Mechanism for Coloration of Alkali Halides at Low Temperatures

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A mechanism for low-temperature coloration of alkali halides is proposed in which double ionization of a halide ion or single ionization of two adjacent halide ions leads to the formation of an uncharged halogen molecule which occupies two adjacent halide ion sites. If the molecule is localized at one of these sites by the jump of a nearby halide ion into the other site, a vacancy and interstitial are formed. Capture of an electron by each of these imperfections leads to the production of the F center and H center.

A PROBLEM of considerable interest in the study of color centers in alkali halides is the origin of defects responsible for the various centers. At temperatures above room temperature a wide variety of conductivity and diffusion measurements[1] appear to indicate that the primary lattice defect is the Schottky defect: a cation-anion vacancy pair. Calculations also argue that the energy of formation of the Schottky defect is less than that for a Frenkel defect.[2] The Frenkel defect considered in this case is an interstitial positive ion and a positive-ion vacancy. Because of the large size of the negative ions, a Frenkel defect in the negative-ion sublattice would require even more energy and would be thermodynamically less stable.

When color centers are formed at room temperature and below by the action of x rays, it is likely that the system will not achieve thermodynamic equilibrium. Under these conditions it is possible that Frenkel as well as Schottky defects can occur. Considering the high density of color centers that can be formed in an alkali halide by x raying at room temperature and assuming that Schottky defects are responsible, Seitz[3] proposed a mechanism in which vacancies diffused into the crystal under the action of x rays. Later it was found that large densities of color centers could also be formed in crystals x rayed at liquid helium temperatures.[4] In this case diffusion over long distances appeared impossible. Again assuming that Schottky defects are primarily responsible, Seitz proposed that pairs of positive- and negative-ion vacancies could be produced at dislocations during x-ray irradiation.[5] Some implications of this model were considered further by Markham[6] and by Dexter.[7]

A very different model for the formation of color centers has been proposed by Varley.[8] He suggested that if a halide ion were doubly ionized it would become a *positive* ion in a region of high electrostatic repulsion. Because of its small size this positive ion could easily be ejected into an interstitial position thus forming a Frenkel defect in the negative-ion sublattice.

It appears from recent work at liquid helium temperatures that the basic effect of x rays is to create an interstitial halogen atom leaving a vacancy in the lattice. This Frenkel defect model arises in part from the atomic nature of the two prominent color centers formed at 4°K: the F center and the H center. The F center has long been regarded as an electron at a halide ion vacancy. Recently Känzig and Woodruff[9] have proposed a detailed model of the H center which, in its simplest terms, consists of an interstitial halogen atom. These centers complement each other in the sense that if they recombine, the perfect lattice is reformed. This model of the H center is derived from paramagnetic resonance spectra[9] and is supported by optical measurements on the symmetry of the H center.[10] Other evidence arises from the work of Rabin and Klick[11] who find that the coloration rate is independent of the initial concentration of negative-ion vacancies in the crystal, the concentration of chemical impurities, and the degree of strain of the crystal. They conclude that Frenkel defects are formed in the perfect lattice and show that the coloration rates among the different alkali halides vary as the atomic dimensions of the ions in a way consistent with a Frenkel defect mechanism. A number of other recent experiments have been interpreted on the basis of Frenkel defects.[12,13]

While Varley's model can be used to explain the production of Frenkel defects, serious objections have been raised to it by Seitz and Koehler[14] and more

[1] For a recent review of this work see A. B. Lidiard, *Handbuch Der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20.

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[7] D. L. Dexter, Phys. Rev. **93**, 985 (1954).

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[13] D. A. Wiegand and R. Smoluchowski, Phys. Rev. **116**, 1069 (1959).

[14] F. Seitz and J. S. Koehler, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 447.

recently by Dexter.[15] Dexter argues that in a time very short compared with that of lattice vibrations, the doubly ionized halide ion will capture an electron from a neighbor. He considers the resulting center from the point of view of band theory as two nearby holes which repel each other and rapidly move apart, and he concludes that the Varley mechanism is not likely to be the correct explanation.

It is also unlikely that the halide ion is directly displaced by momentum transfer from an energetic electron, since efficient coloration of KBr is found for x rays from a 50 000 volt machine. Under these conditions the maximum transfer of energy to the Br is about $\frac{1}{3}$ of an ev which would appear to be orders of magnitude too low for a direct displacement.

