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Enhanced Thermal Expansion in X-Rayed Rocksalt*†

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The volume expansion of NaCl heavily irradiated at room temperature with penetrating x rays has been studied with a photoelastic technique. In the course of the study a new effect was found; the coefficient of thermal expansion of NaCl is increased by irradiation. The magnitude of the fractional increase in expansion coefficient is typically somewhat less than 1%, and is about 14 times the concentration of radiation-induced defects, as measured by the volume expansion. The thermal annealing, above room temperature, of the enhancement of expansion coefficient has been observed; within experimental error the effect anneals concurrently with the volume expansion. The increase in expansion coefficient seems to be correlated only with the total concentration of lattice point defects, and is rather insensitive to their electronic state and spatial distribution.

Complete understanding of the effect in terms of a microscopic model has not been achieved, but the algebraic sign and approximate magnitude of the enhancement can be calculated thermodynamically from the local strain field of a vacancy or an interstitial. A rough dynamical calculation, using a modified Einstein model to represent the lattice vibrations, indicates that the dominant term in the enhanced thermal expansion involves the mixed derivative $(d/dt)(\partial W_s/\partial V)_T$, where W_s is the activation energy for formation of Schottky defects. This quantity, as estimated from the data, is equal to 2×10^8 dynes/cm²-deg.

INTRODUCTION

WORK reported to date on the effects of irradiation on the thermal expansion properties of solid materials has been sparse, and the results have been negative.[1–3] The present paper describes the results of a study of the enhancement of the thermal expansion coefficient of NaCl by irradiation with energetic x rays. This is of interest, not only for its own sake, as a newly discovered effect of irradiation, but also because it bears on the more general problem of anharmonicities in a lattice containing point defects. The effect was discovered accidentally in the process of volume expansion measurements on irradiated alkali halides. The study concerns primarily the dependence of the thermal expansion enhancement upon the total concentration of lattice point defects produced by the irradiation although the effects of defect association and the influence of the electronic state of lattice defects were also investigated.

The change in expansion coefficient was detected with a highly sensitive, though rather indirect, photoelastic technique, which has not previously been applied to thermal expansion measurements. Since this technique depends upon a knowledge of the temperature dependence of certain elastic and photoelastic constants of NaCl, these were checked, over a temperature range of a few hundred degrees above room temperature, by an independent method.

Theoretical analysis has proceeded along two principal lines: (1) a thermodynamical effort to connect the observed increase in expansion coefficient with the elastic strain field of a point defect, and (2) a rough dynamical calculation based on a modified Einstein model of an ionic crystal with defects.

EXPERIMENTAL

Outline of the Method

The method used to measure the x-ray-induced volume expansion is essentially the photoelastic one introduced by Primak *et al.*[4] and modified by Wiegand and Smoluchowski.[5] A slab of single-crystal material is mounted in a lead block in such a way that half the slab is irradiated by the x rays, the other half being shielded. The irradiated portion, which would normally undergo uniform dilatation, is constrained by the undamaged half. The resultant strain is anisotropic and can be detected quantitatively by photoelastic methods.[6] (The geometry of the sample, shield, and strain pattern in our experiments was essentially that shown in Fig. 1 of reference 5.) The free volume expansion which the irradiated portion of the sample would have undergone in the absence of constraints is obtained by solving an elastic problem, which, in the one-dimensional case, is straightforward.[5] An approximation used in obtaining this solution ($2b\ll l$) was, however, found not to be valid in our case. The two- or three-dimensional elastic problem in this geometry has not been solved in closed form. Although a two-dimensional analysis of a mathematically identical problem, suitable for digital computer solution, is available,[7] it was felt that nothing would be gained by the use of the two-dimensional calculation because of other (experimental) limitations.

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[1] G. Mayer and J. Gigon, J. phys. radium **18**, 109 (1957).

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[4] W. Primak, C. J. Delbecq, and P. H. Yuster, Phys. Rev. **98**, 1708 (1955).

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[6] R. W. Goranson and L. H. Adams, J. Franklin Inst. **216**, 475 (1933).

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The one-dimensional treatment assumes the crystal to be infinite in the two dimensions parallel to the plane separating the irradiated and unirradiated portions. It was verified experimentally[8] that edge effects were so small that the errors introduced by this assumption were entirely negligible.

A point defect may contribute to the volume expansion of the irradiated part of the crystal not only because of the lattice relaxation in its immediate neighborhood, but also, in the case of a Schottky defect, because of the appearance of an additional ion on the crystal surface. It is not clear *a priori* that the photoelastic technique described here is sensitive to that part of the volume expansion which arises from these additional surface layers. Experimentally, the volume expansion vs temperature annealing curves for rocksalt crystals obtained by the photoelastic technique are in good agreement with the curves obtained by Kobayashi,[9] who measured density change with a differential flotation technique. If the photoelastic technique were measuring only the relaxation contribution to the volume expansion, then one would expect substantial disagreement between the annealing curves as measured by the two different techniques, especially at higher temperatures.

There is evidence[10–14] that rocksalt single crystals whose surfaces are exposed to the atmosphere are "case-hardened," that is, the material at the crystal surface differs chemically from the bulk crystal, and forms a tough elastic "skin" which prevents dislocations from breaking easily through to the surface. The ions displaced in the formation of Schottky defects can hardly migrate the entire distance to the surface of the crystal in any case, and very likely migrate only to edge dislocations, a crystallographically equivalent situation. Apparently the presence of the "skin" ensures that the volume expansion arising from these Schottky defects displaced ions contributes to the microscopic, non-uniform strain which is the measured quantity in the photoelastic technique.

Since the radiation-induced volume expansion is at most only a few hundred parts per million, whereas the volume thermal expansion of NaCl is one hundred twenty parts per million per degree centigrade, it is clear that even a small difference in the coefficients of thermal expansion of the two halves of the crystal will cause a detectable change in the volume expansion of the irradiated portion relative to the unirradiated portion as the crystal is heated. If there is a temperature range of some extent in which no annealing of the radiation-induced volume expansion occurs, a change in the relative volume expansion may still be observed if irradiation has changed the thermal expansion coefficient of one-half of the crystal.

TABLE I. Spectrochemical analysis on two samples. No. 99—as cleaved. No. 94—cleaved and put through the pretreatment anneal wrapped in platinum foil.

	Impurity content in parts per million Sample No. 99	Sample No. 94
Al	25	10
Ti	<5	10
Fe	10	20
Ca	10	10
Bi	5	10
Si	4	2
Cu	3	1
Ag	1	3
K	<1	<1
Li	<0.3	<0.3
Ba	<5	<5
Mn	<5	<5
Cr	<5	<5
Pt	<10	<10

Samples and Pretreatment

The samples used were slabs of single-crystal NaCl approximately $16\times16\times4$ mm, cleaved from stock supplied by the Harshaw Chemical Company. The process used in growing these crystals includes a step which amounts to a single-pass zone refining operation, and as a consequence the impurity concentration at one end of the ingot may be appreciably higher than at the other end.[15] The three large blocks from which all samples were cleaved were taken from the high-purity end of a single ingot. A spectrochemical analysis for certain elements, given in Table I, is consistent with other published analyses,[16,17] and indicates that the material was quite pure by present day chemical standards. The total impurity concentration might reasonably be estimated at 100-200 parts per million.

Some thermal pretreatment of the samples was necessary, since random strains present in the crystals after cleaving were large compared to the strain arising from the radiation expansion. In order to determine the temperature at which the background strain annealed, polarized light was passed through the crystal and the random strain pattern observed visually as the sample was heated. Figure 1 gives the annealing curve. We note that annealing of the background strains begins at 300°C and is essentially complete at 600°C. Because of the rather poorly defined state of strain in the crystal

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[8] M. F. Merriam, thesis, Carnegie Institute of Technology, 1960 (unpublished).

