superconductivity data, can be interpreted in terms of the theory of polaron transitions, if it is postulated that polaron-intervalley phonon matrix elements are larger by a factor of 1.35 for nearly small polarons than for large polarons.

(4) Predictions of the theory for the normal state could most easily be tested by specific-heat and free-carrier absorption measurements for a given carrier concentration as a function of Zr concentration or of pressure.

ACKNOWLEDGMENTS

I should like to thank L. Friedman for an informative discussion, B. D. Silverman for some comments on the manuscript, and the authors of Refs. 23, 26, and 42 for the use of reports of their work prior to publication.

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Stored Energy in Irradiated Sodium Chloride*†

JAMES M. BUNCH‡ AND EDGAR PEARLSTEIN
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska

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Irradiated NaCl crystals are heated from room temperature to 400°C, and the energy released is measured by calorimetry. F-center densities range from 3×10^{17} to $1.8\times10^{18}/\text{cm}^3$, which are low enough to be measured directly, rather than inferred, as in some previous work. There are three definite peaks in energy release: centered at 135°, 250°, and 350°. The 250° peak is the largest, and is associated with almost all of the coloring changes. The total stored energy is 12.4 eV per F center, of which 8.4 eV is released in the 250° peak and 2.2 eV is released in the 135° peak. Assignment of thermal energies to specific atomic processes is difficult, because there are so many processes but only three experimental peaks. Evidence is good that the 250° peak is mainly a superposition of two unresolved peaks, of which the lower is due to the annealing of the F-center electrons, and the upper to the annealing of vacancies. We suggest that the 350° peak comes from the annealing of M-center divacancies. We do not have good evidence with which to explain the large amount of energy in the 135° peak. A calcium-doped crystal also releases energy in three peaks centered at these temperatures, but here most of the energy, and all of the bleaching, occur under the lowest-temperature peak.

I. INTRODUCTION

THE results are reported here of measurements of the energy released when irradiated NaCl crystals are gradually heated from room temperature to 400°C. As is shown, the data gives a "spectrum" of stored energy release—i.e., a graph of energy-release rate versus temperature shows several peaks. To some extent these peaks can be correlated with measured changes in optical absorption during heating.

Kobayashi[1] used a differential calorimetric technique, similar to that described by Overhauser,[2] to measure the stored-energy spectrum in proton-irradiated NaCl. The energy-release rate had peaks at three fairly well-defined temperatures, which Kobayashi interpreted in terms of specific processes by noting the correspondence in temperature with peaks in the annealing of optical absorption and with peaks in the electrical resistance of irradiated samples. His samples for the thermal measurements were necessarily so heavily colored, because of limitations in calorimeter sensitivity, that the color-center concentrations could only be inferred by extrapolation from less heavily colored samples. Thus, accurate values of the energy could not be assigned to specific centers.

Zavadovskaya[3] and co-workers also used this technique to measure the rate of release of stored energy in several alkali halides, heavily irradiated at room temperature with γ rays. The color-center concentrations apparently were not measured directly; instead, the energy was related to the radiation dose, which is difficult to translate into defect concentration, since the latter depends in fairly complicated fashion on dose rate, irradiation temperature, and trace impurities.

Phelps and Pearlstein[4] measured the *total* stored energy as a function of color-center concentration, using a heat-of-solution method, in NaCl x irradiated at room temperature. They concluded that the energy associated with the annihilation of one F center is 9.2 ± 0.3 eV, which is close to the energy predicted from a simple model. However, as they point out, the interpretation is ambiguous by as much as 3.6 eV per F

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† From a thesis submitted by J. M. Bunch in partial fulfillment of the requirements for the Ph.D. degree at the University of Nebraska.

‡ Present address: Los Alamos Scientific Laboratory, Los Alamos, N. M.

[1] K. Kobayashi, Phys. Rev. **102**, 348 (1956).

[2] A. W. Overhauser, Phys. Rev. **94**, 1551 (1954).

[3] E. K. Zavadovskaya and A. V. Kuz'mina, Fiz. Tverd. Tela **6**, 3348 (1965) [English transl.: Soviet Phys.—Solid State **6**, 2677 (1965)].

[4] F. T. Phelps, Jr., and E. Pearlstein, Phys. Rev. **128**, 1575 (1962).

center, since it is not really known how the ions associated with the F center go into solution.

Our differential calorimeter is significantly more sensitive than those used by Kobayashi or Zavadovskaya; so data can be obtained from samples in which the color-center concentrations are low enough to be measured *directly*, and the growth and annealing of various features of the stored-energy spectra can more easily be related to changes in optical absorption. Also, since the range of sensitivity includes the color-center concentrations used by Phelps, we might draw conclusions concerning the solution chemistry by comparing our results with his.

