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Thermally stimulated depolarization spectra of CaF_2 containing Gd and hydrogen

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Thermally stimulated depolarization measurements on CaF_2 containing Gd and hydrogen reveal the presence of a relaxation of 0.24-eV activation energy whose intensity correlates well with the population of C_{4v} Gd^{3+}-H^- dipolar centers as assayed by infrared spectroscopy. The 0.38-eV activation energy reported from EPR line-broadening data appears to be another relaxation mode of the same complex. A mechanism is proposed for the 0.24-eV relaxation that involves tunneling of the H^- ion between equivalent interstitial sites about the Gd^{3+}.

INTRODUCTION

There has been considerable interest in the relaxation of dipolar defects in rare-earth-doped calcium fluoride. CaF_2 crystallizes in the fluorite structure, which consists of a simple cubic array of anions, with divalent cations occupying the body-center positions of alternate cubes. Trivalent rare earths enter substitutionally for the Ca^{2+} ions, and the excess charge of the aliovalent dopants is usually compensated by fluoride interstitials located at the body-center positions complementary to those occupied by the lattice anions.[1,2] However, when hydrogen is introduced in CaF_2, a portion of the excess charge of the rare earth will be compensated by H^- ions.[3]

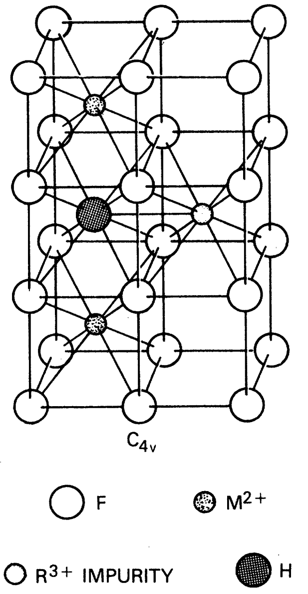

FIG. 1. C_{4v} complex formed by a substitutional trivalent rare earth (R^{3+}) and an interstitial H^- ion.

Local compensation occurs when a rare-earth ion and its compensator form a close pair bonded by Coulombic attraction. The most prominent such complex in rare-earth-doped CaF_2 is seen to be a complex comprised of a fluoride ion in the interstitial position that is the nearest neighbor to the rare earth, forming a dipole of C_{4v} symmetry.[4,5] An analogous center with the fluoride interstitial ion replaced by an H^- ion has been observed in gadolinium-doped CaF_2 treated with hydrogen,[3] and is illustrated in Fig. 1. Electron paramagnetic resonance (EPR) line-broadening measurements have yielded an activation energy for reorientation for this Gd^{3+}-H^- dipole of 0.38 eV.[6]

In this study, we have measured the thermally stimulated depolarization spectrum of similar samples containing both gadolinium and hydrogen. We have observed a relaxation of 0.24 ± 0.03 eV whose population correlates well with the population of C_{4v} Gd^{3+}-H^- dipoles as assayed by infrared (ir) spectroscopy.

EXPERIMENT

CaF_2 crystals were obtained from Optovac, Inc. Nominal doping of Gd^{3+} was 0.01 mole%. CaF_2 from this supplier has been found to be low in oxygen contamination. Hydrogen was introduced into the crystal by the technique of Hall and Schumacher.[7] Gamma irradiations were carried out at the NRL ^{60}Co pool at a dose rate of 1×10^6 rad/h.

Infrared absorption was measured using a Beckman IR-20*AX* spectrophotometer. Thermally stimulated depolarization (TSD) measurements, also known as the ionic thermocurrent (ITC) technique, were carried out in the usual manner.[8] The sample is inserted into a chamber filled with a helium heat exchange gas. An electric field $\sim 10\,000$ V/cm is applied at a temperature where the relaxation time for reorientation is short (~ 1 min or less) preferentially orienting the dipoles. The sample is then cooled to a temperature at which the relaxation time is long, and the field is removed. The depolarization current is monitored using a Cary 401 vibrating reed electrometer while the sample is warmed at a linear rate of 3 to 5 deg/min. A peak in the current is seen as each dipolar complex depolarizes.