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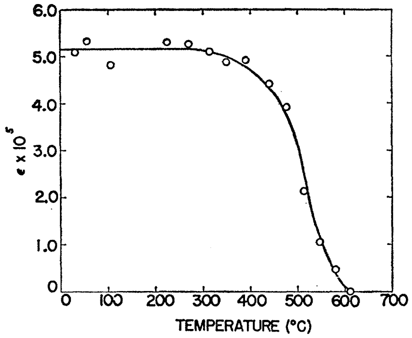

FIG. 1. Annealing of background strains in as-cleaved NaCl. Temperature raised at 2°C/min. Data corrected for temperature dependence of both the elastic and photoelastic constants.

before annealing, little significance can be attached to the detailed shape of the annealing curve between these temperatures. The annealing temperatures are of interest, however, since the random background strain arises from elastic strain fields of dislocations. It is somewhat surprising that dislocations in NaCl move at such low temperatures. Annealing, at comparable temperatures, has recently been observed in the nuclear quadrupole resonance broadening in other alkali halides.[18] Since the broadening is caused by dislocations strain fields this is probably another manifestation of the phenomena here observed.

Removing the random background strain was accomplished by heating to 620°C in dry helium and cooling to room temperature at a well-controlled uniform rate of 1 to 5 degrees per hour so as to keep the frozen-in thermal strains to a sufficiently low level, of the order $\epsilon \approx 10^{-6}$. Most of the crystals were wrapped in platinum foil during the pretreatment anneal. This procedure apparently did not introduce significant platinum impurity into the sample (see Table I).

Irradiations

All samples were irradiated with x rays of sufficient energy to give substantially uniform coloration through the thickness of the crystal. The x rays were obtained from a GE Maxitron 300 therapy unit with a tungsten target operated at 300 kvp and 20 ma. The radiation emerging from the beryllium window of the tube was filtered by 1.6 mm of aluminum to cut out the soft radiation. Samples were irradiated for 49 ± 1 hr in a measured radiation field of 12 000 r/min, except for sample No. 81, for which the radiation field was only 11 000 r/min. Sample holders for the irradiations are shown in Fig. 2. The lower half of the crystal was shielded by lead absorbers of a thickness sufficient to reduce the x-ray intensity by three orders of magnitude or more. The positioning of the sample with respect to the anode of the x-ray tube was such as to minimize asymmetries and geometrical shadowing and to assure uniform irradiation. The irradiations were carried out in air, nominally at room temperature, although during irradiation sample temperatures actually rose somewhat. The temperature, as determined by thermocouples imbedded in dummy samples, rose to 87°C for holder shown in Fig. 2(c) and to 47°C for holder shown in Fig. 2(b).

Measurements

The photoelastic measurements were made with the apparatus illustrated schematically in Fig. 3. The analyzer unit, in addition to its rotatable polarizing prisms, includes a telescope with removable eyepiece for viewing the sample, and a large (10 in.) diameter engraved scale fixed to the polarizing prism, for reading its angular position. This angular position was read, with the aid of a magnifying eyepiece, to ± 0.01 degree of arc. The angular position of the first polarizing prism (the "polarizer") and of the quarter wave plate was accurately fixed at 45° to the vertical for all measurements. The quarter wave plate was nominally intended for use with the 5890-A sodium *D* line, rather than the 5770-A line of Hg which was the light actually used, but no deterioration of the quality of the null which could be attributed to the slight wavelength mismatch was observed.

The irradiated sample was placed in the light beam between the first polarizing prism and the quarter wave plate with its boundary plane (between the irradiated and the unirradiated parts) horizontal or vertical and parallel to the light beam. The furnace shown in Fig. 3 can be removed and a stage equipped with a micrometrically movable slit inserted in the beam if it is desired to map the strain as a function of position. A number of such profiles were made, to see how closely the actual strain pattern approximated the theoretical one. Agreement was quite good, especially in the unirradiated half of the crystal.

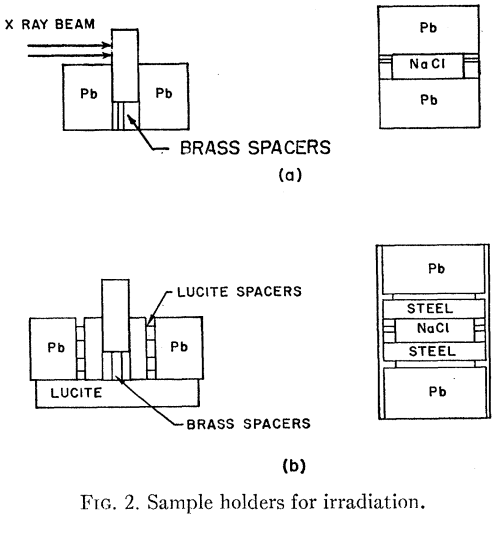

FIG. 2. Sample holders for irradiation.

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[18] G. Clark, thesis, Cornell University, 1960 (unpublished).

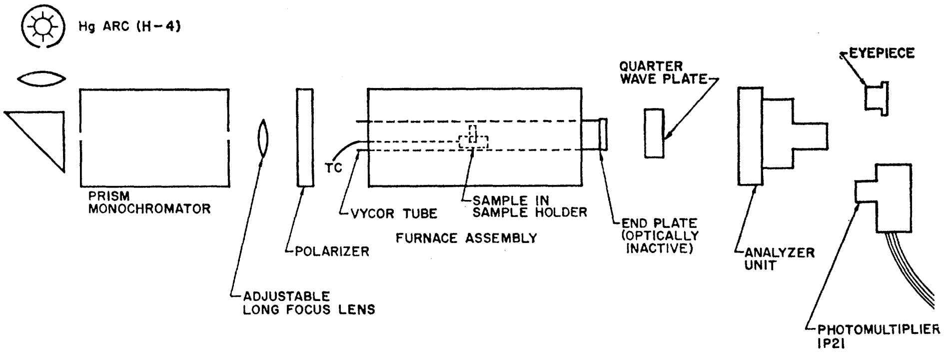

FIG. 3. Polariscope and annealing furnace (schematic).

It is of course essential that the radiation-induced strain in the crystal be entirely elastic. If any slip occurs, the measured optical rotation is no longer proportional to the volume expansion. Attempts were made to observe slip lines on a number of samples, both directly, using a Zeiss Interference Microscope, and photoelastically, using the apparatus described above. No slip lines or other evidences of plastic flow were ever observed. Thus all the photoelastic measurements are interpreted on the supposition that slip did not occur.

When making measurements of strain as a function of temperature the crystal was placed in an aluminum holder, to which a thermocouple was attached. The whole assembly was then inserted in furnace tube, which had one end blocked with a plate of optically inactive glass to minimize drafts and convection. All anneals, except the pretreatment anneals noted earlier, were made in air. The tube was placed into a furnace and the furnace positioned in the polariscope light beam. Since all the crystals used in this study were heavily irradiated, no light passed through the irradiated half of the sample (the *F* band in NaCl absorbs light at the wavelength used) and photoelastic measurements could be made only in the unirradiated part. The optical rotation caused by the radiation expansion could be measured visually simply by observing the crystal through the telescope and noting the analyzer rotation which corresponded to a minimum in the light transmitted through the region in the crystal (in the unirradiated half) where the strain was a maximum. All data presented here, however, with the exception of that in Fig. 1, were obtained photoelectrically. In this case it was necessary to mask the sample before inserting it in the aluminum holder, so that light is transmitted only through the region of the crystal corresponding to the maximum of the strain pattern in the unirradiated half. Details and geometry of the masking are given elsewhere.[8] Since the irradiated portion of the crystal (as well as most of the unirradiated portion) was completely masked, it is practically certain that the optical bleaching phenomena were not present to complicate the thermal annealing studies.

