Thermal Conductivity of the V_k Center in CaF_2

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Abstract: The thermocurrent properties of the V_k center in CaF_2 were investigated. The thermocurrent properties during irradiation as a function of temperature indicate that the number of V_k centers produced per Roentgen decreases with increasing temperature. The V_k lifetime and activation energy were determined.

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INTRODUCTION

The thermocurrent (TC) characteristics of pure CaF_2 have been investigated and reported previously.¹⁻³ When pure CaF_2 is irradiated near 80°K then warmed while applying an electric field, two prominent peaks are observed in the resulting thermally activated currents. The first peak is seen near 180°K and results from motion of V_k centers; the other peak occurs near 290°K but the related color center has not been identified.^{4,5}

It is known that the V_k centers transport charge by moving from site to site and not by producing a mobile hole in the valence band.⁴ Also, the moving charges can produce currents in an external circuit either directly, or by piling-up spatially so as to polarize the sample, or by depolarizing material which had been polarized previously.¹ Conduction currents result when the electrodes can freely supply charge to the bulk of the material; polarization currents are seen when they cannot. Simultaneous conduction and polarization may also occur.

This report is concerned with the thermocurrent properties of the V_k center during and after irradiation. The V_k lifetime and kinetics of the V_k center after irradiation have been determined.

EXPERIMENTAL

Aluminum electrodes were evaporated onto 1 cm squares of pure CaF_2 (Harshaw), a single electrode on one side, and a $\frac{1}{4}$ inch diameter signal electrode surrounded by a guard ring on the other. The electrodes were applied to parallel cleaved surfaces so the electric field was nominally along the 111 axis. The samples were typically 1 mm thick. Currents

were measured with a Keithley model 602 electrometer; the signal electrode was never more than 1 mV above guard potential (usually grounded).

The samples were glued, using Epoxy Technology No. H61, to a copper cold finger in a vacuum chamber; irradiation, with x-rays at about 27KeV effective, and TC measurements were performed under vacuum. Cooled nitrogen gas maintained the sample at constant temperature when necessary. The temperature of the sample was monitored with chromel-alumel thermocouples which were also glued to the cold finger. During the heating portion of the cycle, which is the condition of greatest thermal lag, the cold finger and the face of the sample opposite to the cold finger had a maximum temperature variation of within 2°K . For isothermal measurements no gradient was detected. Clamping instead of gluing was not nearly so effective in eliminating temperature differences.

RESULTS

a) Thermally Activated Currents at High Fields.

Figure 1 shows the thermally activated current produced by a 65R exposure at 80°K followed by heating at 1.6°K/sec . The curve taken with 500V applied during the heating is typical of results reported by others;^{2,3} the V_k peak near 180°K appears with a shoulder on the low temperature side. Raising the electric field gradually shifts the shoulder to lower temperature until at 4000V it has become the resolved peak also shown in Fig. 1. (Note that the two curves are normalized to peak at 1.) This small peak has not been identified, but apparently it results from a center which is field ionized or whose carrier hopping

barrier through the lattice can be altered by an applied field. A possible explanation is given by the following reasoning. V_k centers in CaF_2 are along (100) directions so that all orientations are equivalent with respect to the applied field along the (111) direction. The small peak could result from altered V_k centers whose orientation is different from the (100) direction.

As the applied field is increased, the prominent peaks grow, as shown in Fig. 2. The V_k peak grows sublinearly while the 290°K peak begins to grow supralinearly. This supralinear growth may mark the onset of charge multiplication. If this is truly the cause of the supralinear growth, then this peak must result from carriers whose mean free path is long enough to allow the carriers to acquire several eV of energy. Since V_k centers do not travel more than a single hop at a time, it is reasonable that they do not gain enough energy to cause charge multiplication. Thus the 290°K peak cannot result from V_k centers. Higher fields were not explored because of breakdowns in the insulating glue.

b) Currents During Irradiation.

We are most interested in currents produced during irradiation, especially in the temperature region where V_k centers are mobile. Irradiation at 165°K produces the currents shown in Fig. 3. The lower curve shows the radiation induced currents as a function of time after the beginning of irradiation. At first the current is zero because there are no V_k centers; then as more V_k centers are produced the signal grows until it approaches an equilibrium value. In part this equilibrium is between production of V_k centers by the radiation and their destruction by internal processes. The

equilibrium current is also affected by polarization in the crystal. If the sample is irradiated with no field applied, then a true equilibrium between production and destruction of V_k centers can be inferred, as shown in the upper curve of Fig. 3. Here the irradiation has been applied for more than 60 seconds so the equilibrium concentration of charge carriers is already on hand when the field is applied at time zero. Here the current begins at a high value and falls to the former equilibrium level. Apparently this fall results from internal polarization which acts to reduce the applied field.

The presence of polarization is easily proven. First a sample is irradiated with a field applied and at a temperature where the V_k centers are mobile ($\sim 165^\circ\text{K}$). When irradiation ceases, the sample is cooled quickly to about 80°K with the field still applied. Finally, thermally activated currents are measured during warm-up with no field applied. The resulting thermally activated depolarization current is shown in Fig. 4. Notice it is not V_k centers but rather the low temperature neighbor that causes most of the polarization as evidenced by the height of the thermally activated depolarization peak. The sample can also be polarized by irradiating at 80°K with a field applied, but this technique is only about 10% as effective as irradiating at 165°K where more carriers are mobile.

