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Effect of X-Irradiation on Surface Structure of Sodium Chloride Crystals

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Electron diffraction studies of x-irradiated sodium chloride crystals have shown that after sufficient irradiation the surfaces of these crystals break up into small crystallites which exhibit preferred orientations. The time required to produce surface damage is much greater for water-polished crystals than for untreated ones.

INTRODUCTION

INVESTIGATIONS of the mechanical properties of irradiated alkali halide crystals have shown that marked changes in hardness,[1] internal friction,[2] and creep[3] occur. The changes in properties can be attributed to the presence of *F*-centers and to the changes in vacancy concentration and distribution which accompany *F*-center formation.

Although it has been shown[4,5] that prolonged x-irradiation results in changes in density, little more has been done to learn whether gross alterations in structure of irradiated crystals also occur. The soft x-rays which are most effective in producing *F*-centers are absorbed in passing through the crystal, and the resultant *F*-center concentration drops off very rapidly with distance.[4] Since electron diffraction provides a means for the investigation of the structure of thin surface layers, it seemed an appropriate method for this study.

Sodium chloride crystals which had been irradiated for periods as long as 262 hours were examined. From the viewpoint of studies on radiation damage, x-irradiation offers some distinct advantages over such methods as pile irradiation and high-energy particle beams in that possible complications from extraneous interstitial atoms and mechanical damage by energetic particles are eliminated. Also, problems associated with the dissipation of large amounts of heat in specimens during irradiation are avoided.

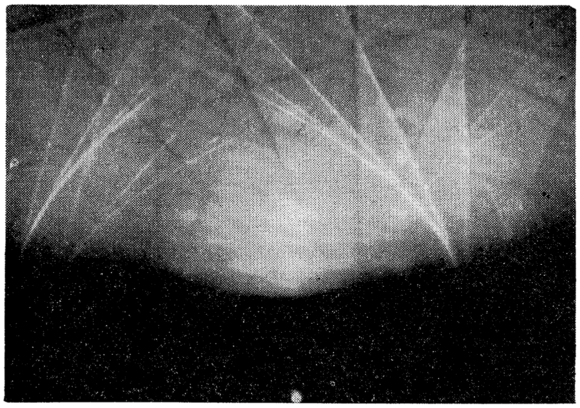

FIG. 1. NaCl cleavage face. Crystal annealed at 600°C and water-polished. Beam in (110) direction.

EXPERIMENTAL

Sodium chloride specimens were cleaved to approximately 2×4×6 mm from larger single crystals which were obtained from the Harshaw Chemical Company. Some crystals were irradiated as cleaved, while others were first either water-polished, or annealed and water-polished. Annealing was done at 600°C for a minimum of 24 hours and was followed by furnace-cooling over a period of six hours. Water-polishing involved dissolution of the surface layer in a stream of water. The water treatment was immediately followed by a rinse in ethanol and then by one in acetone. This procedure has been previously shown to yield a surface free of imperfections and salt crystallites visible in a microscope.[6] The fact that diffraction patterns made prior to irradiation of crystals which had been water-polished, or annealed and water-polished, were characterized by well-defined Kikuchi lines indicated that such treatment produced undamaged surfaces. Likewise, well-defined Kikuchi lines were taken as the criterion for good surfaces when directly cleaved faces were studied.

The irradiations were made with a Machlette *AEG*-50 tube having a tungsten target and a beryllium window.

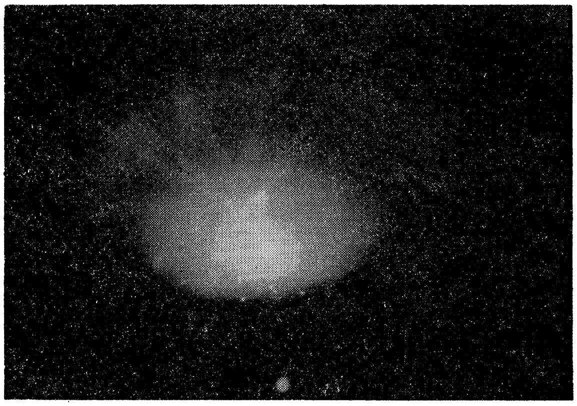

FIG. 2. NaCl cleavage face. Crystal annealed at 600°C and water polished. Irradiated for 140 hours. Beam in (110) direction.

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[1] D. Westervelt, Atomic Energy Research Department, North American Aviation, Inc., Report NAA-*SR*-888, May 1, 1954 (unpublished).

[2] D. R. Frankl and T. A. Read, Phys. Rev. **89**, 663 (1953).

[3] R. A. Lad and F. I. Metz, J. Mech. and Phys. Solids (to be published).