Photoelectric detection has not been used by previous authors[4,5,19] who studied radiation-induced volume expansion with the photoelastic technique, but was found to be essential for the present study. Lack of comparability between sets of data taken at different times, as well as scatter in data taken at any one time, made visual null determination unsuitable. The photoelectric attachment consisted of a 1P21 multiplier phototube in a light-tight housing adapted to fit into the analyzer unit in place of the removable telescope eyepiece. The photomultiplier output was fed directly to a box galvanometer of sensitivity 1.5×10^{-9} ampere/mm.

As mentioned above, when making a visual determination of strain the analyzer was rotated for a null—a minimum of the transmitted light—5 or 10 readings taken and the results averaged. When making a photoelectric measurement, however, it was not practical to detect the null directly in this manner because the detection system is insensitive near the minimum of the transmitted light. The phototube is less sensitive to an absolute minimum in the transmitted intensity than is the human eye. Consequently, when making a photoelectric determination the analyzer was rotated to one side of the null until a certain photomultiplier current was observed at the galvanometer. The analyzer was then rotated back through the null until the same current was again observed. The point midway between these two angular positions was then taken as the angular position of the null. This method, of course, depends upon symmetry about the null position in the curve of transmitted intensity vs analyzer position. Since an asymmetry is conceivable, though not likely, it was verified repeatedly, in nearly every sample, that the position of the null was independent of the galvanometer deflection used to determine it. At no time was any lack of symmetry detected. As an additional check, visual and photoelectric nulls were frequently compared, by interchanging phototube and eyepiece.

Smooth temperature control during anneal is of the greatest importance. Because of the low-thermal conductivity of rocksalt and the high sensitivity of the

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[19] D. A. Wiegand and R. Smoluchowski, Phys. Rev. **110**, 991 (1958).

measurements to transient thermal strains, temperature fluctuations of the order of a few degrees in a few minutes are intolerable. For this reason, only isothermal and constant rate of warmup anneals were used.

The temperature-sensing element was an iron-constantan thermocouple attached to the aluminum sample holder. It was connected to either a Leeds and Northrup Micromax recording controller or a Rubicon portable potentiometer, manually operated, usually with one-microvolt sensitivity. During constant rate of warmup anneals, the rate of rise of temperature was constant against short-term fluctuations to within 0.003°C/min, there were no fluctuations larger than this which could be resolved with the 5-sec response time of the manually operated Rubicon potentiometer. Long-term linearity in the temperature-time function was such that deviations from the programmed temperature were never larger than five percent. Temperatures were controlled manually during isothermal anneals to ±1°C. The thermocouple wire used was not calibrated; it was, however, checked at one point (217°C, the boiling point of naphthalene) for protection against a gross error.

Optical absorption measurements were made with a Beckman DU spectrophotometer equipped with a Warren model 3000 Spectrocord recording attachment and with Mitchell's scale expander.[20] Neutral density filters were used in the Beckman reference beam to measure high optical densities.

RESULTS

Interpretation of the Observed Phenomena

When a crystal which had been irradiated in the manner described above was annealed by raising its temperature at a constant rate, the fractional volume expansion $\Delta V/V$ of the irradiated half, as compared to the unirradiated half, was found to increase linearly with with increasing temperature (Fig. 4) up to about 190°C where a rapid decrease set in. This initial increase has been found to be reversible, that is, if the temperature is raised slowly to any temperature less than 190°C, and then slowly lowered back to room temperature, the linearly increasing curve of $\Delta V/V$ vs temperature observed during the heating period is retraced on cooling. This cycle can be repeated, presumably indefinitely, as long as the 190°C temperature is not exceeded. Above 190°C irreversible annealing takes place until the photoelastically detectable volume expansion disappears entirely at roughly 400°C.

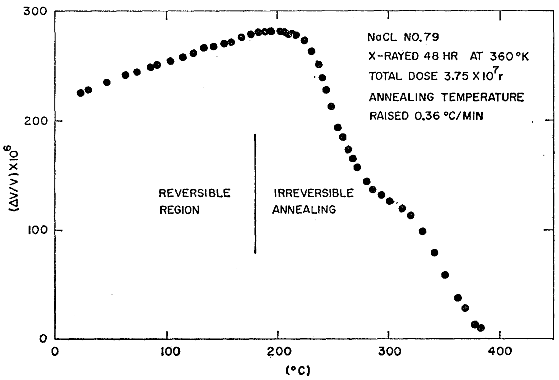

FIG. 4. Observed temperature dependence of $\Delta V/V$ in a typical sample. Only every third point is shown.

The linear increase in the curve of $\Delta V/V$ vs T in the range from room temperature to 190°C is essentially independent of heating rate over a considerable range. It is found also that if the raising of the temperature at a constant rate is stopped short of 190°C, say at 170°C, and the temperature is then maintained constant at that value, no decay of the $\Delta V/V$ takes place. In fact if the crystal is heated very quickly from room temperature to, say, 170°C, and held at that temperature, one observes that $\Delta V/V$ does not change with time after the constant temperature is reached, although the value of $\Delta V/V$ at the constant temperature (170°C) is higher than its value at room temperature by the expected amount. The linear increase from room temperature to 190°C was not seen by Kobayashi[9] whose flotation technique for measuring relative change in density is considerably more direct than the photoelastic method. While otherwise in general agreement with our results, his annealing curve shows no change in $\Delta\rho/\rho$ from room temperature to 200°C. Since all his measurements were made at room temperature (the crystal being raised to annealing temperature between measurements), a reversible effect would not have been detected in any case.

We now consider several possible interpretations of the linear increase in the $\Delta V/V$ vs T curve. The effect cannot be connected with motion or recombination of lattice defects present in the sample since it is unlikely that any such defect annealing would be reversible. Furthermore, there is no reason why any such annealing should yield a *linear* increase of $\Delta V/V$, and be independent of heating rate. Instrumental transient effects can also be ruled out. As noted in the preceding paragraph, they were searched for experimentally and not found.

To obtain $\Delta V/V$ from the observed quantity θ/d, the optical rotation per centimeter, the following equation is used[21]: $\Delta V/V = 1.3k(T)(\theta/d)$, where $k(T)$, which is given explicitly in Appendix I, contains the elastic and photoelastic constants and is fairly strongly temperature dependent. If the temperature dependence of $k(T)$ were incorrect, in just the proper way, one could obtain an erroneous, linear temperature dependence of

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[20] P. V. Mitchell, thesis Carnegie Institute of Technology, 1960 (unpublished).

[21] The factor 1.3 is a geometrical one, arising from the fact that in our samples the breadth of the highly strained region was appreciable compared with the length of the crystal. This factor reduces to unity when the approximation $2b \ll l$ (Fig. 1 of reference 5 is valid; see reference 8).

$\Delta V/V$, as observed. This is not thought to be the case for two reasons. First, the temperature dependence of $k(T)$ was independently checked, and the check, made under the conditions of our experiment, agreed with the temperature dependence from the literature, at least up to 200°C. This is discussed more completely in Appendix I. Furthermore, if the observed phenomena were simply a reflection of an incorrect temperature dependence of $k(T)$, then the magnitude of the initial rise (i.e., the slope of the $\Delta V/V$ vs T curve between room temperature and 190°C) should be proportional to the value of $\Delta V/V$ itself. Although this is usually observed, at least one case, to be discussed later, was found in which $\Delta V/V$ increased and the slope of the $\Delta V/V$ vs T curve decreased.