II. EXPERIMENTAL

A. Calorimetric Method

Two crystals, one of which has been irradiated, are heated inside a metal calorimeter cup. As the temperature of the cup rises, the irradiated sample gets hotter than the "dummy," in any temperature range where the metastable defects are annihilating or undergoing other exothermic modifications. The difference in temperature between the samples is measured with an appropriate thermocouple. It can be shown[2] that the energy released per degree of temperature rise is given by

$$dU/dT = M\,E(T) + N[dE(T)/dT], \qquad (1)$$

where U is the stored energy remaining at a given temperature, T is the sample temperature (the samples are very nearly at the same temperature), E is the difference between the differential-thermocouple emf for the annealing run and for a subsequent "baseline" run, M and N are slowly varying functions of temperature which depend upon, respectively, the thermal conductance from sample to sample and from sample to cup, and the heat capacities of the samples and attached thermocouples and holders.

B. Apparatus

The calorimeter is designed to operate at temperatures up to 400°C, since published data indicate that radiation-induced changes in the properties of NaCl anneal completely when samples are heated to this temperature. Heating is in a helium atmosphere. Because of a thermal transient at the start, all runs begin at -5°C, which is well below the temperature at which energy begins to be released. Our standard heating rate is about 5°C per min.

The calorimeter is similar in construction to those used by the others mentioned above. Careful attention was given to the choice of materials and the method of assembly, in order to eliminate as much as possible irreversible changes in thermal conductance between parts of the calorimeter as it is heated and cooled. The details are described elsewhere.[5] The difference in temperature between samples was measured with a ten-junction chromel-constantan thermopile, in order to average out to some extent the nonreproducible changes that occur in the thermocouple materials when they are cycled in temperature.

Direct calibration of the calorimeter was made by means of a small heater buried in a dummy sample identical in external dimensions and mass to the samples to be irradiated. The heater power was turned off and on periodically and the response $E(T)$ recorded. Then, as indicated in Eq. (1), $M(T)$ is related in obvious fashion to the equilibrium value of $E(T)$ after the power has been on sufficiently long, while $N(T)$ is given by the temperature interval required for equilibration after the heater is turned on or off. The temperature calibration of the thermocouple used to measure T was checked by observing the melting transition in very small reagent-grade samples of indium, tin, bismuth, and lead, sealed in glass tubes and inserted in holes in NaCl crystals. Measured melting temperatures agreed with handbook values to within 1°C.

Usable sensitivity, as determined from the repeatability of consecutive runs with unirradiated samples, is of the order of 0.01 cal/g, integrated over the temperature range of 25 to 400°C. This corresponds to about 10% of the total stored energy released from NaCl containing 10^{18} F centers per cm^3. (Since the energy is released in several peaks, rather than uniformly, we did not need this high a concentration of F centers.) In order to attain this sensitivity, it was necessary to adjust the data as follows: Successive runs of E versus T with nonirradiated crystals do not agree (which we ascribe to changes in thermal contact of the parts of the calorimeter). With our samples, however, there should be no stored energy released at the upper and lower limits of temperature, so that any differences in the differential temperature at these extremes must be instrumental. Therefore, we adjust data so that successive runs agree at room temperature and 400°C, and assume a linear correction for temperatures in between. The sensitivity figure given above is, then, partly the uncertainty due to this procedure.

C. Irradiation Procedure

The samples were irradiated in the dark at 28°C, either in a 10^6-R/h cobalt-60 γ source,[6] or 10 cm from the anode of a 190-kV peak, 20-mA, x-ray tube with filtration consisting of several millimeters of glass and cooling oil.

Because it was expected that impurity content would be different in crystals cut from different boules, an

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[5] James M. Bunch, Ph.D. thesis, University of Nebraska, 1967 (unpublished). Obtainable from University Microfilms, Inc., Ann Arbor, Mich. A few copies are available from the author.

[6] We are grateful to Dr. Clarence Wolf of McDonnell Aircraft Corp. for making the γ irradiations.