[4] Estermann, Leivo, and Stern, Phys. Rev. **75**, 627–33 (1949).

[5] K. Sakaguchi and I. Suita, Technol. Repts. Osaka Univ. **2**, 177 (1952).

[6] R. A. Lad, J. Appl. Phys. **23**, 800 (1952).

The tube was operated at 50 kv and 30 ma. The radiation intensity at the position of the crystal was found to be about 72 000 r/hr. The crystals were irradiated on one face and were kept in a light-tight aluminum foil receptacle during irradiation. They were removed only at intervals to obtain the diffraction patterns. The described experimental steps were performed with as little delay as possible. The observed radiation effects were not complicated by possible moisture adsorption and subsequent recrystallization. Crystals stored under the same conditions but without irradiation were unchanged.

The diffraction apparatus was a General Electric Model *G*-1 instrument with a modified pumping system which produced a working vacuum below 10^{-4} mm. Grazing incidence technique was used in obtaining diffraction patterns.

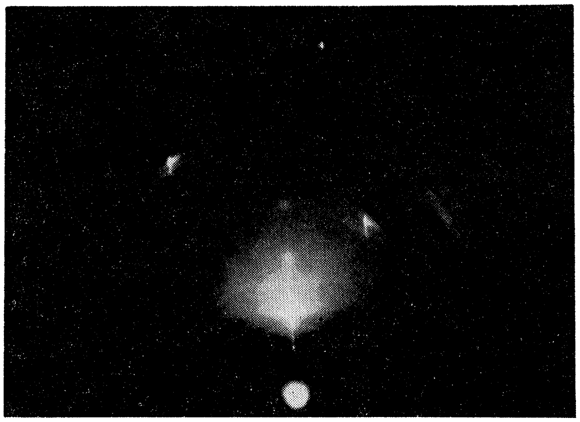

Fig. 3. NaCl cleavage face. Crystal annealed at 600°C and water-polished. Irradiated for 262 hours and then reannealed at 600°C. Beam in (110) direction.

RESULTS

Crystal specimens which had been water-polished, or annealed and water-polished, yielded diffraction patterns which were indicative of a high degree of lattice perfection (Fig. 1). The well-defined Kikuchi lines arising from extensive ordered areas were always obtained. After prolonged irradiation, the sharp patterns of Kikuchi lines became less distinct and after irradiation times of about 120 hours, patterns consisting of extensive arrays of spots and arcs appeared (Fig. 2 is typical). These arcs and spots were taken to be an indication of the presence of small oriented crystallites on the surface. Preliminary studies indicate that certain orientations are preferred. However, this aspect of the problem has not been completely investigated as yet.

The effect of heating the irradiated crystals to 600°C was to alter the arced patterns to ones consisting of fairly uniform diffraction rings (Fig. 3). This behavior indicates that the heating treatment results in a random distribution of the crystallites on the surface.

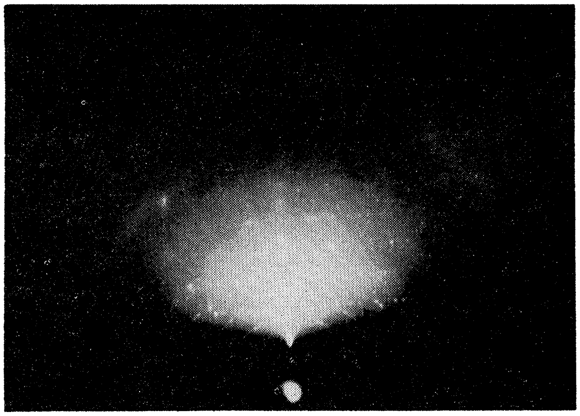

Fig. 4. NaCl cleavage face after 117 hours of irradiation. Beam in (110) direction.

The sharpness of rings and arcs on the diffraction patterns is generally similar to that obtained from powders in the size range of several hundred angstroms or more.

Unirradiated cleaved crystals yielded diffraction patterns of well-defined Kikuchi lines; no evidence of lattice distortion was observable. However, they showed arced and spotted patterns after only one hour of irradiation. On continued irradiation extensive arrays of spots in a layer-line pattern and sharp rings appeared (Fig. 4). Heat treatment at 600°C gave the same results as those obtained from water-polished crystals, namely sharp, continuous rings (Fig. 5).