The correct interpretation of the initial rise is believed to be the following: Let us suppose that the thermal expansion coefficient of NaCl is increased by irradiation, and that consequently the volume difference between the irradiated and unirradiated halves of the crystal increases with rising temperature, because of the differential thermal expansion. Only a rather small change in expansion coefficient, of the order of a fraction of 1%, is necessary to yield an effect of the magnitude observed. This is so because the radiation expansion is quite small compared to thermal expansions; it usually does not exceed the thermal expansion associated with a 1°C temperature rise. This interpretation gives naturally the linearity which is the most striking feature of the observed effect.

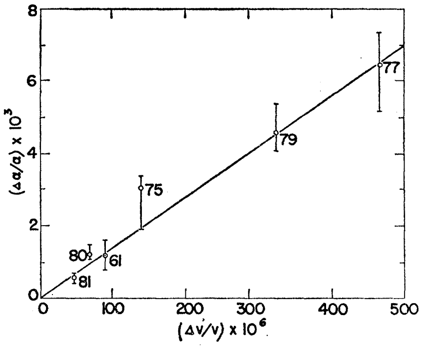

FIG. 5. Increase of thermal expansion coefficient as a function of the increase in volume. Corrected for the effect of elastic strain on the expansion coefficient.

Enhanced Thermal Expansion

The net fractional increase in linear thermal expansion coefficient is obtained from the initial rise according to the relation:

$$\frac{\Delta\alpha}{\alpha}=\frac{1}{3\alpha\Delta T}\left[\Delta\left(\frac{\Delta V}{V}\right)\right].$$

The fractional increase in α caused by irradiation is actually about 20% larger than the net observed value.

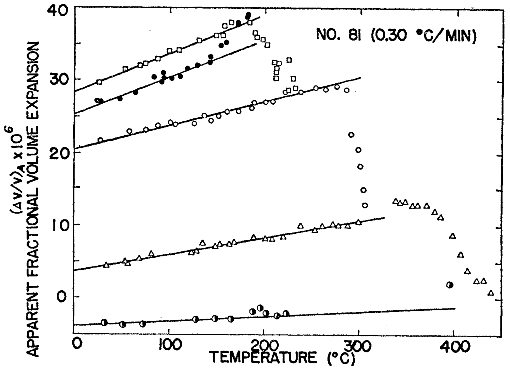

FIG. 6. Cyclic annealing of $\Delta\alpha/\alpha$ and $\Delta V/V$. Only rising temperatures are shown: ●—after irradiation (note annealing of background strain 140–185°); □—after heating to 185°C; ○—after heating to 233°C; △—after heating to 306°C; ◑—after heating to 441°C.

The correction[8] arises from the effect of the elastic strain in the crystal on its expansion coefficient, according to the thermodynamic relation

$$\left(\frac{\partial\alpha}{\partial\epsilon}\right)_T=-\frac{1}{E}\left(\frac{\partial E}{\partial T}\right)_\sigma, \tag{1}$$

where ϵ represents linear elastic strain, E is Young's modulus, and σ is stress.

It was soon discovered that those samples having the largest volume expansions also showed the greatest enhancement of thermal expansion coefficient. A plot of $\Delta\alpha/\alpha$ vs $\Delta V/V$ for a number of samples annealed by constant rate of warmup is given in Fig. 5. The enhancement of thermal expansion coefficient is seen to be roughly proportional to the radiation-induced volume expansion. It is also to be noted that $\Delta\alpha/\alpha$ is a full order of magnitude larger than $\Delta V/V$. If the contribution to $\Delta V/V$ from lattice relaxations around defects is neglected in comparison with the contribution from creation of additional atomic sites, then

$$\Delta V/V=n/N,$$

where n/N is the concentration of lattice point defects. The data shown in Fig. 5 give, however, $\Delta\alpha/\alpha=14\times(n/N)$. If the observed effect is connected with the defects present, then one would expect it to anneal out simultaneously with the volume expansion. In order to check this, a crystal was annealed cyclically by alternate heating and cooling, heating on each cycle to a higher temperature than on the preceding one. The data shown in Fig. 6 clearly indicate a decrease in initial slope for successive cycles. Figure 7 shows the simultaneous annealing of $\Delta\alpha/\alpha$ and $\Delta V/V$ as obtained from the data of Fig. 6. While the limits of error are rather large, the enhanced thermal expansion does in fact show the same general annealing behavior as the volume expansion.

The heavily irradiated crystals used in these experiments have, of course, very high F-center concentra-

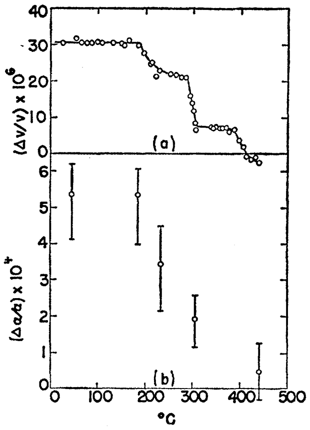

FIG. 7. Simultaneous annealing of volume expansion and of enhanced thermal expansion coefficient in sample No. 81.

tions, in excess of $10^{18}/\mathrm{cm}^3$. It is an interesting fact that removal of the electrons from F centers does not seem to have a very strong effect upon the enhancement of expansion coefficient. The initial rise portion of the $\Delta V/V$ vs T curve is linear and reversible right up to the temperature at which annealing of $\Delta V/V$ sets in, although irreversible thermal bleaching of F centers, together with simultaneous growth of bands attributed to more complex centers, begins at a considerably lower temperature.

One experiment was performed in which annealing of F centers may have played a role. An irradiated crystal was heated at a uniform rate to 173°C and then the temperature raised rapidly to 210°C where it was held for many hours. The temperature was then slowly lowered to room temperature and the sample examined visually under white light. It was optically clear, i.e., the F centers had disappeared. The temperature was then raised again at a constant rate. The results are shown in Fig. 8. It is to be noted that even though a considerable increase in $\Delta V/V$ took place during the rapid rise in temperature and that, even though some annealing, resulting in a monotonic (but slight) decrease in $\Delta V/V$ occurred during the isothermal bleaching at 210°C, the crystal, at the start of the second rise, showed a *larger* $\Delta V/V$ than at the beginning of the annealing. This increase in $\Delta V/V$, which amounts to about 10%, presumably arises from the lattice relaxation associated with annealing of the F centers. To our knowledge this relaxation and consequent volume increase has not been previously observed. It appears also that the slope of the second rise is less than that for the first heating; i.e., that $\Delta\alpha/\alpha$ has been decreased by removing the F centers. This difference may not be due to the F-center electrons directly. Certainly extensive clustering of the lattice defects, as well as some annealing, occurred during the long anneal at 210°C. The cause of the change in $\Delta\alpha/\alpha$ is thus not clear.

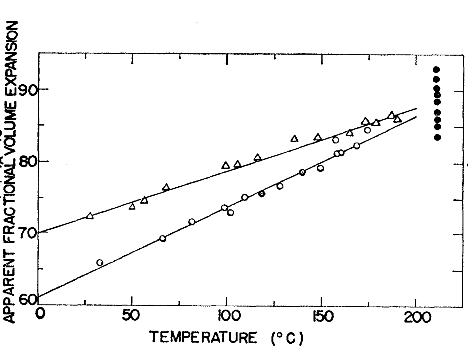

FIG. 8. Effect of thermal bleaching on volume expansion and thermal expansion coefficient. Open circles—heated at constant rate after irradiation; solid circles—4-hour bleaching anneal at 210°C; triangles—heated at constant rate after bleaching. The value of $\Delta V/V$ at 210°C declines monotonically with time by the amount indicated.