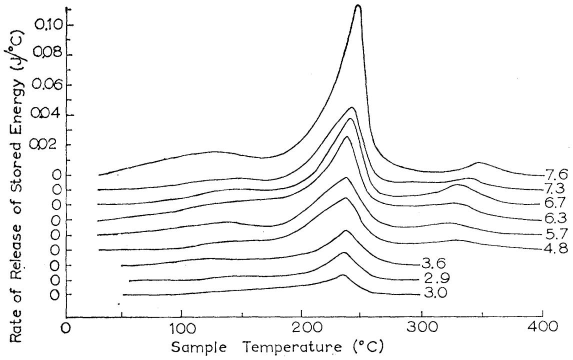

FIG. 1. Stored-energy spectra from Harshaw NaCl irradiated at 28°C. Ordinates are shifted to avoid overlapping. Numbers at the right are initial F-center densities, in units of $10^{17}/\text{cm}^3$. Mass of samples: 7.3 g. The specimen for the top curve was irradiated by γ rays; all the other by x rays.

attempt was made to minimize this source of uncertainty by making all measurements on a number of samples cut from adjacent positions in one large crystal. In order to obtain a sufficient number of samples for all the runs, these few samples were annealed and reirradiated several times, on the assumption that annealing restores a sample to its preirradiation condition. Other research in this laboratory justifies that assumption.

III. DATA

A. Coloration

The time dependence of the growth of the F band is consistent with results reported elsewhere,[7,8] in that the growth occurs in two stages, consisting of a rapid initial rise, followed by a nearly linear increase, with a tendency toward saturation at large doses. The initial rate of coloring and the saturation level increase with radiation intensity, and are much larger in our calcium-doped sample than in the "pure" samples, for given intensity. The M-band peak absorption for a given radiation intensity was found to be proportional to the square of the F-band peak absorption, but the concentrations of the R and higher-aggregate centers were so small in most of the samples that the existence of similar conditions for them could not be established.

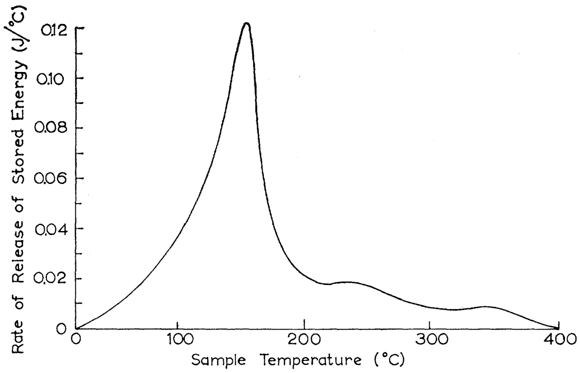

FIG. 2. Same as Fig. 1, but sample is doped with calcium. 1.9×10^{18} F centers/cm^3.

There was a broad absorption band, peaking at about 200 nm, in all the samples, which apparently consisted of a superposition of the OH, U, and V_2 bands.[9] The absorption in these bands increased with dose, but a detailed study of the growth kinetics was impractical because of the poorly resolved character of the bands.

B. Stored-Energy Release Rate

The energy release rate dU/dT was determined from the thermocouple data by using Eq. (1). When dU/dT is plotted as a function of temperature, there are in general (except for the calcium-doped sample, which will be discussed separately) three peaks: at about 135, 250, and 350°C. The 250°C peak is much larger than the others and can be seen even in the least heavily colored samples, while the peaks at 135 and 350°C become prominent only in more heavily colored samples. Figure 1 shows these curves for several radiation doses, with ordinates shifted to avoid overlapping. The curves are labeled with the appropriate F-center concentrations, since F centers are the predominant defects. Data from the calcium-doped sample are shown in Fig. 2. In this case there are still three peaks, but the lower peak is the largest, rather than the middle one as in the case of the pure samples. Note that the center peak in Fig. 1 moves toward higher temperatures for the heavier colorations.

C. Total Stored Energy

Figure 3 shows values of total energy per unit volume, obtained by integrating dU/dT, versus the sum of the

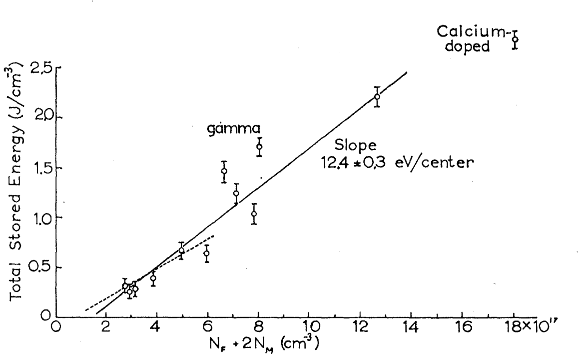

FIG. 3. Total stored energy versus the F-center plus twice the M-center concentration. The line is least-squares-fitted (without weighting) to all points except the ones marked "gamma" and "calcium-doped." The dashed line is Phelps's result.

