüfner have pointed out that it cannot be argued from first principles which contribution will be the more important (*1*). They suggested that in "hard" crystals (less compressible ones) the phonon contribution is the more important one, whereas in "soft" crystals (more compressible ones) the lattice expansion term yields the greater contribution (*1*).

For a clearer understanding of the effect of temperature on Eu^{3+} ion luminescence lines, we try here to separate the temperature dependence of the line position into two different parts arising from different mechanisms and to discuss the details of tempera-

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ture effects based on our experiments with C-type (body-centered cubic) and B-type (monoclinic) Eu_2O_3.

Experimental

Europium sesquioxide (C type), with a certified purity of 99.9%, was obtained from Ventron (Beverly, MA). Prior to the optical studies, all samples were cleaned of adsorbed contaminants and water by heating the oxide at 1000°C for 5 hr. B-Type Eu_2O_3 was prepared from cleaned C-type material by heating for 2 hr at 1350°C. Raman scattering analysis (*6*) and X-ray diffraction of the powder samples confirmed that they were indeed exhibiting the C-type and B-type crystal structures, respectively.

The treated Eu_2O_3 powder was loaded into a quartz capillary which was placed in a furnace. Temperature was measured by a Pt–Pt/10% Rh thermocouple. B-Type Eu_2O_3 powder was also loaded into a diamond anvil cell (DAC) for measurements at high pressure; the DAC is similar to the Merrill and Bassett-type DAC and has been described previously (*7*). Slight modifications made the DAC compatible with the microscope attachment to our Raman spectrometer. The applied pressure was measured via the ruby fluorescence method. Silicone oil was used as the pressure transmitting medium.

Luminescence spectra were recorded at different temperatures at ambient pressure and different pressures at room temperature with a Ramanor Model HG.2S spectrophotometer (Jobin Yvon/Instruments SA) having a resolution of 0.5 cm^{-1} at 514 nm. A Nicolet 1170 signal averager was used to accumulate the spectra from multiple scans. The 465.8-nm line of an argon-ion laser was used as the excitation source. Spectral slits widths were maintained at 400 μm.

The computer program SpectraCalc (Galactric Industries Corp.) was used to determine the energy (± 1 cm^{-1}) of the $^5D_0 \rightarrow {}^7F_0$ transition from the luminescence spectra recorded at the various temperatures and pressures. These data were then fit to separate polynomial expressions, from which the pressure and temperature derivatives were evaluated numerically at room temperature and room pressure, respectively.

Results and Discussion

Only the $^5D_0 \rightarrow {}^7F_0$ transition in both Eu^{3+} samples will be presented and discussed, because the luminescence line from this transition is simple ($J = 0$) and does not overlap with other transitions. In Fig. 1 are shown representative luminescence spectra obtained from C-type Eu_2O_3 at various temperatures up to 375°C and from B-type Eu_2O_3 up to 350°C. In both cases the luminescence tends to be blue-shifted with increasing temperature but with different rates. The temperature dependence of the luminescence was determined by measuring the energy of the emission nearest 17,200 cm^{-1} as a function of temperature, for this peak is the one for which the pressure dependence had already been determined by us (see Table I).

Previous theories considered the contribution from the interaction between the ion and the lattice vibrations and led to a calculation of the temperature dependence of the shift in energy, with the assumption that the phonon spectrum approximates a Debye spectrum of acoustic phonons. Imbusch *et al.* (*4*) derived an expression for this shift in energy (frequency) $\Delta\nu(T)$

$$\Delta\nu(T) = [\alpha\hbar/(2\pi)^2\rho_m v] \times \int_0^{\omega_D} d\omega\{\omega^3/[\exp(\hbar\omega/kT) - 1]\}. \quad (1)$$

The meaning of the various parameters is explained in Ref. (*4*). An important fact is that the mass density of the crystal lattice, ρ_m, was taken as being independent of temperature.