The most interesting and surprising aspect of the results presented above is the magnitude of the irradiation-induced change in the thermal expansion coefficient. The various properties of materials vary greatly in their sensitivity to irradiation. The so-called "defect" properties such as electrical conductivity and mechanical strength usually change drastically upon irradiation, whereas the "bulk" properties, for example, mass density, are expected to change only in proportion to the density of defects introduced. Thermal expansion is usually considered a bulk property. We found, however, the change in thermal expansion coefficient to be a full order of magnitude larger than the volume expansion in the irradiated crystal. Our assumption that the fractional volume expansion is equal to the defect concentration is probably not rigorously true, but it seems unlikely that it could be in error by more than a factor of 2. It would thus appear that thermal expansion of an ionic crystal cannot be regarded as a bulk property, at least so far as its sensitivity to irradiation is concerned.

Classical Theory

Before attempting to analyze the effect of point defects, it is useful to review briefly the usual description of the thermal expansion process, limiting ourselves to alkali halides. The potential between two ions in these crystals is usually taken as the sum of two terms, Coulombic attraction at large separation r and a Born-Mayer repulsion at small separation. The equilibrium separation r_0 of the ions at $T=0$ corresponds to the minimum of the potential well. Since the well is asymmetric the equilibrium separation shifts to higher separations as the temperature is raised, resulting in thermal expansion (see Fig. 9).

The potential energy at low temperature of one ion in the field of all its neighbors can be written

$$V(x)=cx^2-gx^3-fx^4+\cdots,$$

where $x=r-r_0$ is now the departure of the ionic separation from the equilibrium value at $T=0$, and c, g, and f are parameters. The average displacement, to first order, is $\bar{x}=\frac{3}{4}(g/c^2)kT$ and the linear thermal expansion

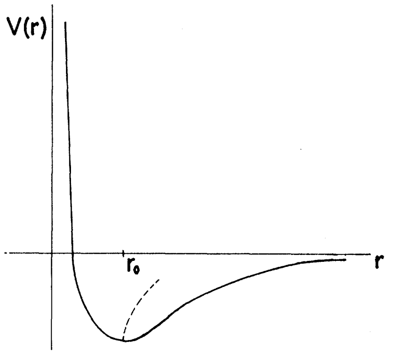

FIG. 9. Interionic potential in an alkali halide crystal showing anharmonicity about the equilibrium separation. The dashed line is the locus of points midway between the extreme values of r for each $V(r)$.

coefficient is, in this approximation $\alpha=\frac{3}{4}(kg/r_0c^2)$. If α is to be the linear thermal expansion coefficient for a macroscopic crystal, the potential must be invariant under translation by any primitive lattice vector. This treatment of the thermal expansion is, of course, rather crude; for example it yields α independent of temperature. Qualitatively α depends linearly on the anharmonic parameter, and inversely on the square of the harmonic parameter of "hardness."

Point Defects at Low Temperatures

Let us consider the effect of point defects upon the thermal expansion coefficient at temperatures sufficiently low so that the total number of defects is independent of temperature. It is not obvious *a priori* whether a defect, for example, a vacancy, will give rise to an increase or a decrease in expansion coefficient. It seems reasonable that any sort of point defect will increase the anharmonicity of the potential felt by surrounding ions. One might, therefore, expect an increase in expansion coefficient. However, this sort of qualitative reasoning is not reliable for two reasons. First, since the measured change in α is an average over all atoms, effects of the point defect upon distant neighbors may be important, and these are very hard to visualize. Second, since the interionic potential is not invariant under translation in the vicinity of the defect, conclusions about changes in the average position of ions near the defect cannot readily be extended to conclusions about changes in the macroscopic dimensions of the crystal. To illustrate the latter point, one might say (incorrectly) that vacancies should decrease the thermal expansion coefficient of a crystal, since neighboring atoms would be able to relax into the vacancies. It is possible, however, to make simple thermodynamical arguments which will give us an idea of what to expect.

Continuum Model

If one considers the crystal as an elastic continuum, one can use simple thermodynamical arguments and hope to understand at least the sign of the change in α. In NaCl both the vacancy[22] and the interstitial atom[23] act as point centers of dilation, i.e., the nearest neighbors move outward. According to Eshelby[24] the effect of a statistically uniform distribution of point centers of dilation in an elastic continuum is to produce a dilational strain which is uniform and isotropic throughout the specimen. This is true for strains of any magnitude.[25] From this we see that a crystal with internal centers of dilation approaches the condition of a perfect crystal under a negative external hydrostatic pressure, in the limit of numerous, weak, uniformly distributed centers of dilation. If we go to this limit, we can apply a thermodynamic relation between thermal expansion coefficient and dilatational elastic strain, which is analogous to the relation between thermal expansion coefficient and linear strain, Eq. (1) above, and is derived in a parallel fashion. The relation is

$$\left(\frac{\partial\alpha}{\partial\bar{\epsilon}}\right)_T=-\frac{\chi}{3}\left(\frac{\partial(1/\chi)}{\partial T}\right)_p, \qquad (2)$$

where α is again the linear thermal expansion coefficient, $\bar{\epsilon}$ refers to dilational strain, p is pressure, and χ is the isothermal compressibility, or reciprocal bulk modulus. The right-hand side of (2) is known for[26] NaCl and it is positive at the temperatures of interest. The change in expansion coefficient will therefore be of the same sign as $\bar{\epsilon}$, i.e., negative for a hydrostatic compression, positive for a dilatational expansion. In our case then $\Delta\alpha$ should be positive, in agreement with experiment.

The right-hand side of Eq. (2) at, say, 100°C is 2.15×10^{-4} $(°\mathrm{K})^{-1}$ and the problem of calculating

$$\frac{\Delta\alpha}{\alpha}=-\frac{\chi}{3}\left(\frac{\partial(1/\chi)}{\partial T}\right)_p\frac{\langle\bar{\epsilon}\rangle}{\alpha}, \qquad (3)$$

is reduced to calculating $\langle\bar{\epsilon}\rangle$, the mean dilatational strain introduced into the crystal by defects. This strain and thus the change in α can be estimated for several types of defects. Applying Eshelby's continuum model to this problem we introduce defects in the following way[27]: (1) Cut out the regions which are to contain the defects; (2) produce one defect in each region; and (3) force the damaged regions back into the original cavities. The volume of the regions cut out will, in general, be changed by the defects and these regions, when replaced, will

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act as centers of dilation in the solid, causing length and lattice parameter changes.

Using linear elasticity theory, and assuming the defect distribution to be statistically uniform the average strain is:

$$\langle\bar{\epsilon}\rangle = 4\pi(1-\sigma)n^*c/(1+\sigma),$$

where σ is Poisson's ratio, n^* the number of centers of dilation per unit volume, and c the strength of a center of dilation. For a prototype defect consisting of a sphere of radius r_0 of the same material, where the relaxed misfit strain is ϵ_d, we have

$$c = \epsilon_d r_0^3(1+\sigma)/3(1-\sigma),$$

and thus c is proportional to the misfit strain and to the volume of the defect region. If several types of defects are present then the effects are simply additive.

Applying this model to an estimate of the relaxation strain around a vacancy, we take the radius r_0 as the normal nearest neighbor distance (i.e., the Na^+—Cl^- spacing) and the misfit strain ϵ_d as twice the fractional displacement of the nearest neighbors of the vacancy of interstitial. We take twice the fractional displacement because the nearest neighbor displacement corresponds to the unrelaxed misfit strain of our prototype sphere, and the relaxed misfit strain, which is one-third the fractional volume expansion of the sphere *before* it is forced into the cavity, will be larger. If $\epsilon_d \ll 1$, the relaxed misfit strain is twice the unrelaxed misfit strain.