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[7] P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **121**, 484 (1961).

[8] W. A. Sibley, E. Sonder, and C. T. Butler, Phys. Rev. **136**, A573 (1964).

[9] H. W. Etzel and D. A. Patterson, Phys. Rev. **112**, 1112 (1958).

F-center plus twice the M-center concentration. This method of plotting was chosen on the assumption that the energy from an M center should be nearly twice the energy from an F center; and such a plot is in fact noticeably more linear than when the energy is plotted against only the F-center concentration. Since the M centers contribute only about 20% of the energy in the more heavily colored samples, the error made in determining the energy of an F center from the slope of this curve should be fairly small even if the M-center energy differs considerably from twice the F-center energy.

The error bars in Fig. 3 denote the uncertainty expected on the basis of repeatability of runs with unirradiated samples. Systematic errors in calibration, and errors in measurements of sample masses, color-center concentrations, etc., are estimated to be negligible.

D. Thermal Bleaching

Figure 4 shows the results of measurements, on a γ irradiated sample, of the peak absorption coefficients of the F, M, R, and N bands measured at the actual bleaching temperatures while the crystal was being heated at 5° C min^{-1}. The absorption of the F band is also shown corrected for temperature broadening, on the assumption that the broadening occurs in such a way that the band area would remain constant in the absence of bleaching. Since it was difficult to resolve accurately the R and N bands, the curves for these are rough estimates only.

The R and higher-aggregate bands seem to bleach at temperatures in the vicinity of 130°C, while the M band first increases slightly and then bleaches rapidly above 200°C, and the F band (corrected for broadening) remains nearly constant up to about 200°C and then bleaches rapidly. A new band, apparently the colloid band,[10] grows as the F band bleaches and then persists to slightly higher temperatures than the F band. Results for x-irradiated samples were similar except that the initial concentrations of the aggregate centers were smaller in these less heavily colored samples.

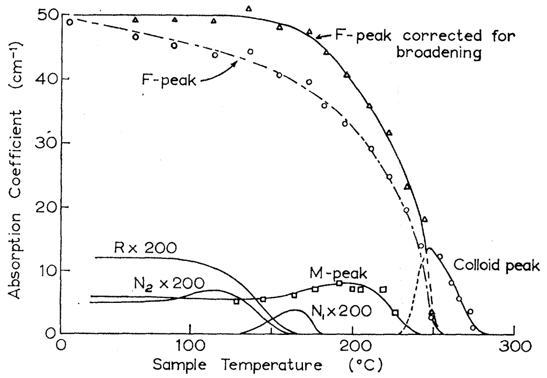

FIG. 4. Thermal bleaching of color centers for a γ-irradiated NaCl crystal. Measurements made at the temperature indicated, while warming at 5°C/min.

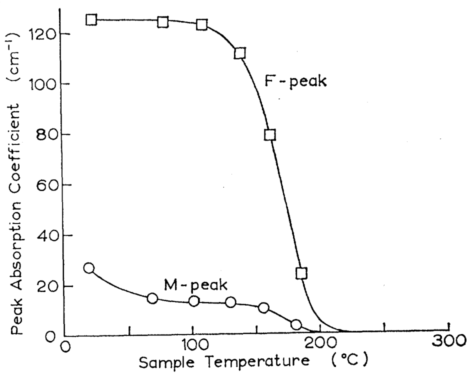

FIG. 5. Same as Fig. 4, but for NaCl doped with calcium.

Figure 5 shows the bleaching of the calcium-doped sample. In this case, only the F and M bands are present, and they bleach roughly simultaneously starting at about 130°C. This is quite a bit different from the pure crystal.

The thermal bleaching was also studied with another experimental procedure: the crystals were heated to the temperature of interest, and then quickly cooled to room temperature, where the optical measurements were made. This method gave results[5] similar to those of Fig. 4, but shifted downward in temperature by about 30°C. We feel that measurements made *during* the heating, as in Figs. 4 and 5, should be more amenable to correlation with the stored-energy release.

E. Thermoluminescence

Some simple thermoluminescence experiments were done, in which irradiated crystals were heated at 5°C/min, with the luminescence looked at by a photomultiplier tube. A typical result is shown in Fig. 6.

