identical with those used to measure the relative changes in the Seebeck coefficient $(\Delta Q)/Q_0$. A chopper technique was used to eliminate the effect of the temperature gradient on the resistivity measurements. The relation between $(\Delta Q)/Q_0$ and $(\Delta \rho)/\rho_0$ gives directly a simple function of the parameters K and L. A second relation involving K, Q_{\parallel} , and Q_{\perp} is obtained from the zero-strain value of the Seebeck coefficient.

We have used the K values given by Goldberg² to calculate Q_{\parallel} and Q_{\perp} . Subtracting the electronic part of these as estimated from low-field Hall data, we have found the ratio of the components of the phonon-drag Seebeck tensor for a single valley, $Q_{p,\parallel}/Q_{p,\perp}$, to have the value 9.6 ± 0.3 at 82° K and 9.5 ± 0.5 at 95.5° K. These agree very well with the values obtained by Herring <u>et al.</u>³ from an analysis of thermomagnetic effects. They found a value of 9.6 which was independent of temperature in the range 60° K to 100° K.

¹C. Herring and E. Vogt, Phys. Rev. <u>101</u>, 944 (1956). ²C. Goldberg, Phys. Rev. <u>109</u>, 331 (1958).

³Herring, Geballe, and Kunzler, Phys. Rev. <u>111</u>, 36 (1958); see also Geballe, Herring, and Kunzler, J. Phys. Chem. Solids <u>8</u>, 347 (1959), and Herring, Geballe, and Kunzler, Bell System Tech. J. (to be published).

COLOR CENTER FORMATION IN SODIUM CHLORIDE

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Recent experimental work in this laboratory on the F-center production in synthetic sodium chloride at room temperature by ionizing radiation has revealed growth curves for synthetic crystals which differ from those obtained for halite. From Fig. 1 it can be seen that the nat-



FIG. 1. Growth of the number of F centers produced in NaCl by x-ray radiation as a function of the energy absorbed.

ural crystal from Baden, Germany has a simple growth curve whereas in the synthetic crystals the growth curve is somewhat complicated. In recent publications^{1, 2} the influence of hydroxyl ions inadvertently introduced into synthetic alkali halide crystals by growth in air, has been noted. It is evident from the figure that as the amount of hydroxyl ion (which is related to the absorption coefficient at 1850 A) is reduced, the growth curves for the synthetic crystals approach that of the natural crystal. If the natural crystal contains any impurities, they are not apparent in the growth curve data.

The color center formation in synthetic crystals has been compared to that in natural crystals using 40-kvp x-rays, 2-Mev electrons, and 1.2-Mev γ rays. The flux from these sources has been calibrated and the energy absorbed by the thin crystals (d=0.22 mm) calculated. The number of F centers created per unit absorbed energy agrees within 30% for the 40-kvp x-rays and the 2-Mev electrons where the flux was comparable (6×10¹⁹ ev/cm²-hr). In the Co⁶⁰ γ -ray exposure, the rate of energy absorption was a factor of 100 less, and the coloration for a given energy absorbed was a factor of 3 lower than that for the other radiations. Despite the low rate of F-center production under γ rays, the shape of the growth curves for the different radiations is the same and the energy initially required to form an F center agrees with that found using xrays and high-energy electrons.

In Fig. 1 the growth curves under x-rays are shown for the various specimens. Up to about 10^{20} ev/cm³ energy absorbed, the rate of coloration varies by as much as a factor of 30 between crystals. It will be noted that the faster-coloring synthetic crystals attain the same color-center concentration and production rate as the natural crystals after prolonged irradiation. This indicates that the entity responsible for the enhanced initial coloration rate in the synthetic crystals is no longer effective for F-center production after prolonged irradiation. This entity is not removed from the crystal, however, because a still higher initial coloration rate is produced if the color centers are optically bleached and the crystal is irradiated again with x-rays. If the entities responsible for the initial enhancement are vacancies, it may be possible that vacancy pairs or higher order complexes are formed under prolonged irradiation which are ineffective for trapping electrons. However, no abnormal growth of the M band or the presence of other higher order bands is observed which can account for the loss of these F centers in synthetic crystals.

In order to facilitate the extrapolation of the data of Fig. 1 to the origin to determine the energy required to form an F center, the data of Fig. 1 are replotted as follows. The abscissa E, the energy absorbed/cm³, is divided by n, the number of F centers/cm³, and this ratio is plotted as the ordinate in Fig. 2. The abscissa is the same in both plots. With the exception of the data for the natural crystal, the curves obtained in Fig. 2 are straight lines over a sufficient en-



FIG. 2. The x-ray energy absorbed per number of F centers formed in NaCl crystals as a function of energy absorbed.

ergy range to be represented by the equation E/n = mE + b, where n is the color-center concentration, m is the slope, b is the intercept on the E/n axis, and E is the energy absorbed. The data then indicate that the energy required to form an F center in Harshaw Company NaCl is 96 ev, in NRL NaCl batch C is 85 ev, in NRL NaCl batch J is 73 ev, and in NaCl:Ca is 70 ev. It should be noted that in this plot, the natural crystal data do not give a straight line over any part of the dose range illustrated. By using thick crystals and γ -ray exposures of $(2-5) \times 10^{15}$ ev/cm², it has been determined that the energy required to form an F center in the natural crystal is about 85 ev.