If the relaxation time τ is of the Arrhenius form,

$$\tau = \tau_0 \exp(E/kT), \tag{1}$$

the current will obey the equation

$$I = \frac{AP}{\tau_0}\exp\left(\frac{-E}{kT}\right)\exp\left[-(b\tau_0)^{-1}\int_{T_0}^{T}\exp\left(\frac{-E}{kT'}\right)dT'\right], \tag{2}$$

where A is the sample area, b is the linear heating rate, P is the initial polarization due to the dipolar species, E is the activation energy for relaxation of the dipole, and τ_0, the "reciprocal frequency factor," is a constant usually ~ 10^{-13} sec.[8] The relaxation parameters P, E, and τ_0 are determined by a least-squares fit of Eq. (2) to the data.

DISCUSSION AND RESULTS

As-received $\mathrm{CaF_2}$:Gd crystals show no structure in the TSD spectrum between liquid-nitrogen temperature and 131 K, where the 0.4-eV relaxation of the C_{4v} $\mathrm{Gd^{3+}}$-$\mathrm{F^-}$ center is observed.[9] After the introduction of hydrogen, a new peak appears at 87 K with an activation energy of 0.24 ± 0.03 eV and a reciprocal frequency factor, τ_0, of 7×10^{-13} sec.

To determine whether the new relaxation is associated with the C_{4v} $\mathrm{Gd^{3+}}$-$\mathrm{H^-}$ dipolar complex, an effort was made to correlate the intensity of the 0.24-eV peak with the population of C_{4v} centers as determined by infrared spectroscopy. The C_{4v} center has two prominent absorptions in the infrared at 1017 and 1104 $\mathrm{cm^{-1}}$ (Ref. 10). In these materials the 1104-$\mathrm{cm^{-1}}$ peak was better resolved, and was taken as a measure of the C_{4v} population.

The hydrogenated sample was irradiated to a dose of 1.16×10^6 rads in the NRL ^{60}Co gamma pool and then subjected to a series of isochronal anneals. The sole purpose of these treatments was to vary the population of the C_{4v} $\mathrm{Gd^{3+}}$-$\mathrm{Hi^-}$ dipoles to allow correlation with the 0.24-eV TSD peak intensity.

After each treatment the TSD and ir spectra were observed. In Fig. 2, the intensity of the 0.24-eV TSD peak is shown as a function of the 1104-$\mathrm{cm^{-1}}$ ir absorption. The two parameters are highly correlated, with the rms deviation of the TSD peak intensity from linearity being about 3%, the accuracy of the TSD measurement. It is thus suggested that the 0.24-eV TSD relaxation is associated with the C_{4v} $\mathrm{Gd^{3+}}$-$\mathrm{H^-}$ center.

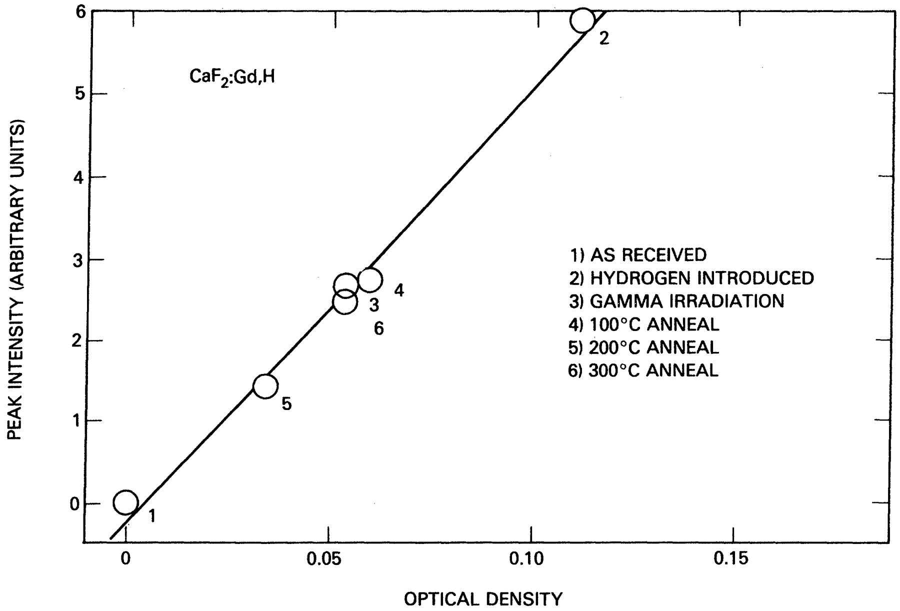

FIG. 2. Intensity of the 0.24-eV TSD peak vs optical density of the 1104-$\mathrm{cm^{-1}}$ ir absorption line, measured following each of the indicated treatments.