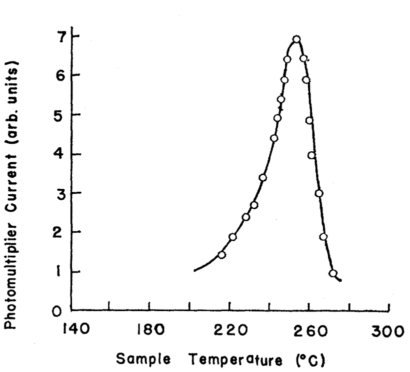

FIG. 6. Thermoluminescence from an irradiated crystal of NaCl (Harshaw). Temperature increasing at 5°C/min. Phototube has S-11 (blue) response.

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[10] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1963), p. 256.

We estimate that the energy in this luminescence is of the order of 10^{-5} of the total stored energy.

IV. DISCUSSION

A. Total Stored Energy

If, as all evidence seems to indicate, there are two mechanisms for F-center production—the early stage, which uses vacancies already existing or easy to produce, and the late stage, in which the radiation must create the vacancies—then the graph of total stored energy versus color-center concentration should show a "knee" at the concentration corresponding to early-stage saturation, with the slope for the region above the knee higher by the energy necessary to create vacancies. Our data seem to follow the expected trend, as shown in Fig. 3, in that the straight-line fit does not go through the origin. (All of the points are in the late stage of coloration.) But there is considerable scatter in the data, especially for the more heavily colored samples; more, in fact, than expected from test runs with unirradiated samples. It appears that the data might just as well be fitted with a curve concave upward, in which case one must assume that defects other than F and M centers contribute to the energy from the heavily colored samples.

Our total energy of 12.4±0.3 eV per F center does not compare well with that of Phelps[4]: 9.2±0.3 eV. However, a straight-line fit to only our six lowest points of Fig. 3, which are in the same coloration range as Phelp's data, gives an energy of 8.1±1.1 eV per center. Phelps's figure includes 3.6 eV per center added to the measured stored energies, on the assumption that the chemical state of a solution of irradiated NaCl is different from that of a solution of nonirradiated NaCl by the formation of one OCl^- ion for each F center. We conclude that our data at least partially support that assumption.

Note that the energy for the γ-irradiated samples is significantly above the trend established by the x-irradiated samples. The most plausible source for this excess energy, as well as for the apparent excess from some of the x-rayed samples, is the R and higher-aggregate centers. This is supported by the fact that the γ-irradiated samples were irradiated for a long time after the F- and M-band growth had saturated, during which time the R and higher-aggregate bands continued to grow. These bands do not seem, on first inspection, to be large enough to account for what is roughly 20% of the total energy. However, they appear as broad shoulders on the F and M bands, and it is difficult to decide accurately how to decompose the optical spectrum. We were able, with proper choice of irradiation time and dose rate, to produce an x-rayed sample with nearly the same F- and M-band peak absorptions as the γ-irradiated samples, but negligible R and higher-aggregate bands. The optical spectra from the two kinds of samples could then be subtracted, to obtain what is presumably the absorption spectrum of just the R and higher-aggregate bands. This is shown in Fig. 7. It can be seen that the area under the "difference" spectrum is a large fraction of that under the F and M bands. Unfortunately we do not know the oscillator strengths to assign to this absorption, through which defect concentrations could be calculated.

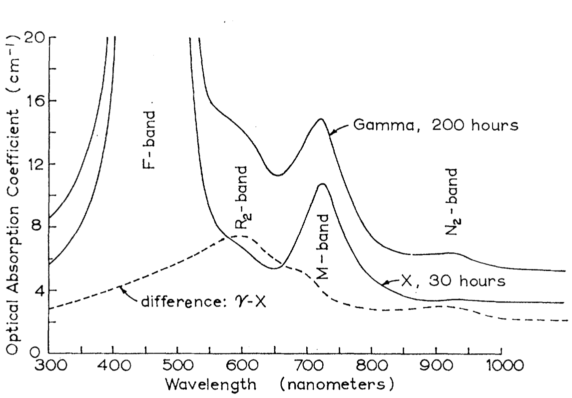

FIG. 7. Comparison of optical absorption in our γ-irradiated and x-irradiated samples, with nearly equal F and M absorptions.

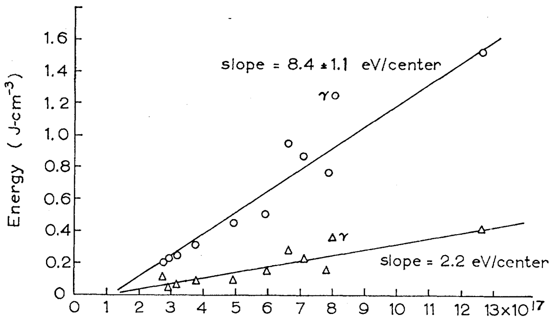

FIG. 8. Stored energy under the peaks at 135 and 250°C versus F-center plus twice the M-center concentration. Top line: least-squares fit to energy released between 170 and 290°C. Bottom line: least-squares fit to energy released between 30 and 170°C.