DISCUSSION

The surface layers of a cleaved crystal are undoubtedly far from equilibrium. The cleaving process itself introduces strain. In addition, the new surface layers may not have adjusted to the new equilibrium surface spacings. These spacings have been computed to be of the order of 6% less than those for the interior in both the directions parallel and normal to the surface.[7] Possible mechanisms by which the adjustment can be made involve crack formation and ion diffusion from the bulk to the surface. Recent work at this labo-

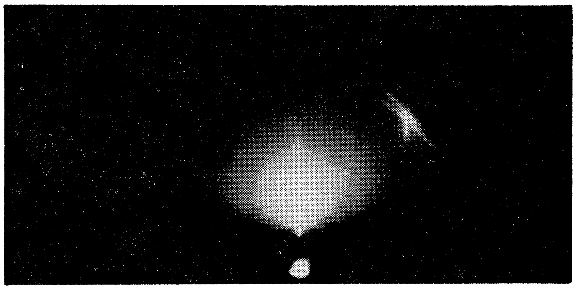

Fig. 5. NaCl cleavage face. Crystal irradiated for 117 hours and then annealed at 600°C. Beam in (110) direction.

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[7] J. E. Lennard-Jones and B. M. Dent, Proc. Roy. Soc. (London) **121**, 247 (1928).

ratory[3,8] has given evidence that cracking is effective in relieving surface strain and that it is a rate process. The rate is quite low at room temperature and is accelerated by radiation and mechanical working. The experiments described in the present paper show that cleaved faces require less irradiation to produce significant damage than those which have been water-polished. This fact may be interpreted to mean that the energy density introduced by cleavage is higher in a relatively thin layer at the surface.

The tendency of the crystallites to assume preferred orientations is interesting in light of other work. Linear surface defects formed by irradiation and heat treatment of sodium chloride also occurred in preferred directions.[3]

The present study indicates that the predominant orientations have the (100) direction of the crystallites parallel to the cube edge of the substrate and parallel to the diagonal of the substrate. A more extensive analysis of the diffraction patterns is needed to confirm this relationship.

ACKNOWLEDGMENTS

The author wishes to thank Florence I. Metz for her cooperation in performing the irradiations. He also thanks Dr. Robert A. Lad and Dr. Frances D. Coffin for many helpful discussions.

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[8] H. R. Leider and L. A. Girifalco (to be published).

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Electron Spin Paramagnetism of Lithium and Sodium[*]

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The paramagnetic susceptibility χ_p^e of conduction electron spins is isolated experimentally from the total magnetic susceptibility in metallic lithium and sodium by studying the intensity of the conduction-electron spin resonances. The absolute intensity of absorption is calibrated by comparison with the nuclear resonance of the metal nuclei in the same sample and at the same frequency, the two resonances being observed merely by changing the static magnetic field. In this manner χ_p^e is measured in terms of the nuclear static susceptibility, χ_p^n, which in turn can be calculated accurately from the Langevin-Debye formula. A narrow band modulation technique gives improved signal to noise over our earlier work. The values of χ_p^e are $(2.08\pm0.1)\times10^{-6}$ cgs volume units for lithium at 300°K and $(0.95\pm0.1)\times10^{-6}$ cgs volume units for sodium at 79°K, in rather good agreement with the theory of Pines and Bohm, but in substantial disagreement with the simple Pauli model, or the results of Sampson and Seitz. Experimental precision does not permit conclusions to be drawn about the diamagnetism of conduction electrons.

I. INTRODUCTION

THE static magnetic susceptibility of a metal, χ_0. is in general composed of two terms, χ_p and χ_d, χ_p is the paramagnetic contribution arising from polarization of the conduction electron spin moments. χ_d is the diamagnetic contribution arising from the orbital motion of the conduction electrons and of the core electrons of the metal atoms. In practice χ_p and χ_d are comparable in magnitude. Conventional methods of susceptibility measurement (e.g., via Gouy balance) determine the total magnetic susceptibility, χ_0, which is the sum of the various contributions to χ_p and χ_d, whereas theories of metallic susceptibilities give the various terms separately. Thus a comparison between theory and experiment is unsatisfactory even when numerical agreement is found between theoretical and experimental values of χ_0.

Recently the interest in susceptibilities of metals has been revived by the major new advances of Bohm and Pines[1] in the theory of electrons in metals. Largely as a result of their work, we have been stimulated to isolate experimentally for the first time the spin contribution χ_p to the total magnetic susceptibility χ_0.[2] One might wonder how it is possible to isolate the spin paramagnetic contribution to χ_0, if this cannot be done by conventional techniques. We will work out mathematical details below, but in brief, the technique involves the study of the conduction-electron spin resonance. Since the conduction-electron spin resonance arises solely from the spin magnetization, the presence or lack of spin magnetization determines the strength of the resonance, enabling us to measure χ_p. As will be shown below, the integrated area under the conduction-electron absorption curve is proportional to χ_p with well-known constants of proportionality. Thus an absolute intensity measurement will determine χ_p. Such measurements are always difficult, although for

