

Density Change of Sodium Chloride Produced by Proton Irradiation and Its Thermal Annealing*

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The density change of sodium chloride crystals upon irradiation with 350 Mev protons with a total flux of 1×10^{16} protons/cm² has been measured and found to be -8.3×10^{-4} g/cm³. The number of negative-ion vacancies calculated from this density change is of the same order as the number of *F* centers estimated from the stored-energy measurements. The recovery of the density change with thermal annealing has also been studied. A relation between the behavior of the density change and of color centers is discussed.

INTRODUCTION

THE electrical conductivity,¹⁻³ stored energy release,³ and absorption spectrum³ of sodium chloride crystals irradiated with high-energy protons have been studied, particularly as a function of progressive annealing. The purpose of this paper is to describe the change of density of sodium chloride crystals caused by irradiation with 350-Mev protons, its recovery process at successively higher temperatures, and the relation between the density changes and other properties.

EXPERIMENTAL

The methods of treatment of the crystals and the irradiations at room temperature were the same as those previously reported.³ The measurements of the density change were made by observing the difference of flotation temperatures⁴ between irradiated and non-irradiated crystals in 1,2-dibromo-ethane. This liquid was purified three times and was transferred into the measuring cell by vacuum distillation. Particular care was taken in heating the crystals for the purpose of thermal annealing. Since the density measurement is very sensitive to the surface condition of the crystal, a transfer of crystals from the measuring cell to a separate annealing system had to be avoided. In order to do so, after each measurement the liquid was removed from the measuring cell to a storage cell and the crystals were dried completely by a vacuum distillation. The crystals were then heated in vacuum in the measuring cell at a rate of 2°C/min which is the same rate as was used in previous work.³ After they reached the desired temperature, the crystals were cooled rapidly to room temperature, the suspension liquid was transferred back into the measuring cell, and the measurement was repeated.

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¹ E. A. Pearlstein, *Phys. Rev.* **92**, 881 (1953); see also "Proceedings of the effect of radiation on dielectric materials," Office of Naval Research Report ACR-2, 31, (1954).

² R. Smoluchowski, *Report of Bristol Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 252.

³ K. Kobayashi, *Phys. Rev.* **102**, 348 (1956).

⁴ For example: Estermann, Leivo, and Stern, *Phys. Rev.* **75**, 627 (1949); M. Hacskeylo and G. Groetzinger, *Phys. Rev.* **87**, 789 (1952).

RESULTS AND DISCUSSION

Figure 1 shows the density changes of crystals irradiated by a total flux of 8.1×10^{15} protons/cm² and of 7.1×10^{15} protons/cm², as a function of annealing temperature; the changes of concentrations of several color centers for the same conditions of heating are also given. The latter were taken from a previous report.³ It can be seen that, while up to about 200°C the density change remains constant, there are large changes in the type and the concentration of color centers. In this region, with the continuous decreases of the *F* and *V₃* bands, the *M* and *N* (840 mμ) centers increase at first and then decrease, being accompanied by the growth of *R'* centers⁵⁻⁸ which are probably large aggregates of vacancies such as early stages of colloid centers. These results show that when the simpler color centers disappear, some probably by changing to more complicated ones, the density change remains unaltered and, therefore, no appreciable annealing of vacancies takes place.

At the instant when the *R'* centers start to dissociate at about 200°C, the density change drops drastically, and reaches about half of its initial magnitude at around 240°C, where all color centers have practically disappeared. This suggests that the mechanism of the disappearance of vacancies can be described in terms of the disappearance of highly-aggregated color centers, particularly *R'* centers. Above this temperature, where no color centers are observed, the presence of further density change indicates the existence of stable vacancy clusters. In this range, the density change decreases almost linearly with temperature, ending at 400° with a complete recovery of the crystal. This complete recovery temperature is in good agreement with those obtained by other methods.³

The density changes, $\Delta\rho$, are measured to be -6.5×10^{-4} g/cm³ and $-6.0_2 \times 10^{-4}$ g/cm³ just after irradiations with 8.1×10^{15} and 7.1×10^{15} protons/cm², respectively. This gives about -8.3×10^{-4} g/cm³ for an irradiation of 1.0×10^{16} protons/cm². The possible error

⁵ A. B. Scott and W. A. Smith, *Phys. Rev.* **83**, 982 (1951).

⁶ A. B. Scott and L. P. Bupp, *Phys. Rev.* **79**, 341 (1950).

⁷ G. W. Neilson and A. B. Scott, *Report of Bristol Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 297.