There is good evidence[11,12] that the formation of aggregate centers is affected by traces of impurities; so perhaps the scatter in some of our data can be explained by concentration gradients of these impurities in the large crystal from which our samples were cut.

B. Structure in the Stored-Energy Spectra

1. Pure Crystals

Figure 8 shows the energy released in the two lower-temperature regions as a function of coloration. (The high-temperature energy release will be discussed later.) The particular temperature intervals chosen are bounded by minima in the energy-release rate and also

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[11] N. A. Tsal' and M. V. Pashkovskii, Fiz. Tverd. Tela **6**, 780 (1964) [English transl.: Soviet Phys.—Solid State **6**, 607 (1964)].

[12] E. Sonder and W. Sibley, Phys. Rev. **129**, 1578 (1963).

correspond roughly to the most rapid bleaching of, respectively, the R and higher-aggregate bands, and the F and M bands.

If a one-to-one correspondence existed between the bleaching in a given temperature range and the release of stored energy in that range, then the following would be expected: (i) The energy released below 170°C should increase faster than linearly with N_F+2N_M. The lower set of points in Fig. 8 actually seem to fit a straight line, but the scatter is large. (ii) The energy released between 170 and 290°C should be linearly related to N_F+2N_M. The upper set of points of Fig. 8 shows that this seems to be true; but, again, with large scatter. (iii) The "excess" energy from the γ-irradiated samples should all be released below 170°C, if this excess is associated with R and higher aggregate centers, as suggested earlier. This is clearly not the case; most of this energy is released between 170 and 290°C.

Other indications that the relation between details of structure in the stored-energy spectra and specific processes is complicated are as follows: (iv) A fairly large fraction of the energy between 170 and 290°C is released *after* the F and M centers have bleached, and (v) The position of the peak at 250°C occurs at slightly higher temperatures for the more heavily irradiated samples (which contain relatively larger concentrations of R and higher-aggregate centers).

A plausible explanation of points (iii), (iv), and (v) above, which is consistent with Kobayashi's[1] interpretation of the peaks, is that the energy released below 170°C comes from electronic transitions or clustering processes involving R and higher-aggregate centers, and the energy from the destruction of the vacancies associated with these centers is released at temperatures slightly above where the F and M centers bleach. This temperature range is where the colloid band appears and then bleaches, but it is not clear whether there is any direct relationship.

2. Calcium-Doped Sample

Only one calcium-doped sample was investigated, so the growth kinetics of the features in the stored-energy spectra cannot be examined. Comparison of the stored-energy spectrum, Fig. 2, and the thermal-bleaching data, Fig. 5, shows that, as in the case of the nominally pure samples, the main stored-energy peak occurs at the temperature of maximum bleaching of the F and M bands. But both processes occur at lower temperatures than in the pure samples. A peak is present at about 250°C, at which temperature the F and M bands have bleached completely. The R and higher-aggregate bands were absent from this sample, as was the colloid band, so vacancies from any of these sources cannot be responsible for this peak. The peak could correspond to the annealing of the lattice defects associated with the F centers, in which case the 250°C peak in the pure samples probably contains a contribution from this source also.

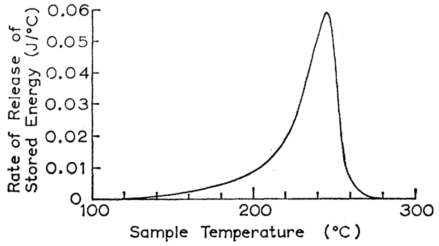

FIG. 9. Stored energy from a γ-irradiated crystal which had been heated to 230°C and then cooled to room temperature.

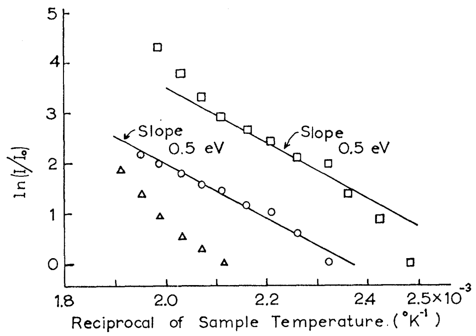

FIG. 10. Kinetics of the "initial rise" of quantities associated with the stored-energy peak near 250°C. I is the quantity, measured with respect to the baseline I_0. □: stored-energy-release rate from sample previously heated to 230°C. ○: F-band bleaching rate. △: thermoluminescence.