There is one difficulty with this assignment. Measurements by Edgar and Welsh[6] of the relaxation time of the Gd^{3+}-H^- center by EPR line broadening indicate an activation energy of 0.38 eV which is much larger than the 0.24 eV observed by TSD. However, these two measurements may not be in conflict. The EPR line-broadening data were taken at higher temperatures than the TSD measurements, and it appears that the two experiments may be observing different relaxation modes of the same center. Figure 3 exhibits the relaxation rate as a function of temperature as measured in this study (curve 3) and in the work of Edgar and Welsh[6] (curve 1). For a single relaxation of the Arrhenius form, the logarithm of the relaxation rate should vary linearly with $1/kT$ and have a slope equal to the activation energy for relaxation. The value of 0.38 eV was obtained by Edgar and Welsh from the highest temperature points in the EPR data. At lower temperatures the measurements deviate from linearity, suggesting a second relaxation mode of lower activation energy. Extrapolation of the data of this work to the higher temperatures of the EPR measurements shows that ascribing the 0.24-eV TSD peak to a second relaxation of the C_{4v} Gd-H^- center is reasonably consistent with the EPR line-broadening data within the accuracy of the TSD measurements.

The 0.38-eV relaxation mode is very similar from the standpoint of energy to the 0.4-eV relaxation of the analogous C_{4v} Gd^{3+}-F^- dipolar complex. It seems likely that the 0.38-eV relaxation proceeds by a jump of the H^- ion between equivalent ⟨100⟩ nearest-neighbor interstitial sites. The mechanism involved in the 0.24-eV relaxation mode is less clear, but it appears that this mode may involve tunneling of the H^- ion from one interstitial site to the next.

Because of the small mass of the hydrogen atom, the center will exhibit local vibrational modes similar to those of a simple harmonic oscillator. If reorientation of the center were to proceed by tunneling of the hydrogen in its vibrational ground state, relaxation would be temperature independent. However, at the temperatures of interest, the tunneling rate from an excited vibrational state would be

$$1/\tau = (1/\tau_0)\exp(-\Delta E/kT), \qquad (3)$$

where $\exp(-\Delta E/kT)$ is the probability of finding the center in a state ΔE above the ground state, and $(1/\tau_0)$ is the rate of tunneling from that state. Note that Eq. (3) is equivalent to the Arrhenius form, as given in Eq. (2), and is consistent with the temperature dependence of the TSD peak. The 0.24 ± 0.03 eV measured activation energy is within experimental error of the ΔE of 0.26 eV of the second excited vibrational state as measured by ir spectroscopy.[3,10,11]

The value of $1/\tau_0$ measured by the TSD experiment is 1.4×10^{12} $\sec^{-1}$, with an accuracy of about a factor of 5. To determine whether this value