Temperature effects are more complex

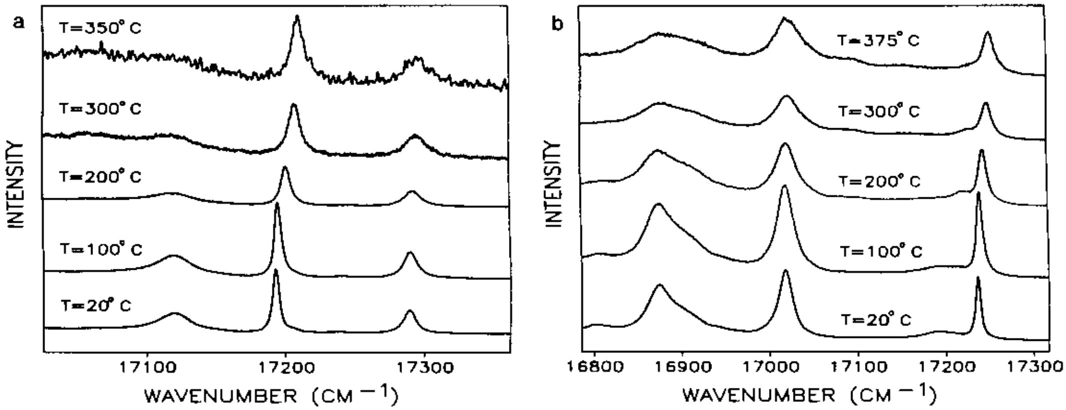

FIG. 1. (a) Luminescence spectra from the $^5D_0 \rightarrow {}^7F_0$ transition in Eu^{3+} ion (three crystallographic sites) in *B*-type Eu_2O_3 at room temperature to 350°C. (b) Luminescence spectra from the $^5D_0 \rightarrow {}^7F_0$ transition in Eu^{3+} ion (two crystallographic sites) in *C*-type Eu_2O_3 at room temperature to 375°C.

than are pressure effects. A change in pressure alters the equilibrium interatomic spacings. A change in temperature, in addition to its effect on the interaction between the ion and the lattice vibrations, also alters the interatomic spacings because of thermal expansion. Thus, the temperature dependence may be regarded as being composed of an implicit contribution attributable to the accompanying volume change and an explicit contribution attributable to the effect of temperature on a clamped (constant volume) crystal.

The temperature dependence of each luminescence line observed at constant pressure is a function of both temperature and volume, i.e., $\nu = \nu(T, V)$. In this way, the first-order derivative of the frequency with respect to the temperature consists of two distinct contributions:

$$\begin{aligned} d\nu/dT &= (\partial\nu/\partial T)_V + (\partial\nu/\partial V)_T(\partial V/\partial T)_P \\ &= (\partial\nu/\partial T)_V - (\alpha/\beta)(\partial\nu/\partial P)_T \\ &= (\partial\nu/\partial T)_V - \gamma(\partial\nu/\partial P)_T \qquad (2) \end{aligned}$$

where ν is the frequency of the luminescence line; V, the crystal volume; α, the volume expansivity $(1/V)(\partial V/\partial T)_P$; β, the compressibility $[-(1/V)(\partial V/\partial P)_T]$; and γ, the thermal pressure coefficient (α/β). The left side of Eq. (2) is the total observed temperature coefficient. The first term on the right is the contribution at constant volume, which reflects the pure temperature effect,

TABLE I

RELATIVE SENSITIVITY TO PRESSURE AND TEMPERATURE AND FRACTION, η, OF THE PURE TEMPERATURE-DRIVEN CONTRIBUTION TO THE TOTAL TEMPERATURE SHIFT OF THE $^5D_0 \rightarrow {}^7F_0$ LUMINESCENCE TRANSITION IN Eu^{3+} ION IN Eu_2O_3

Sample	$d\nu/dT$ (cm^{-1}/K)	$(\partial\nu/\partial P)_T$ (cm^{-1}/kbar)	$(dT/dP)_\nu$ (K/kbar)	η
Eu_2O_3 (*C* type)	0.039	-0.427[a]	11	0.81
Eu_2O_3 (*B* type)	0.023	-0.053	2.3	0.94

[a] Result obtained from Ref. (*8*).

i.e., the interaction between the ion and the lattice vibrations. The second term on the right is the contribution from the effect of the change in equilibrium atomic positions via thermal expansion. Such a change in the equilibrium atomic positions can change the crystal field, and thus, this term reflects the effect of a change in the crystal field. The higher-order derivative of the frequency with respect to the temperature can also be derived in a similar way. Because of the complexity of this calculation, we consider here only the linear part of the temperature shift, by which we show how to pick up the pure temperature term.