3. Kinetics of Bleaching, Annealing, and Thermoluminescence

In an effort to untangle what are evidently several processes occurring between 170 and 290°C, a crystal which had been γ-irradiated was heated to 230°C and quickly cooled to room temperature, in order to remove the energy contribution from processes corresponding to the low-temperature peak. (This procedure is analogous to that used to "burn off" low-temperature peaks in thermoluminescence studies.) The stored-energy spectrum from this sample is shown in Fig. 9. This curve is obviously similar to the thermoluminescence curve, Fig. 6, and to the derivative of the F-band thermal-bleaching curve. To examine this similarity more closely, the "initial rise" method of examining the kinetics, often used to investigate thermoluminescence kinetics,[13] was applied to these three curves, as shown in Fig. 10. Both the stored energy and thermal bleaching are consistent with monomolecular kinetics and an activation energy of about 0.5 eV. The departure of the data points from the straight lines at the low-temperature limit can be explained by errors in the measurement of small quantities and at high temperatures by failure of the initial-rise approximation. The thermo-

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[13] J. J. Hill and P. Schwed, J. Chem. Phys. 23, 652 (1955).

luminescence kinetics, on the other hand, appears to be different from that of the thermal bleaching and stored-energy release. This, along with the fact that the energy released in the luminescence is only about 10^{-5} of the energy released thermally, implies that the thermoluminescence represents at most a minor fraction of the F centers, and that these bleach by a route different from that taken by the majority.

C. Relation of Stored Energy to Volume Changes

Merriam, Wiegand, and Smoluchowski[14] studied the annealing of the volume increase in irradiated NaCl, both isothermally and at various constant heating rates. For samples heated at rates comparable to ours, the rate at which the volume increase anneals has peaks at temperatures corresponding to the middle and upper peaks in our stored-energy spectra. No volume annealing occurs below 200°C; thus, if the volume increase in irradiated samples is intimately related to the presence of negative-ion vacancies, this implies that the stored energy released below 200°C, and the corresponding changes in optical-absorption spectra, must involve electronic transitions and/or other processes, such as clustering, which do not change the number of vacancies. This agrees with the conclusions of the previous discussion concerning the distribution of the energy between the peaks in our stored-energy spectra. Merriam *et al.* analyze the kinetics of the volume annealing just above 200°C, and show it to be consistent with a monomolecular process having an activation energy of 1.3 eV. The details of their annealing kinetics at higher temperatures do not seem to be amenable to such simple analysis. Their data seem to imply that the lattice damage associated with the F centers anneals at temperatures somewhat above the bleaching temperature of the F centers. Our data also fit this picture, in that much of the stored energy in the large peak near 250°C is released above the temperature where the F and M bands have completely bleached. It has been suggested already that at least part of this energy may come from vacancies associated with R and higher-aggregate centers, but it is possible that some of it may also come from vacancies associated with F centers. This could mean that during thermal bleaching, electrons from the F centers must initially enter low-energy trapping levels which are not detected optically, and then at higher temperatures participate in processes leading to the return to the perfect lattice. The difference between our thermal-bleaching activation energy and Merriam's volume-annealing activation energy seems also to support this picture. The former energy would correspond to the activation of an electronic transition, and the latter to the motion of a lattice defect. 0.5 eV is too low an energy for the direct ionization of the F center, but seems a reasonable value for the activation of hole states, which must exist in equal numbers with the F centers somewhere in the lattice, although they have not yet been detected in room-temperature-irradiated crystals.

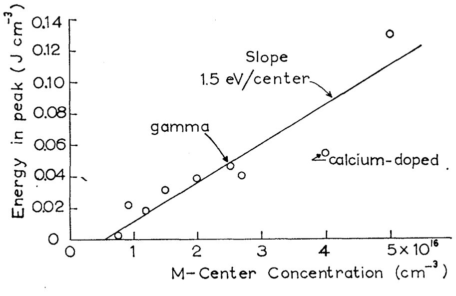

FIG. 11. Stored energy under the peak at 350°C versus initial M-center concentration.

D. Stored-Energy Peak at 350°C

This is discussed separately because the samples are completely bleached at this temperature. (This statement should be qualified by noting that the absorption in the uv, near 200 nm, is still bleaching at this temperature. However, there are not sharp changes in bleaching rate which can be related to the stored energy peak at 350°C, the uv absorption is only a little larger than in unirradiated samples to start with, and bleaches slowly over a wide temperature range.)