When the temperature is raised, polarization effects play a diminishing role during irradiation, as can be seen by a comparison of the equilibrium currents for 183°K and 165°K (Fig. 3). The equilibrium current at 183°K is 90% of the maximum current whereas at 165°K , it is 60% of the maximum current. As the temperature is raised further, the signal becomes a step response (for our slow measuring system) when the field is applied. The

same behavior is evident when radiation is applied subsequent to the application of the electric field.

Once polarization is accounted for, the equilibrium current seems to represent the equilibrium between production and destruction of V_k centers. Figure 5 shows how this current varied with reciprocal temperature. The equilibrium current falls with increasing temperature so that the maximum current decreases exponentially with decreasing reciprocal temperature.

In Fig. 5 we are plotting the maximum current in an experiment like that shown in Fig. 3; that is, the highest current seen in the upper curve is the one used in Fig. 5. As the temperature is raised above about 185°K the two curves of Fig. 3 become more like step functions with the same height, so at these temperatures it is this constant response that is plotted in Fig. 5. Experiments could be carried to higher temperature, but this is more difficult since carriers from the 290°K peak begin to contribute to the response.

If the final equilibrium current (e.g. right hand side Fig. 3) is plotted against reciprocal temperature without any correction for polarization, then, at temperatures where the response is slow and the two curves of Fig. 3 are distinctly different than square waves, the equilibrium current levels off rather than increasing exponentially with reciprocal temperature. From this result we infer that the step-response does not result from a quickening in the polarization process, but rather from an absence of polarization.

c) Currents After Irradiation: V_k Lifetime.

When irradiation ceases in an experiment like that shown in Fig. 3, the current falls exponentially with time to zero. (Initially the drop is

somewhat faster -- see below.) By timing this decay at several temperatures, the kinetics for V_k destruction were determined; Fig. 6 shows a semilogarithmic plot of the decay constant against reciprocal temperature. The straight line drawn through the points represents an activation energy, $E = 0.30 \pm 0.01$ eV and an "attempt" frequency, $s = 1.8 \times 10^{-8} \text{ sec}^{-1}$. Notice that since we were monitoring current during irradiation and could watch the isothermal decay immediately, the V_k lifetime was measured up to over 200°K, a considerable extension over other techniques. The decay parameters agree quite well with those reported by others, and in fact these experiments demonstrate that the currents observed during irradiation are due primarily to mobile V_k centers.

Not all of the current observed during irradiation is due to normal V_k centers, however. Immediately after radiation ceases, 10-20% of the signal is lost at a rate faster than that characteristic of normal V_k centers. There is evidence of several contributors to this extra current. First, Compton currents are seen even at zero bias. Second, at 80°K where V_k centers are immobile, the current during irradiation is larger than the Compton current, demonstrating the existence of additional carriers. Finally, the centers causing the thermally activated current peak just below the V_k peak will also add to the current.

The maximum current plotted in Fig. 5 is not corrected for these other contributors; this figure can be taken to show an orderly change in the equilibrium current due to V_k centers, but probably not the true temperature dependence. In any case, there is no doubt that the equilibrium current due to V_k centers decreases with increasing temperature. This fact indicates that as the temperature is raised, irradiation produces fewer V_k centers per

second. This lower production rate can be seen by noting the result to be expected if irradiation produced a constant concentration of V_k centers per second. For the first order decay seen in the lifetime data, the equilibrium current seen during irradiation would be expected to be constant as a function of temperature. The equilibrium concentration of V_k centers is obtained when the rate of destruction $\frac{dm}{dt} = -\frac{m}{\tau}$ is equal to the constant production rate, C ; that is, $m = \tau C$. The current depends on this equilibrium concentration and on the carrier velocity, in this case the hopping rate $\propto \frac{1}{\tau}$. The product $m\tau$ is proportional to the rate of production and independent of the lifetime or temperature.

CONCLUSIONS

The V_k center dominates the currents produced during irradiation, at least from 150 to 250°K; the number of V_k centers produced per Roentgen decreases with increasing temperature. A polarization appears to be present during irradiation. The V_k center lifetime can be measured at relatively high temperatures (to 230°K) by monitoring the current decay when irradiation ceases. These lifetimes are consistent with values measured at lower temperature.

Finally, the results imply that CaF_2 might be used like a proportional counter during irradiation if high enough fields ($\sim 40,000$ V/cm) are applied. Polarization would probably be a problem, however.

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Fig. 1 Thermally activated currents induced by a 65R exposure at 80°K . The heating rate was 1.6°K/sec . and the sample thickness was 1.14mm. The voltages applied are indicated on the two curves.

Fig. 2 Peak heights for thermally activated currents as a function of voltage applied during read-out. The sample was irradiated with 70R at 80°K before each reading. Sample thickness = 1.14mm.

Fig. 3 Currents observed during irradiation at 165°K . The exposure rate was 0.2R/sec . The lower curve begins at time zero with the electric field (500 V/mm) already applied. In the upper curve, the electric field (500V/mm) is applied at time zero with irradiation already in progress for more than 60 sec.

Fig. 4 Thermally activated depolarization currents read by heating at 1.6°K/sec . in short circuit. The sample was polarized by irradiating (140R) near 165°K with 500V/mm applied and cooling quickly to 80°K when irradiation ceased.

Fig. 5 Maximum current observed during irradiation (0.2R/sec.) when 500V/mm is applied to the sample.

Fig. 6 Decay constant for currents observed when radiation ceases. The decay is typical of mobile V_k centers.