The model described here is an attempt to describe in some detail a way in which Frenkel defects might be formed and which is free of some of the objections raised by Dexter to the Varley mechanism. The various stages of this mechanism are illustrated schematically in the drawings of Fig. 1. Figure 1(a) shows the perfect lattice. In Fig. 1(b) the central halide ion has lost two electrons by an encounter with an x-ray photon or a high-speed electron. Varley has estimated that about 10% of the ionization may be of this double kind. As proposed by Dexter, Fig. 1(c) shows that the doubly ionized halide ion has captured an electron from a neighboring halide ion so that two neutral halogen atoms are formed. In this process a large amount of energy is supplied to the center. The configuration of Fig. 1(c) can also be reached by having each of two neighboring ions separately ionized and the subsequent steps may follow equally well in this case. Dexter next proposes that electrons from outer halide ions are transferred to these atoms; this is equivalent to saying that two holes are repelled outward. In the model proposed here it is suggested that another effect may occur with high probability. The two halogen atoms may quickly alter their electronic configurations to that of a somewhat separated halogen molecule bound together by exchange forces. This would lead, in Fig. 1(d), to the moving together of the atoms to form a more normal halogen molecule. The molecule is small and is neutral so that its energy is nearly independent of its position within the two neighboring vacancies. In the case drawn here, which is roughly that for KCl, the molecule could fit nicely into one vacancy alone. The center would be in a state of high vibration for a short period of time due to the transfer of an electron as illustrated in Fig. 1(c). Under these conditions it may frequently be possible for a neighboring halide ion to jump into one of the vacancies. One possible resulting configuration is shown in Fig. 1(e). This step is the one in which an interstitial is formed; it is believed that the mechanism illustrated here for producing interstitials
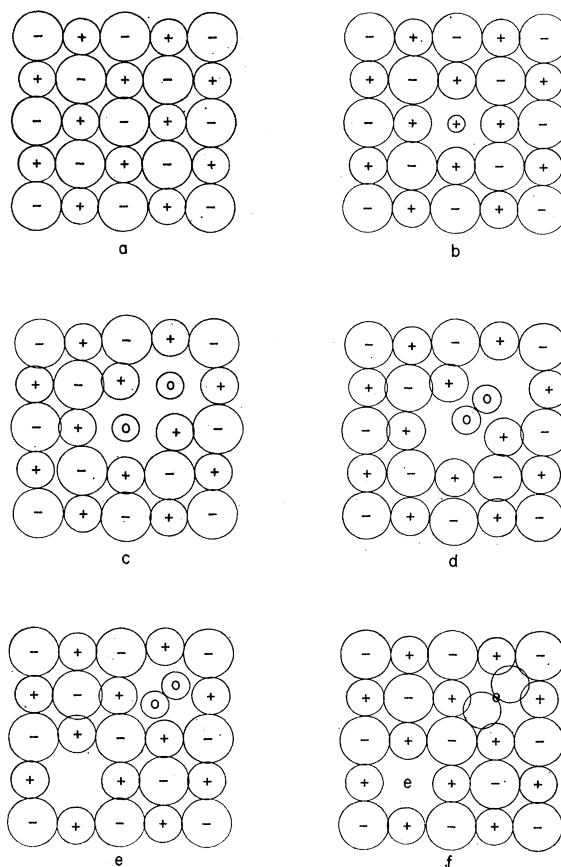

FIG. 1. Schematic illustration of a proposed model for production of color centers by x rays at low temperatures. (a) The perfect lattice; (b) after double ionization of a halide ion; (c) after transfer of an electron to the doubly ionized halide ion; (d) formation of a neutral halogen molecule; (e) formation of a vacancy and interstitial halogen by the jump of a halide ion; (f) capture of an electron by the vacancy to form an F center and capture of an electron by the halogen molecule to form the H center.

requires little energy compared with that necessary to displace a halogen atom directly to a region sufficiently distant from the vacancy so that back diffusion is unlikely. Finally, in Fig. 1(f), the capture of one of the free electrons by the vacancy gives rise to the F center; the capture of the other electron at the halogen molecule gives rise to the H center.