The shift in frequency expressed by Eq. (1) seems to be the pure temperature term in Eq. (2). To determine the effect of the "thermal expansion" term on the total shift $d\nu/dT$, we need to examine the shifts of the Eu^{3+} ion luminescence lines with both pressure at constant temperature and temperature at constant pressure.

The independent measurements of both the pressure and the temperature dependencies have been performed for both B-type and C-type Eu_2O_3. The pressure dependence of the ${}^5D_0 \rightarrow {}^7F_0$ transition in C-type Eu_2O_3 was reported in Ref. (*8*). The pressure dependence of the ${}^5D_0 \rightarrow {}^7F_0$ transition in B-type Eu_2O_3 was measured in the present work (see Fig. 2). Such independent measurements permit a separation of the temperature dependencies into volume-derived and temperature-derived terms, which should help our understanding of the mechanism of the temperature dependence of the luminescence lines. Then using Eq. (2), one should be able to get separately pure volume-derived and temperature-derived terms for the first-order derivative of frequency. The results of this approach are listed in Table I.

The tabulated experimental ratio $[-(\partial\nu/\partial P)_T]/(d\nu/dT)$ is abbreviated as $(dT/dP)_\nu$. This quantity is interpretable as the decrease in temperature dT which compensates for an increase in pressure dP in the sense of canceling the effect on frequency to keep ν constant. The various parameters determined for the ${}^5D_0 \rightarrow {}^7F_0$ transition of the Eu^{3+} ion in C- and B-type Eu_2O_3 are compiled in Table I. The value of $(dT/dP)_\nu$ is 11 K/kbar for C-type Eu_2O_3, meaning that a temperature decrease of 11 K produces the same upshift in frequency as does a pressure increase of 1 kbar. The value of 2.3 K/kbar for B-type Eu_2O_3 has the same meaning.

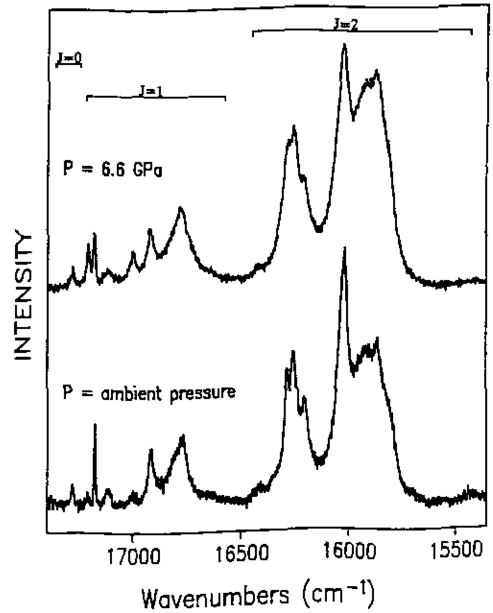

FIG. 2. Luminescence spectra from *B*-type Eu_2O_3 at ambient pressure and 6.6 GPa. Emission is from the ${}^5D_0$ level in Eu^{3+} ion to the ${}^7F_J$ level indicated at the top of the figure.