The peak is small, so data are inaccurate. A plot of energy released above 290°C versus N_F+2N_M shows much scatter. However, if we plot only the energy *in the peak* (defined as that portion of the stored-energy curve above the straight line drawn from the dip near 290 to 400°C), we get a fairly smooth curve. Figure 11 shows the energy in this peak as a function of initial M-center density. (A graph in terms of the square of the F-center density also gives a straight line[5], with somewhat less scatter than Fig. 11.) Note that even the point for the calcium-doped sample comes close to the line, in spite of the fact that this sample was drastically different from the pure samples in its growth kinetics and its ratio of F- to M-center concentration.

Since the M band (and all others, too) has completely bleached at this temperature, the energy must come from lattice defects. The slope of the line drawn in Fig. 11 is 1.5 eV per M center, which is reasonable for a lattice-annealing process.

V. CONCLUSION

Detailed assignment of the three stored-energy peaks to various mechanisms cannot be reliably made. There are too many processes going on: growth, conversion, and bleaching of several known color centers; and motion, coagulation, and annihilation of vacancies and interstitials. We can, however, make some general statements based on the available data.

At temperatures below 170°C, about 20% of the stored energy is released, yet there is no bleaching of

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the F band or annealing of the volume expansion. There is, to be sure, growth and annealing of aggregate centers, but these are in much too small a concentration to account for the energy. Thus, most of the energy must come either from electronic transitions not showing up in our optical measurements, or from atomic rearrangements which do not change the volume. The former might be electrons and holes in shallow traps annihilating, and the latter might be the annihilation of interstitials at vacancy clusters. An electronic mechanism seems to offer more possibility for accounting for the large energy.

In the temperature region 170–290°C, all known coloring bleaches, most of the stored energy is released, and volume annealing begins and is nearly completed. The data indicate that the F- and M-band bleaching occur at lower temperatures than the volume annealing. We suggest, then, that the stored-energy spectrum at these temperatures consists of at least two unresolved peaks. The case of the calcium-doped specimen seems to support this, since its optical bleaching occurs at a much lower temperature. It might be significant that the temperature of maximum energy-release rate is higher for the higher colorations.

Between 290 and 400°C there are no more optical effects, but there is still considerable stored-energy release and volume annealing. Since the stored energy here is proportional to the *initial* M-center concentration, a plausible model is that the M-center divacancies are migrating to surfaces. The energy of 1.5 eV per M center, Fig. 11, seems reasonable.

In the calcium-doped specimen, all of the bleaching, and most of the stored-energy release occurs in the lowest of our three temperature ranges. One might be inclined to ascribe the stored-energy release under the 135°C peak for the pure specimens to impurities similar to calcium. We think that the evidence is against this. The pure specimens show no bleaching to correspond to that peak, even though it has appreciable energy. Note also that the stored energy per F center in the doped crystal is about the same as that of the pure crystals, in spite of the very different annealing behavior. Perhaps the calcium acts as a kind of catalyst that enables the F centers to bleach at lower temperatures without changing the net energy release.

It might be fruitful to study stored energy in other alkali halides. With luck, one might find a compound where the various processes occur at more widely separated temperatures, thus giving more peaks and enabling the assignment of energies to processes.

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Refractive Indices of the Condensed Inert Gases

A. C. SINNOCK*
Department of Applied Physics, Brighton College of Technology, Brighton, Sussex, England

AND

B. L. SMITH
School of Mathematical and Physical Sciences, University of Sussex, Falmer, Sussex, England

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The refractive indices of condensed argon, krypton, and xenon have been measured for wavelengths between 3612 and 6439 Å by the spectroscopic method of minimum deviation. The Lorentz-Lorenz functions f_{LL} are found to remain constant to within about 3% over the entire range studied, with a small decrease (~1%) on freezing. At higher solid densities, the f_{LL} functions decrease with increasing density at an accelerating rate. This behavior is in moderate agreement only with theoretical predictions based on the tight-binding exciton model.

I. INTRODUCTION

It has recently been proposed[1–3] that the low-frequency dielectric properties of the solidified inert gases could be described in terms of a tight-binding exciton model. Existing experimental data[4–6] are not sufficiently extensive to provide an adequate test of theories based on such a model. We have therefore measured the refractive indices (n) of solid argon, krypton, and xenon[7] over a wide range of temperature and at wavelengths in the region 3612–6439 Å. In addition, we report the results of measurements on the liquids in equilibrium with their vapors at temperatures close to the triple points.

According to the Lorentz local-field model, the

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