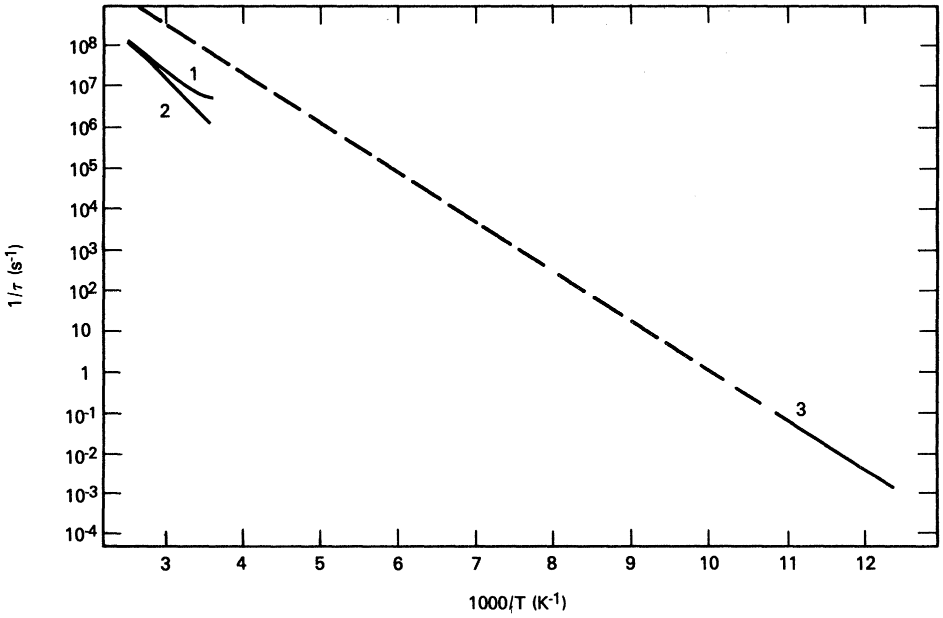

FIG. 3. Relaxation rate ($1/\tau$) vs reciprocal temperature. Curve 1: as determined from the EPR line-broadening data of Edgar and Welsh for the Gd^{3+}-H^- dipole. Curve 2: as determined from the EPR line broadening of Edgar and Welsh for the Gd^{3+}-D^- dipole. Curve 3: as determined from the TSD data of this work for the 0.24-eV relaxation.

is reasonable for the center, the tunneling rate was calculated for a simple one-dimensional, two-well model of the center. The two wells correspond to adjacent equivalent nearest-neighbor interstitial sites which are available to the H^- ion. The parameters available to define the potential-energy function of the model are (a) the barrier height, determined by Edgar and Welsh by EPR line broadening, (b) the center-to-center separation of two wells, defined by the crystal structure, and (c) the curvature of the bottom of the wells, determined by the wavelengths of the infrared local-mode absorption lines of the defect.

The uniform spacing of the vibrational levels of the center as observed by ir spectroscopy suggest that the individual wells are reasonably harmonic, with a harmonic oscillator energy level spacing $\hbar\omega_E$ of 0.13 eV. Therefore the first potential considered was the double harmonic oscillator, shown in Fig. 4(a). However, this type of potential is not consistent with the values of the parameters cited above. If the separation and curvature are chosen properly, the resulting barrier height V_0 will be greater than 7 eV, much larger than the desired values of 0.38 eV. This potential was modified by truncating the barrier at the desired height as shown in Fig. 4(b). While this model of the potential may not be precisely correct, it is the simplest modification of the double harmonic well consistent with the curvature and barrier height predicted by ir (Ref. 10) and EPR (Ref. 6) data. In this formulation, the potential retains the harmonicity of the wells to a sufficient degree and yields the correct barrier height. Since the experimentally measured barrier height is the height above the vibrational ground state, the value of V_0 was chosen to be $0.38 + 0.13/2$ or 0.446 eV.

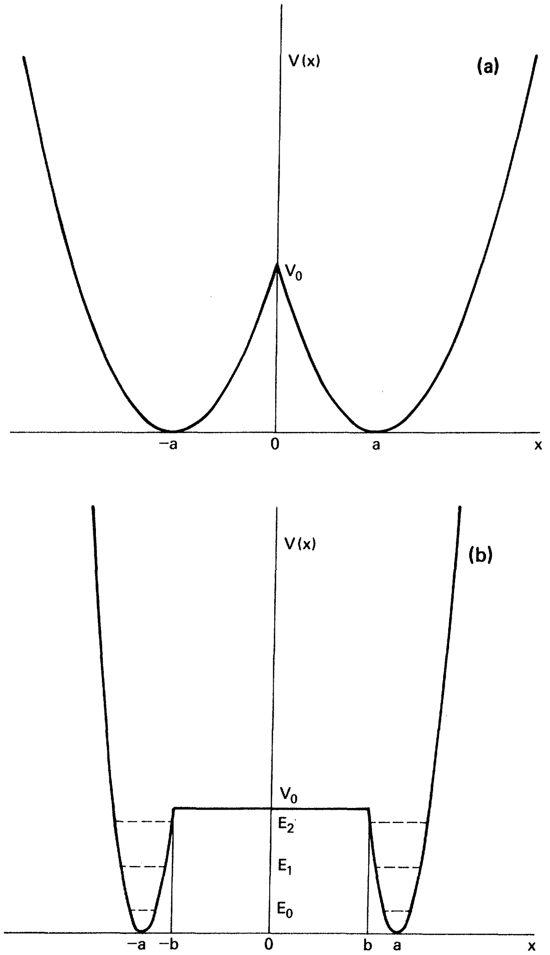

FIG. 4. Potential energy $V(x)$ vs position for (a) a simple double harmonic well with barrier height V_0 and separation $2a$, and (b) a truncated double harmonic well with barrier height V_0, separation $2a$, and curvature determined by the spacing of the simple harmonic vibrational levels, E_0, E_1, and E_2.