Since $(N/4)a^3$ is the unit volume if N is the number of ion pairs per unit volume and a the lattice parameter, and introducing $n = n^*/2$ as the number of pairs of centers of dilation (e.g., a positive and a negative ion vacancy would constitute such a pair), we obtain

$$\langle\bar{\epsilon}\rangle = (8/3)\pi[\epsilon_d^*(+) + \epsilon_d^*(-)](n/N),$$

where $\epsilon_d^* = \epsilon_d/2$ is the fractional nearest neighbor displacement, n/N is the concentration of Schottky pairs, and $\langle\bar{\epsilon}\rangle$ is the mean dilational strain in the crystal arising from lattice relaxation around n pairs of vacancies. For the fractional nearest neighbor displacement we use the values of ϵ_d^* calculated by Tosi and Fumi.[22] These authors obtained $\epsilon_d^*(-) = 0.104$ for the nearest neighbors of a negative-ion vacancy and $\epsilon_d^*(+) = 0.070$ for the nearest neighbors of a positive-ion vacancy. These values yield $\langle\bar{\epsilon}\rangle = 1.46(n/N)$ which, when substituted into (3), gives $\Delta\alpha/\alpha = 7.6(n/N)$ for the fractional enhancement of expansion coefficient arising from a concentration (n/N) of Schottky pairs. If we consider a crystal whose vacancies have been generated by a Varley-type mechanism,[28] then the n pairs of F centers and interstitial halogen atoms give, using the nearest neighbor displacements calculated by Hatcher and Dienes[23] for the halogen interstitial, $\langle\bar{\epsilon}\rangle = 1.47(n/N)$ or again $\Delta\alpha/\alpha = 7.6(n/N)$. Since the same value is obtained for both models, measurements of $\Delta\alpha/\alpha$ are not likely to be helpful in distinguishing between the proposed mechanisms for vacancy formation. We note that the value calculated for $\Delta\alpha/\alpha$ is smaller than the experimental value by about a factor of 2, which is not too surprising in view of the crudeness of our numerical estimate.

In making the estimate of $\langle\bar{\epsilon}\rangle$ the calculated ionic displacements for the nearest neighbors of an empty vacancy were used. One may ask whether this is appropriate for an irradiated crystal, in which, presumably, most of the vacancies contain trapped electrons or holes, which would be expected to reduce the relaxation substantially. The justification for proceeding as we did is the experimental observation, noted earlier, that the enhancement of expansion coefficient is not greatly changed if all electrons and holes are removed from lattice vacancies by a mild heat treatment.

In connection with this approach it is worthwhile to inquire to what extent a continuum model with linear elasticity can represent an ionic crystal in the badly strained region near a defect. The model will certainly be applicable to regions of the crystal far enough from a defect. The only question is whether "far enough" is one lattice parameter or ten. Bassani and Fumi[29] and Tosi and Fumi[22] calculate various formation and association energies in NaCl and obtain rather good agreement with experiment by treating only nearest, and sometimes next nearest, neighbors as discrete ions. This indicates that our approximation of the crystal as an elastic continuum at distances greater than half a lattice parameter from the center of the defect may not be too bad.

If the defects are present as clusters the average value of strain in the crystal as a whole is not affected, since, as Simmons and Baluffi[27] point out, the strength of a cluster of n defects is just n times the strength of an individual defect if no overlap of the nonelastically strained regions of the defects occurs. Whether or not such overlap occurs is essentially the problem of the validity of the linear approximation as discussed in the preceding paragraph. We conclude that the enhancement of the expansion coefficient is independent of the fine scale distribution of the point defects within the elastic approximation. This is in agreement with the experimental observation that the initial rise in the $\Delta V/V$ vs T curve remains linear and reversible up to 190°C, even though large irreversible changes occur in the optical absorption properties of the crystal at considerably lower temperatures. We need only postulate that the total number of electrons and holes trapped at vacancies remains constant up to 190°C, the observed growth of complex absorption bands at the expense of the F band representing simply a rearrangement of vacancies and trapped electrons and holes, without any change in the total number of either.

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Dynamical Model

Although the calculation above is in many ways informative, and gives good agreement with experiment, a continuum approach can provide only limited physical understanding of the increase in expansion coefficient. A better insight may be obtained using a simplified discrete (Einstein) model. For a perfect crystal of volume V, consisting of N atoms vibrating at a single frequency ν, and having lattice energy per atom $E(V)$, the free energy is given by[30]

$$F=N[E(V)+3kT\ln(h\nu/kT)],$$

if $h\nu<kT$. Minimizing F at constant pressure, and defining, in the low-temperature limit, an average linear expansion coefficient $\bar{\alpha}$ by $V-V_0=3V_0\bar{\alpha}T$, where V_0 refers to volume at 0°K, one obtains

$$\bar{\alpha}=-\frac{k}{V_0}\left(\frac{d^2E}{dV^2}\right)_{V_0}^{-1}\frac{d\ln\nu}{dV}.$$

If the crystal is not perfect, but contains $n\ll N$ Schottky defects, with a formation energy $W_s(V,T)$, which alter the vibrational frequencies of their x neighbors from ν to ν' in the direction joining the neighbor and the vacancy and do not otherwise affect the frequencies, then a similar calculation of $\bar{\alpha}$ can be made[8] taking into account the fact that at 0°K the equilibrium volume is no longer V_0. The result is

$$\bar{\alpha}'=-\left[3(V_0-\Omega)\left(\frac{d^2E}{dV^2}\right)_{V_0}\right]^{-1}\left[\frac{n}{N}\frac{d}{dT}\left(\frac{\partial W_s}{\partial V}\right)+3k\frac{d\ln\nu}{dV}+\frac{nx}{N}k\frac{d\ln\nu'}{dV}\right],$$

where the volume derivative of W_s is taken at constant temperature and the temperature derivative is to be evaluated at $T=0$.

In deriving this expression the substitution,

$$\left[\left(\frac{\partial W_s}{\partial V}\right)_T-\left(\frac{\partial W_s}{\partial V}\right)_{T=0}\right]\frac{1}{T}\rightarrow\frac{d}{dT}\left[\left(\frac{\partial W_s}{\partial V}\right)_T\right]_{T=0},$$

valid in the low-temperature limit, is used.

Before proceeding further we estimate the quantity Ω given by

$$\Omega=\frac{n}{N}\left(\frac{\partial W_s}{\partial V}\right)_0V_0\left[V_0\left(\frac{d^2E}{dV^2}\right)_{V_0}\right]^{-1}=\frac{n}{N}\left(\frac{\partial W_s}{\partial V}\right)_0V_0\chi,$$

where χ_0 is the isothermal compressibility at 0°K of a crystal without defects. For NaCl χ_0, according to Slater,[31] is $\chi_0=3.3\times10^{-12}$ cm/dyne. No experimental value is available for $(\partial W_s/\partial V)_0$; however, Mott and Gurney[32] estimate $|(d\ln W_s)/(d\ln V)|\approx2$, on the assumption that W_s is independent of T. This gives

$$|V_0(dW_s/dV)_0|\approx2W_s\approx4\text{ ev}=6.4\times10^{-12}\text{ dyne-cm},$$

using Etzel and Maurer's value[33] for W_s in NaCl. A negative sign for dW_s/dV follows from LeChatelier's principle and it is intuitive that compression will increase W_s. Thus $\Omega\approx-(n/N)(2W_s\chi_0)=-(n/N)(2.1\times10^{-25}\text{ cm}^3)\approx2\times10^{-29}$ cm^3 which is to be compared with $V_0=4.5\times10^{-23}$ cm^3, the volume per ion pair. It follows that $V_0\gg\Omega$ and