We use η to denote the fraction of the total linear temperature coefficient attributable to the explicit contribution $(\partial\nu/\partial T)_V$:

$$\eta = (\partial\nu/\partial T)_V/(d\nu/dT). \qquad (3)$$

In the present work (see Table I), $0 < \eta < 1$. If $\eta = 1$, the total temperature coefficient is determined only from the interaction between the ion and the lattice vibrations. In such a case, Eq. (1) describes the total shift in frequency induced by a change in temperature. If $\eta = 0$, the total temperature coefficient is determined only from the volume change as a result of thermal expansion. In such a case, the total shift in frequency is due to the variation of the crystal field induced by this volume change. Therefore, Eq. (1) cannot describe this sort of temperature dependence.

The value of η is important to clarify the origin of the temperature-induced $4f$ level shift. For C-type Eu_2O_3, $\eta = 0.81$, meaning that $0.81(d\nu/dT)$ is from the contribution of electron–phonon coupling, which can be described by Eq. (1). We have discussed elsewhere the pressure-induced shift of the Eu^{3+} ion luminescence line in C-type Eu_2O_3 (*8*). It was shown that the shift is due to the change in the value of the spin–orbit coupling constant ζ_{4f}, when pressure induced a variation of the crystal field. Thus, the total shift induced by temperature in C-type Eu_2O_3 comes from changes in both the electron–phonon coupling and the spin–orbit coupling constant. The latter is pictured as the magnetic coupling between the spinning electron and the magnetic field due to the relative orbital motion of the nucleus and electrons and has been correlated to the radial extent of the $4f$ orbital. Therefore, for the cases when $0 < \eta < 1$, the total temperature effect on the $^5D_0 \rightarrow {}^7F_0$ transition is determined from both the electron–phonon coupling and the electronic character. The value of η determines the fraction of the electron–phonon contribution to the total temperature coefficient. Therefore, we can apportion quantitatively the contributions from the different mechanisms to the total temperature effect on the shift in frequency of the luminescence line of Eu^{3+} ion.

In addition, the parameter η should be an intrinsically important parameter. As discussed before (*8*), in B-type Eu_2O_3, the Eu–O bond has greater covalent character than in C-type Eu_2O_3. Correlating this with the results in Table I, it seems that the more covalent Eu–O bonding is associated with a higher value of η. A more detailed study is needed to test this possible relationship between the intrinsic metal–oxygen bond character and the value of η.

Equation (1) is the same, apart from a multiplicative constant and a certain arbitrary Debye temperature θ_D, as that for the total heat or internal energy, which was measured in an experiment involving V^{2+} ions doped into MgO (*4*). However, the same approximation did not give a comparably good fit to the line-shift data obtained from V^{2+} ions doped into α-Al_2O_3 (*4*). Because Eq. (1) includes only the explicit temperature term, the validity of the equation is confirmed only when $\eta \approx 1$, as discussed above. It is likely that in the experiment with V^{2+} ions doped into α-Al_2O_3, it is the term $(\alpha/\beta)(\partial\nu/\partial P)_T$, the effect of the change in equilibrium atomic positions via thermal expansion, that makes a significant contribution to the observed line shift. As a result Eq. (1) fails to describe the temperature-induced line-shift data obtained from this crystal.

For "hard" crystals, $(\partial\nu/\partial P)_T$ is usually smaller than that for "soft" crystals, so from Eq. (2), we see that the volume-derived term may contribute less to the total temperature coefficient. Thus, we can understand the effect of "hardness" on determining whether the electron–phonon coupling or lattice expansion is the more important contribution to the total temperature coefficient.

Independent measurements of both the pressure and temperature dependencies provide a clearer picture for understanding the mechanism of the shift in frequency of a Eu^{3+} ion luminescence line and a more accurate way for using the previous calculation which yielded Eq. (1). The present work has shown that by just multiplying the parameter η by $d\nu/dT$, one can better approximate the pure effect of temperature alone.

Independent measurements of both the pressure and temperature dependencies of the luminescence line shift for samples with different Eu^{3+} ion site symmetries could be useful to understand the site symmetry influence on the temperature- and volume-derived contributions. We believe that, in addition to the "hardness" of the crystal, the metal ion site symmetry could be another factor which influences the mechanism of the temperature-induced shift in frequency of the luminescence line.

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