Despite the wide variation in the rate of colorcenter production in the various crystals, the energy to form an F center is about the same for all crystals studied although there is some slight variation. This energy is a measure of the efficiency with which an electron in a given crystal is freed from within the lattice and trapped at a negative-ion vacancy to form an F center. The fact that the F-center coloration varies considerably in the mid-range of energy absorbed indicates the presence of a readily available source of vacancies which is dependent upon the crystal history. It is known² that air-grown synthetic NaCl has an absorption at 1850 A associated with an hydroxyl ion concentration to which the coloration is proportional. In NaCl doped with calcium, it is known that the irradiation-produced F-center coloration is proportional to the calcium concentration.³ Preliminary coloration experiments with x-rays on calcium-doped NaCl indicate that the growth curve is well represented by $n = (m + b/E)^{-1}$ to color-center concentrations in excess of 2×10^{18} F centers/cm³. The fact that the data shown in Fig. 1 are, in the initial rapidcoloring stage, represented by $n = (m + b/E)^{-1}$ in both hydroxyl-bearing and calcium-bearing crystals suggests that a common entity is introduced into these crystals by the impurities. Arguments have been presented for the presence of positiveion vacancies as being responsible for the enhanced coloration observed in calcium-doped alkali halides.⁴ The excess positive-ion vacancies are thought either to aid in the diffusion of negative-ion vacancies from dislocations or to act as traps for holes, reducing the electron-hole recombination. If it is to be assumed that there is an excess positive-ion-vacancy concentration in the hydroxyl-bearing crystals, it would require that the hydroxyl ion substitute for two chlorine

ions in the lattice. Whether this occurs or not could perhaps be verified by measuring the ionic conductivity of a group of crystals having different hydroxyl concentrations.

Finally, it is of interest to note that not only is the energy required to form an F center about the same for these diverse crystals, but for prolonged irradiations the various crystals appear to have the same color-center concentration and rate of production. It would seem then, that the only region in which it would be safe to use the data of synthetic crystals which contain inadvertent impurities for kinetic studies of F-center formation is in the high-dose range where the effects of these impurities are no longer present.

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ELECTRON FREE PRECESSION IN PARAMAGNETIC FREE RADICALS*

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Free magnetic induction signals from the unpaired electron in the organic free radicals, $\alpha - \alpha$ diphenyl- β -picryl hydrazyl, α - γ bisdiphenylene- β -phenylallyl, and picryl-*n*-amino carbazyl, have been observed. Transverse relaxation times, T_2 , in the range 30-100 millimicroseconds were measured directly using pulsed resonance techniques originated by Hahn.¹ Measurements were made on polycrystalline samples at 300°K with an extremely fast time-resolution pulsed spectrometer operating at microwave X-band frequencies (9.3 kMc/sec). Recently, Gordon and Bowers² have used pulse methods at 23 kMc/sec to measure T_2 's in the range 100-1000 microseconds for paramagnetic resonances in impuritydoped silicon.

A detailed description of the spectrometer used for these measurements will be published later. It utilizes a ferrite circulator and a magnetron which generates 150-watt, 50-millimicrosecond pulses at 9.3 kMc/sec. A terminated TE_{102} transmission cavity ($Q \sim 30$) containing the spin sample in a dc magnetic field is placed in the antenna arm of the circulator. The pulse power and duration produces approximately a 45° pulse in this cavity. One-half of the free precession signal originating in this cavity following a pulse appears in the receiver arm of the circulator and is detected in a broadband superheterodyne system. The output is displayed directly on the plates of a Tektronix 517A oscilloscope. Figures 1(A), (B), and (C) are oscilloscope photographs of free precession decays following application of a single microwave pulse in the hydrazyl, phenylallyl, and carbazyl radicals, respectively. Samples used contained approximately 10^{20} spins. The first two spikes preceding the spin signal are reflections from leading and trailing edges of the transmitter pulse. The signal minimum occurring shortly following the pulse has been shown by Nelson³ to arise from dispersion in the angle of rotation of the spin ensemble



FIG. 1. Free precession signal decay following single pulse in (A) hydrazyl, (B) phenylallyl, and (C) carbazyl. The time scale is 50 millimicroseconds/scale division.

¹J. Rolfe, Phys. Rev. Lett. 1, 56 (1958).