$$\frac{\bar{\alpha}'-\bar{\alpha}}{\bar{\alpha}}=\frac{\Delta\bar{\alpha}}{\bar{\alpha}}=-\left(3k\frac{d\ln\nu}{dV}\right)^{-1}\left[\frac{n}{N}\frac{d}{dT}\left(\frac{\partial W_s}{\partial V}\right)+\frac{6n}{N}k\frac{d\ln\nu'}{dV}\right]$$
$$=+\frac{n}{N}\left[\frac{1}{3k}\frac{V}{\gamma}\frac{d}{dT}\left(\frac{\partial W_s}{\partial V}\right)_T+2\frac{d\ln\nu'}{d\ln\nu}\right],\qquad(4)$$

where $\gamma\equiv(d\ln\nu)/(d\ln V)$ is the Grüneisen constant, equal to 1.6 for NaCl. Grüneisen's constant is usually associated with a Debye model; however, its use here is as justifiable as the use of the Einstein model itself. The temperature dependence of γ is very weak; Sheard's calculations[34] for NaCl give $\gamma=1.2$ in the low-temperature limit and $\gamma=1.6$ in the high-temperature limit which is reached at room temperature.

The quantity contained in the square brackets is equal to (N/n) $(\Delta\alpha/\alpha)$ which, according to our experiments, is about 14. On the other hand, as shown in Appendix II, the quantity $2(d\ln\nu')/(d\ln\nu)$ is of the order of unity or smaller. It follows that (a) the change of the thermal expansion coefficient produced by the presence of Schottky defects can be associated with the mixed derivative

$$\frac{d}{dT}\left[\left(\frac{\partial W_s}{\partial V}\right)_T\right]=\left[\frac{\partial}{\partial V}\left(\frac{\partial W_s}{\partial T}\right)\right]_T,$$

and that (b) the shifts in lattice vibration frequencies arising from the presence of defects are not important in affecting the thermal expansion coefficient directly.

The mixed derivative, according to our experimental results, should be about -2×10^8 dynes/cm^2-degree. As yet there is no independent measurement of the quantity available for comparison. Its physical significance is clearly the simultaneous temperature and volume dependence of the non-Coulombic, i.e., repulsive forces associated with the formation of a Schottky defect. High-temperature and high-pressure measurements of ionic conductivity in pure and doped NaCl could in principle lead to a determination of this quantity.

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It is interesting to inquire into the physical consequences of a nonzero value of dW_s/dT. At constant pressure $W_s(T) = W_{s0} + (dW_s/dT)_0 T + \cdots$. Since

$$\exp(-W_s/kT) = \exp\left[-\frac{1}{k}\left(\frac{dW_s}{dT}\right)_0\right]\exp(-W_{s0}/kT),$$

the effect of dW_s/dT is to increase or decrease the pre-exponential factor, according to whether dW_s/dT is negative or positive. The change in this factor may be considerable. If we take the simplest possible approach and suppose W_s to be independent of temperature except through volume, i.e.,

$$(\partial W_s/\partial T)_V = 0, \quad dW_s/dT = (dW_s/dV)(dV/dT) = 3\alpha V dW_s/dV,$$

and use, as before, Mott and Gurney's estimate,

$$-VdW_s/dV \approx 2W_s \approx 4 \text{ ev},$$

we get, using the room temperature value of α, $-(1/k)$ $(\times dW_s/dT) = -5.6$ which gives

$$\exp\left(-\frac{1}{k}\frac{dW_s}{dT}\right) \approx e^{5.6} = 2.7\times 10^2.$$

If a high temperature value of α (7×10^{-5}) is used instead one obtains

$$\exp\left(-\frac{1}{k}\frac{dW_s}{dT}\right) \approx e^{9.75} = 1.7\times 10^4.$$

The effect is apparently large enough to see if it could be separated from other complications. Present knowledge, both experimental and theoretical, of pre-exponential factors is too inexact to determine even the sign of dW_s/dT from conductivity measurements.

All the calculations above leading to Eq. (4) were made in the "low-temperature limit." It can be shown that the pertinent approximations are either also valid at room temperature or that there is no evidence against them. In particular, the experimental approximate independence of $\Delta\alpha/\alpha$ on temperature as indicated by Eq. (4) is experimentally confirmed.

SUMMARY

When point defects are introduced into sodium chloride by irradiation, an increase in the linear thermal expansion coefficient measured between room temperature and 200°C is observed. The fractional increase in the expansion coefficient is approximately 14 times the defect concentration. An increase of approximately this magnitude is predicted by a rough thermodynamical calculation using an elastic continuum model. This calculation also indicates that the change in α should be insensitive to clustering and rearrangement of lattice defects, in agreement with experiment. A rough dynamical calculation based on an Einstein model indicates that the dominant term in the enhanced thermal expansion involves the mixed derivative $(d/dT)(\partial W_s/\partial V)_T$, where W_s is the activation energy for formation of Schottky defects. This quantity can be estimated from our data and is approximately -2×10^8 dynes/cm^2-degree. Shifts in lattice vibration frequencies arising from the presence of the defect are apparently not important in changing the thermal expansion coefficient directly. The increase in expansion coefficient resulting from irradiation has been observed to anneal roughly simultaneously with volume expansion.

ACKNOWLEDGMENTS

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APPENDIX I

Temperature Dependence of the Elastic and Photoelastic Constants

The constant k relating $\Delta V/V$ (the relative volume expansion) and θ/d (the observed optical rotation) is given by the formula[5]

$$k = \frac{2\lambda}{180}\left[\frac{3c_{11}}{(c_{11}+2c_{12})}\right]\frac{1}{r},$$

with

$$r = \tfrac{1}{2}n^3(p_{11}-p_{12}),$$

where λ is the wavelength of the polarized light, c_{11} and c_{12} are elastic constants, and p_{11} and p_{12} are photoelastic constants. It is of course, a function of temperature. For NaCl the temperature dependence of the elastic[20,35–37] and photoelastic[38] constants has been measured in the temperature range of interest. All the measurements of elastic constants as functions of temperature are in substantial accord; we use the data of Hunter and Siegel.[26] Combining the various independent measurements of the temperature gives for the temperature dependence of k the heavy curve in Fig. 10. The points shown are at the temperatures of the photoelastic observations; the actual elastic data have been graphically interpolated to obtain values for these temperatures. All the experimental data were reduced using the value of $k(T)$ obtained in this way.

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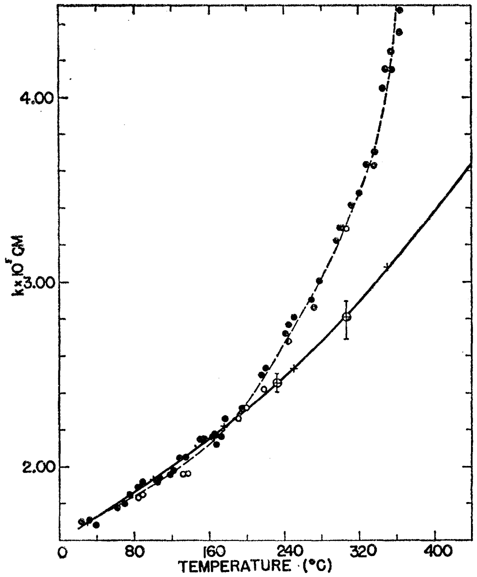

FIG. 10. Temperature dependence of the constant k relating volume expansion and optical rotation. +—deduced from photoelastic data of reference 38 and elastic data of reference 26; ●—crystal No. 79, rising temperature; ○—crystal No. 79, falling temperature; ⊕—crystal No. 81.