It has been pointed out by Maurer[16] that the substitutional molecule in Fig. 1(e) corresponds to the model proposed by Känzig and Woodruff for the V_1 center.[9] If, therefore, some of the free electrons are trapped at F centers to form F' centers or are trapped elsewhere than at the molecule, V_1 centers as well as H centers may be formed. While it is not certain that V_1 centers are formed on x raying at low temperatures, it has been suggested that the slight shift of the H band on bleaching may be due to the presence of the V_1 band nearby.[10]

One feature of the present mechanism is that some

[15] D. L. Dexter, Phys. Rev. 118, 934 (1960).

[16] R. J. Maurer (private communication).

of the F and H centers could be close to each other. As a result one might look for effects of one center on the other. Two experiments have been attempted both of which failed to find such an interaction. In one case irradiation in the H-absorption band failed to produce F-center luminescent emission which should have occurred if the H center transferred energy to the F center.[17] In the other experiment no effect was found on the polarization of the F center if the H centers were turned so that most of them were oriented in one direction rather than being randomly distributed.[10] The details of the spin-resonance spectrum also argue against

a close proximity of the F and H centers.[18] It thus seems likely that the centers move apart even at these low temperatures. One mechanism may be the propagation of the H center along the row of halide ions in the $\langle 110 \rangle$ directions. The details of such a motion have, however, not been investigated.

ACKNOWLEDGMENT

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Nuclear Quadrupole Resonance in Superconducting Gallium*

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The nuclear quadrupole resonance (NQR) of Ga^{69} is investigated between 0.8 and 4.2°K. (The superconducting critical temperature is 1.084°K.) Progressive saturation of the resonance is produced at increasing rf power levels of a frequency-modulated marginal oscillator. The nuclear spin-lattice relaxation rate $1/T_1$ (sec^{-1}) is approximately $\frac{1}{2}T$ (°K) in the normal state. The contact part of the hyperfine interaction appears to be predominant in producing relaxation. Although the saturation method does not permit a precise determination of the constant of proportionality, the comparison of normal and superconducting relaxation rates is considerably more reliable. The rf fields are assumed to obey the London law of penetration, and an average rf field is determined in the superconductor. The relaxation rate shows a maximum enhancement by a factor 1.8 at approximately 0.95 T_c, a result which agrees with that obtained by Slichter and Hebel, and Redfield for the nuclear magnetic resonance of aluminum, and which serves as an additional experimental justification for certain features of the Bardeen-Cooper-Schrieffer theory of superconductivity. Unsaturated signal intensities in normal and superconducting states furnish a basis for estimating the penetration depth in superconducting metal spheres: $\lambda(0) = 1200$ A for an average particle diameter of 2.7 μ. The NQR frequency of Ga in the superconductor shifts by $(+)5 \times 10^{-5}$ of the normal frequency [the corresponding result for indium is found to be approximately $(-)10^{-2}$]. This means that the contribution of the conduction electrons to the average nuclear quadrupole coupling is modified by the rearrangement of the conduction band in the superconductor. It is demonstrated that, if the quadrupole term in the hyperfine interaction were to predominate, the spin relaxation rate in the superconductor would have a temperature dependence like that of the ultrasonic attenuation.

I. INTRODUCTION

IN searching for nuclear quadrupole resonance (NQR) in metals one anticipated the possibility of observing the resonance in a superconducting metal. Since NQR is performed in zero magnetic field (except for a small rf field), the requirements on the particle size are much easier to satisfy than they are for an experiment on the nuclear magnetic resonance (NMR) in superconductors.[1–3] Following the discovery of the NQR in gallium,[4]

the present work became possible. In succeeding sections we shall discuss the nuclear spin relaxation rate and the penetration depth in superconducting gallium. A separate report will be made on these effects in indium,[5] including a more complete discussion of the observed NQR frequency shift in both superconductors.

The relaxation mechanism in metals is based on interactions between nuclear spins and conduction electrons near the Fermi surface. Since, in any theory of superconductivity, rearrangements take place in the conduction band, it is to be expected that the relaxation rate will change when the metal becomes superconducting. It was in fact found experimentally that the rate increases to a maximum at approximately ninety-

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