⁸ F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

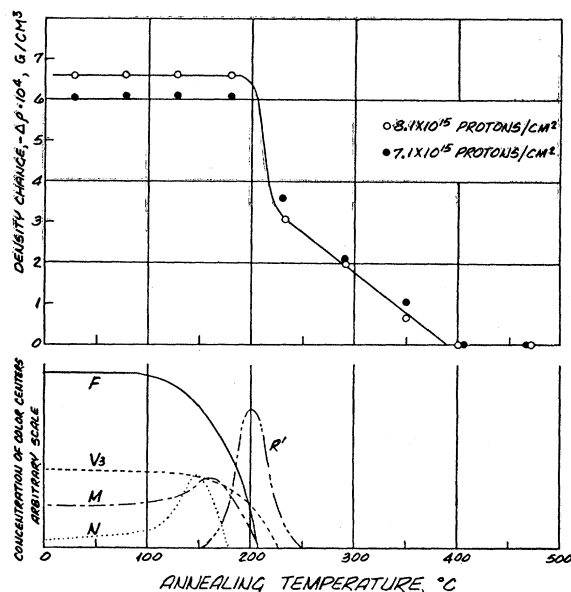


FIG. 1. Density changes of NaCl crystals irradiated with 350-Mev protons, with a total flux of 8.1×10^{15} protons/cm² (open circles) and of 7.1×10^{15} protons/cm² (solid circles), as a function of thermal annealing temperatures. The curves in the lower graph are changes in the concentrations of color centers (arbitrary scale) which are taken from Fig. 6 of the previous report.³

in the density change is $\pm 1\%$ and in the proton flux $\pm 10\%$. If we assume that the number of negative-ion vacancies is about 2.3 times the number of positive ones, as has been suggested in the previous paper,³ the number of negative-ion vacancies can be estimated from the density change as $(1.1 \pm 0.1) \times 10^{19}$ /cm³ for an irradiation of 1.0×10^{16} protons/cm². This number, however, would be reduced to $(8.6 \pm 0.9) \times 10^{18}$ /cm³ for the same amount of irradiation had we assumed that the number of negative-ion vacancies is the same as the number of positive ones.

In principle, the number of negative-ion vacancies can be compared to the concentration of *F* centers. Unfortunately, here the concentration of *F* centers was too high to measure the optical density of the crystal. The number of *F* centers, however, can be estimated very roughly from stored-energy data. As indicated in a previous paper, a peak in the stored-energy curve³ between 150 and 250°C is believed to be associated with a disappearance of color centers. The integrated heat under this peak would correspond to the energy difference between a crystal at 150°C and at 250°C, and this quantity may be expressed as a function of the number of *F* centers as follows: The energy released thermally when an electron is removed from an *F* center and combines with a hole at a neutral chlorine atom is about 4–5 ev.³ Thus, if *n* is the number of *F* centers, about $4n$ – $5n$ ev will be released by this electronic process when all *F* centers are bleached out. The maximum additional effect due to electron recombination with holes at the *V*₃ centers, other than the

neutral chlorine atoms, would probably be within 30% of this. There is also the energy associated with the annealing out of vacancies. The fact that about half of the density change recovers at the temperature which corresponds to the end of the peak in the stored-energy release indicates that about half of the vacancies, presumably most of which had originally been associated with color centers, disappear at this temperature. Since the energy of formation of a pair of isolated vacancies of opposite sign is 2 ev,⁸ an energy of about $2(n/2)$ ev will appear in this process, if one assumes that the number of negative-ion vacancies which disappear is the same as the number of positive ones. It has been suggested, however, that the number of negative-ion vacancies may be much greater than the number of positive ones after irradiation, and therefore, it would be possible that some of the negative-ion vacancies disappear without the simultaneous disappearance of positive-ion vacancies. The energy released when a negative-ion vacancy alone disappears would be equal to the energy required to remove a negative ion from the interior of the crystal and place it on the surface. This energy would be much less than the energy that is necessary to remove a negative ion from the interior of the crystal to the outside, which is 5.2 ev.⁹ Therefore, the possible error in the above estimate, which is based on the assumption that the number of negative-ion vacancies which disappear is the same as the number of positive ones which disappear, is less than $(5.2 - 2)n/2$ ev or less than 25% of the total energy release. The remaining half of the vacancies will presumably form clusters at this temperature, and this process will contribute to the total released energy an amount $0.9(n/2)$ ev, if one assumes that the energy of clustering is about 0.9 ev⁸ per pair. Then the total energy released between 150°C and 250°C may be expressed as about $6n$ ev with a possible error of 30%. Thus, with this expression, the number of *F* centers, *n*, can be estimated from the measured stored energy in this range, and it is found to be $(1.2 \pm 0.4) \times 10^{19}$ per cm³ of the crystal irradiated with 1.0×10^{16} protons/cm². This is in good agreement with the number of negative-ion vacancies estimated from the density change mentioned above. It can be concluded, therefore, that most of the vacancies produced by proton irradiation are in the form of color centers.