This procedure for obtaining $k(T)$ is open to criticism on several grounds. For one thing, the elastic data, obtained by the usual acoustic techniques, are characteristic of the behavior of sodium chloride at very small strains, of the order of 10^{-6}. The photoelastic data, on the other hand, relate to strains two orders of magnitude larger, of the order 10^{-4}, which is roughly the magnitude of the strains in our experiment. Furthermore, the measured quantities in the photoelastic work are the stress-optical coefficients, whereas the quantities appearing in the $k(T)$ are strain-optical coefficients. These were obtained from the corresponding stress-optical coefficients by the use of Hooke's law with the ordinary (low strain) elastic constants. There is no reason to think that the elastic behavior of NaCl at strains of 10^{-4} is characterized by constants measured at strains of 10^{-6}. For that matter it is not even clear that sodium chloride is elastic at strains of 10^{-4}.[39]

There is some possibility of stress relaxation by plastic strain, i.e., slip, in the photoelastic measurements of Bhagavantam and Murty.[38] The stress used by these authors was 19 kg/cm^2. The stress required to initiate slip in NaCl is usually quoted between 7 and 10 kg/cm^2.[40–42] On the other hand, if the birefringence is studied as a function of applied stress it is found that the stress birefringence relation is linear up to 20–25 kg/cm^2, at room temperature.[43,44] Data on the temperature dependence of the yield point are contradictory,[41,42] and the sensitivity of the mechanical properties of NaCl to environmental conditions is well known.[10] Bhagavantam and Murty would probably have detected appreciable amounts of slip, since their photoelastic observations were made visually, and visual photoelastic observation detects slip readily.[40,45] Also, they made their measurements at 5890 A, whereas we used 5770 A, but this is not a source of error, since the dispersion of the photoelastic constants is small in this spectral region.[43,46]

The dashed curve of Fig. 10 represents an independent measurement of $k(T)$, which was accomplished using a sample which had a temperature independent $\Delta V/V$. The temperature dependence of $k(T)$ was then measured simply by observing θ/d as the temperature of the sample was varied. Since $\Delta V/V=1.3k(\theta/d)$, and $\Delta V/V$ is temperature independent, we have

$$k(T)=k(T_0)\theta(T_0)/\theta(T),$$

where T_0 refers to room temperature. The value $k(T_0)$ is obtained from published data. This point is fairly reliable since a number[43,44,47,48] of mutually consistent measurements of the photoelastic properties of NaCl have been made at room temperature.

The sample used (No. 79) was a crystal which had been irradiated in the usual manner and annealed by slowly raising the temperature to over 400°C. After this anneal, a small residual *negative* $\Delta V/V$ remained in the sample. This negative $\Delta V/V$, which was stable at temperatures below 400°C, was observed in more than one crystal.[8] (The origin of the effect is not clear, but it may be connected with impurity precipitation.) The temperature independence of $\Delta V/V$ below 400°C was checked with several experiments, and may be seen in the dashed curve of Fig. 10, where the points obtained while the temperature was rising are consistent with those taken while the temperature was falling.

The two curves for $k(T)$ shown in Fig. 10 agree within experimental error from room temperature to 200°C and diverge at higher temperatures. The agreement up to 200°C lends support to the interpretation of the linear initial rise in $\Delta V/V$ as evidence for enhancement of the thermal expansion coefficient by irradiation. The disagreement at higher temperatures is probably due to systematic errors in measurement of the dashed curve as discussed elsewhere.[8] The coincidence of the dashed and solid curves below 200°C gives confidence in the use of the data from the literature, even in the region above 200°C, since it indicates that the measure-

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ments of Hunter and Siegel and of Bhagavantam and Murty, are applicable to the conditions of this experiment.

The validity of the heavy curve above 200°C, the one obtained from the literature values of the elastic and photoelastic constants separately, is also confirmed by two additional independent measurements made with crystal No. 81. This crystal was cycled in temperatures, and during portions of the cycling no annealing of $\Delta V/V$ took place. It is thus possible to deduce[8] the value of $k(T)$ at the two temperatures indicated on Fig. 10.

An additional rough, but independent, check of the temperature dependence of k is provided by the background strain annealing observations. In this case we expect no complications arising from change in expansion coefficient. Consequently a plot of background strain as a function of temperature should be horizontal until annealing begins, after the data has been corrected for the temperature dependence of both the elastic and photoelastic constants. This is observed, within experimental error (Fig. 1).

APPENDIX II

Effect upon Thermal Expansion Coefficient of the Shift in Lattice Frequencies of Ions Near a Vacancy

In evaluating the term

$$2\frac{d\ln\nu'}{d\ln\nu}=2\frac{d\ln\nu'}{D\ln V}\,\frac{d\ln V}{d\ln\nu},$$

which occurs in Eq. 4 as a contribution to the calculated value of $\Delta\alpha/\alpha$, it is tempting to apply the Grüneisen principle directly to our case and write

$$\frac{d\ln\nu}{d\ln V}=\frac{d\ln\nu'}{d\ln V}=-\gamma.$$

This is, however, not justifiable because Grüneisen's theory yields the thermal expansion coefficient itself, whereas we are after a higher order effect, the change in α. In our model, moreover, ν' is drastically different from ν (it was created to take into account a quantitatively different force field), and we would not expect it to vary with volume in the same manner as ν, even though the various frequencies of the perfect crystal, which we have represented by the single frequency ν, do have the volume dependence postulated by Grüneisen.

One can estimate the dependence of ν' on volume, using the expression,

$$V=A\lambda/r^n-\mu e^2/r,$$

for the interionic potential. If the volume is slightly reduced, for example by isothermal compression, then the change in ν' will be less than the change in ν. This follows from the fact that the force between two ions separated by a vacancy, being essentially a Coulomb repulsion, will increase only as the inverse square of their separation as the lattice is compressed slightly, whereas the repulsive force between two ions not near a vacancy increases with a very large inverse power of their separation under the same conditions. A higher restoring force means, of course, a higher frequency.

To put this more quantitatively we suppose the lattice volume to have been reduced by isobaric cooling. If the temperature is lowered by 1°C, the fractional change in linear dimension is α, the thermal expansion coefficient. We compute the change in ν' arising from this change in linear dimension: $(\nu')^2\propto F'\propto 1/(2r_0)^2$, or $\nu'\propto\sqrt{F'}\propto 1/2r_0$ where $r_0=2.82\times10^{-8}$ cm. This gives $\Delta\nu'\propto\Delta\sqrt{F'}\propto -2\Delta r/(2r_0)^2$ or $\Delta(\nu')/\nu'=-2\Delta r/2r_0=-\alpha$. On the other hand, the change in ν (using $n=9.4$ for the exponent in the repulsive term of the potential[8,49]) is given by $\nu^2\propto F\propto 1/(r_0)^{-10.4}$ or $\nu\propto\sqrt{F}\propto 1/(r_0)^{5.2}$. This gives $\Delta\nu\propto\Delta\sqrt{F}\propto[5.2/(r_0)^{6.2}]\Delta(r_0)$ or $\Delta\nu/\nu=-5.2\Delta(r_0)/r_0=-5.2\alpha$. Thus

$$\frac{d\ln\nu'}{d\ln\nu}=\frac{d\nu'/\nu'}{d\nu/\nu}=\frac{1}{5.2}.$$

The second term in Eq. (4) then is

$$T_2=d\ln\nu'/d\ln\nu=2(1/5.2)\approx0.4,$$

and we conclude that it is (at most) of order unity.

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[49] C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., Chap. 3.