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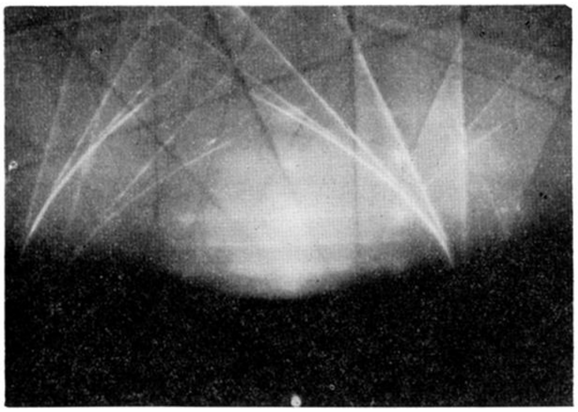
[1] D. Bohm and D. Pines, Phys. Rev. **82**, 625 (1951); D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953); D. Pines and D. Bohm, Phys. Rev. **85**, 338 (1952); D. Pines, Phys. Rev. **92**, 626 (1953); D. Pines, Phys. Rev. **95**, 1090 (1954).

[2] Schumacher, Carver, and Slichter, Phys. Rev. **95**, 1089 (1954).



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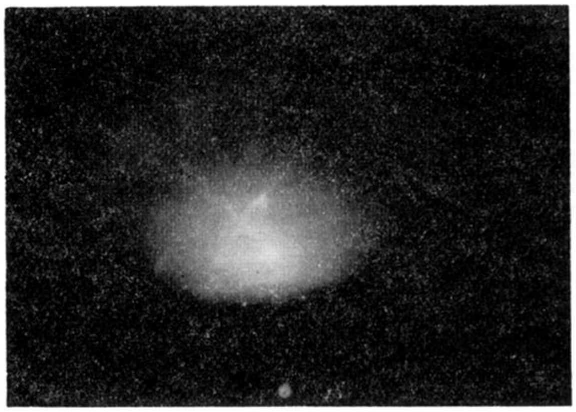
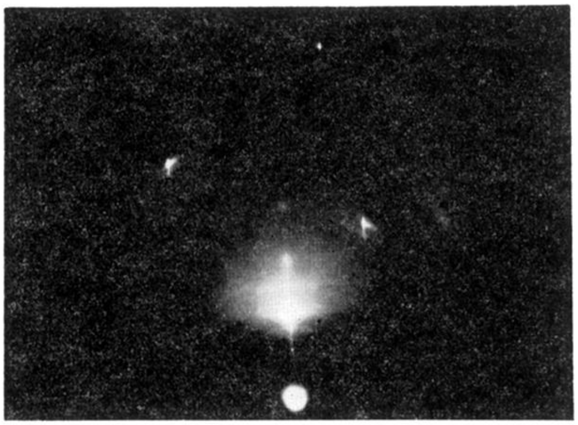


FIG. 2. NaCl cleavage face. Crystal annealed at 600°C and water polished. Irradiated for 140 hours. Beam in (110) direction.



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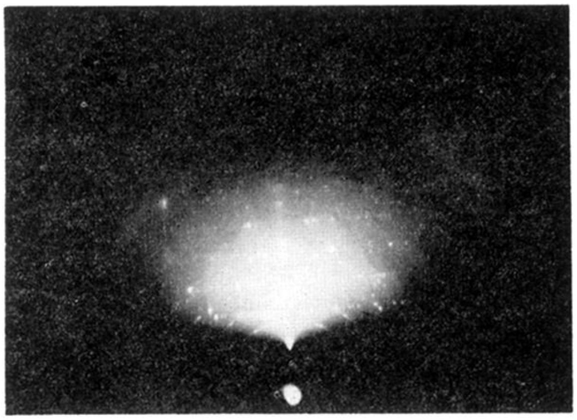

FIG. 4. NaCl cleavage face after 117 hours of irradiation. Beam in (110) direction.

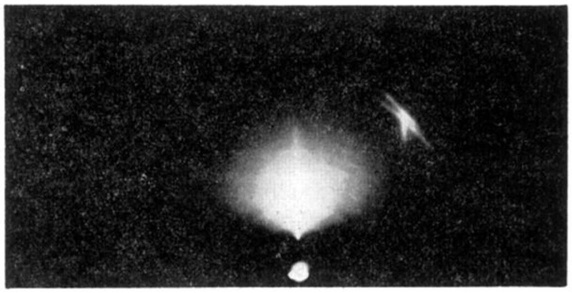

FIG. 5. NaCl cleavage face. Crystal irradiated for 117 hours and then annealed at 600°C. Beam in (110) direction.