When two simple harmonic oscillator wells are brought close to each other, the vibrational levels will each be split by an amount E_t, called the tunnel splitting. The tunneling rate is then simply given as $\omega_t = E_t/\hbar$.[12] The Wentzel-Kramers-Brillouin (WKB) approximation predicts the splitting E_t to be

$$E_t = \frac{\hbar\omega_E}{\pi\theta}, \tag{4}$$

where $\hbar\omega_E$ is the harmonic-oscillator energy-level spacing and θ is a measure of the opacity of the barrier given by

$$\theta = \exp\left(\int_{-b}^{b} \frac{2m}{\hbar^2}\{[V(x) - E]^{1/2}\} dx\right),$$

where b and $-b$ are the classical turning points of the oscillator, m is the H^- ion mass, and E is the energy of the ion.[13]

For the model potential of Fig. 4(b), the calculated values of the tunneling parameters are

$$E_t = 2.35 \times 10^{-3}\ \text{eV}$$

and

$$\omega_t = 3.6 \times 10^{12}\ \text{sec}^{-1}.$$

The value of ω_t is very sensitive to the details of the potential barrier, but the excellent agreement between the predicted ω_t of 3.6×10^{12} sec^{-1} and the measured $1/\tau_0$ of 1.4×10^{12} sec^{-1} indicates that it is not unreasonable to expect relaxation of the defect via tunneling. In the vicinity of 87 K, the temperature of the TSD measurements, relaxation of the defect appears dominated by this tunneling process. However, the 0.38-eV relaxation is dominant at higher temperatures, because the probability of surmounting the barrier thermally exceeds the tunneling probability.

If tunneling were involved in the lower energy relaxation mode of the C_{4v} Gd^{3+}-H^- center, this mode would be strongly suppressed by substitution of deuterium for hydrogen in the center. This agrees with observations made both in this study and in the work of Edgar and Welsh.[6] Their EPR line-broadening measurements on the C_{4v} Gd^{3+}-D^- center (Fig. 3, curve 2) exhibit a strictly linear dependence of $\log_{10}(1/\tau_0)$ on reciprocal temperature, showing no hint of a second relaxation mode. The activation energy calculated by Edgar and Welsh is 0.42 eV, which is close to the value of 0.38 eV of the Gd^{3+}-H^- center. We have surveyed the TSD spectrum of the CaF_2:Gd sample treated with deuterium and have observed no peak whose population correlates with the C_{4v} Gd^{3+}-D^- population. The 0.42-eV relaxation peak of the Gd^{3+}-D^- center, if present, would be unresolvable from the 0.4-eV C_{4v} Gd^{3+}-F^- relaxation which dominates the spectrum. It must be pointed out, however, that the 87-K 0.24-eV peak assigned to the C_{4v} Gd^{3+}-H^- dipole falls near the low-temperature limit of our TSD apparatus, and if there were a Gd^{3+}-D^- peak at slightly lower temperature it would be unobservable with our apparatus. The absence of evidence for a lower energy relaxation in the deuterium-doped samples is consistent with the proposed tunneling mechanism.

CONCLUSIONS

Strong evidence for the identification of the 0.24-eV TSD peak is provided by the high correlation between the TSD peak intensity and the population of C_{4v} Gd^{3+}-H^- dipoles as assayed by infrared spectroscopy. This is not in conflict with the 0.38-eV relaxation energy of this center determined by Edgar and Welsh by EPR line broadening, as the 0.24- and 0.38-eV activation energies appear to be associated with two relaxation modes of the same center. A possible mechanism of the lower energy relaxation mode involves motion of the H^- ion from one interstitial site to the next via tunneling from its second excited vibrational state.

The values of $1/\tau_0$ and E predicted by using the tunneling model are 3.6×10^{12} sec^{-1} and 0.26 eV, in good agreement with the experimentally determined values of 1.4×10^{12} sec^{-1} and 0.24 eV. The tunneling mechanism would be expected to be less important in the defect involving deuterium than that involving mass-1 hydrogen. Consistent with this mechanism, the 0.24-eV relaxation has not been observed in CaF_2:Gd samples treated with deuterium, and Edgar and Welsh[6] observe deviations from simple Arrhneius behavior for the hydrogen defect, but not for the deuterium defect. The most likely mechanism for the low energy relaxation of the Gd^{3+}-H_i^- dipole appears to be tunneling from the second excited vibrational level of the center.

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