As mentioned above, at about 250°C, approximately half of the vacancies still remain in the crystal in the form of clusters which disappear at 400°C. One can estimate roughly how much energy would be evolved in this temperature range owing to the disappearance of these clusters. Since the energy of formation of a pair of isolated vacancies of opposite sign is 2 ev, and the energy of formation of a neutral pair from isolated ones is 0.9 ev as indicated above, it can be assumed that an

⁹ N. F. Mott and M. J. Littleton, Trans. Faraday Soc. 34, 485 (1938).

energy of the order of 1 ev or a little less per vacancy pair would likely be released when a vacancy cluster disappears into the perfect lattice. As the number of vacancy pairs remaining at 250°C in one cc of crystal irradiated with 1.0×10^{16} protons/cm² is about 5×10^{18} , one can estimate that about 0.2 cal or a little less would be evolved from this crystal in the temperature range, 250–400°C. The corresponding observed value from the stored-energy measurements³ is about 0.6 cal. The agreement is rather poor and this discrepancy may

possibly be due to energy release associated with the elimination of strains from a crystal.

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F^{19} Nuclear Magnetic Resonance Line Shapes in CaF_2 †

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The F^{19} magnetic resonances have been measured in CaF_2 with the magnetic field along the [100], [110], and [111] crystal directions and these data are compared with the data of Pake and Purcell. Calculations of the second and fourth moments for the new data further confirm the theory of Van Vleck on magnetic dipole interactions in solids since improved agreement with theory is obtained in the case of the magnetic field along the [111] crystal direction. Corrections of the moments for modulation broadening were small.

THE measurements by Pake and Purcell¹ of the F^{19} magnetic resonance line shapes confirmed the theory proposed by Van Vleck² on magnetic dipole interactions in solids. Their data were taken in the very early days of nuclear magnetic resonance before the effect of modulation on line shapes³ was known and, though the second moments of the resonances with the magnetic field aligned along the [100] and [110] crystal directions were in excellent agreement with theory, the result for the [111] direction was in doubtful agreement. Therefore, the experiment has been repeated using the same fluorite crystal that was used by the early investigators but employing a spectrometer of later design and correcting for modulation broadening.

A conventional single-coil spectrometer with phase-sensitive detection was used. The magnetic field was that of a permanent magnet with an inhomogeneity of 0.01 gauss over the one-milliliter sample volume. The field was modulated at 30 cps. A crystal-controlled oscillator operating at 25.81 megacycles provided the radio-frequency field. The nuclear paramagnetic absorption signal was isolated by means of a bridge network.⁴ The radio-frequency signal was preamplified by a cascode amplifier⁵ and then amplified and demodu-

lated by a National HRO-7 receiver. The derivative of the absorption curve obtained from the phase-sensitive detector⁶ was displayed on a Leeds-Northrup recorder. The recorder chart drive was used to sweep the magnetic field through resonance thereby assuring a constant relationship between the magnetic field and chart abscissa. This relationship was determined by amplitude modulating the oscillator at a known audio-frequency and measuring the spacing between resonances arising from several of the side-band frequencies.

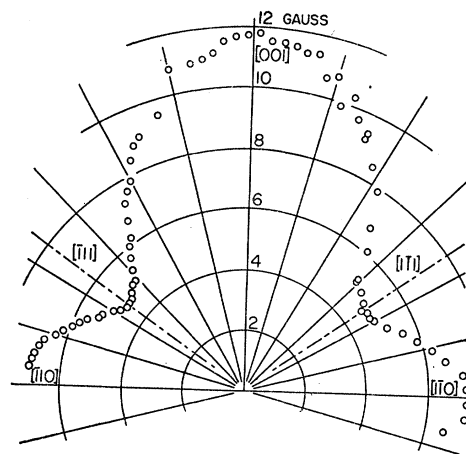


FIG. 1. F^{19} resonance width measured between points of maximum slope as a function of the magnetic field direction in a single CaF_2 crystal.

⁶ N. A. Schuster, *Rev. Sci. Instr.* **22**, 254 (1951).

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¹ G. E. Pake and E. M. Purcell, *Phys. Rev.* **74**, 1184 (1948).

² J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

³ E. R. Andrew, *Phys. Rev.* **91**, 425 (1953).

⁴ H. L. Anderson, *Phys. Rev.* **76**, 1460 (1949).

⁵ Wallman, Macnee, and Gadsden, *Proc. Inst. Radio Engrs.* **36**, 700 (1948).