Spin-Lattice Relaxation of F Centers in KCl: Isolated F Centers*

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Spin relaxation of F centers in KCl has been observed by a field-sweep-inversion recovery technique between 2.1°K and 150°K in external magnetic fields from 1 Oe to 10 000 Oe. The intrinsic spin relaxation time is best fitted by:

$$1/T_1 = AH^2T + B(T/\theta)^7 J_6(\theta/T),$$

where $A = 5.1 \times 10^{-12}$ sec^{-1} Oe^{-2}(°K)$^{-1}$, $B = 7.8 \times 10^4$ sec^{-1}, $\theta = 210$°K, and $J_6(\theta/T)$ is a tabulated "transport" integral. These results are interpreted in terms of spin-lattice relaxation of isolated F centers by means of phonon modulation of the electron-nuclear hyperfine interaction.

INTRODUCTION

IF paramagnetic centers are placed in a magnetic field, there will be a distribution of the centers among the various spin states. If the centers interact among themselves, this distribution will be a Boltzmann distribution defining a spin temperature[1,2]; if the centers are coupled more closely to the lattice in which they are embedded than to any other heat sink, this spin temperature will be the lattice temperature. Many different processes have been identified[3-11] by which such a system of non-interacting or weakly interacting spins can relax or come into equilibrium with the lattice. In some cases[4] this occurs by means of an interaction between the spin moments of the individual centers and the thermal vibrations of the lattice. In other cases, equilibrium is accomplished by cooperative processes[7] involving pairs or larger groups of the centers or by spin coupling to other paramagnetic defects rather than to lattice waves directly. If the interactions of the isolated spins with the lattice are very weak, the cooperative processes are likely to dominate.

The F center in the alkali halides is a very attractive candidate for spin-relaxation measurements. Its structure is rather well understood[12] in comparison to other paramagnetic centers; its resonance spectra[12] and ex-

cited states[13] have been extensively investigated. Its approximate wave functions have been determined.[12,14] The alkali-halide lattices are simple enough so that they have been studied experimentally and theoretically[15] in some detail and have been found to exhibit thermal properties which are well fitted by a Debye model.[16]

Spin relaxation of F centers in alkali halides has been investigated both theoretically and experimentally by several authors[17-23] in the last few years. Inasmuch as earlier measurements on our part[20] indicated relaxation times in KCl at low temperatures that were considerably longer than those reported previously, it may be reasonably assumed that the shorter values were due to cooperative effects. Short relaxation times depending upon sample properties such as purity, F-center concentration, and light exposure, have also been observed by us and are discussed more fully in a subsequent paper.[24]

It is the purpose of this paper to present those results which appear to exhibit the intrinsic spin-lattice relaxation time of the isolated F center and which are detailed enough to allow an identification of the dominant interaction between the F-center magnetic moment and the lattice. Magnetic-dipole and crystal-field interactions are considered. Each type of interaction would cause a specific dependence of the spin-lattice relaxation time on temperature and magnetic field as is discussed in

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detail below. The identification of the dominant inter-action is accomplished by a comparison of the experimentally observed temperature and field dependence with that predicted for each of the various models.

THEORY

Because the theory of spin-lattice relaxation of weakly coupled paramagnetic centers has been treated rather extensively,[4,9–11,25,26] it will only be outlined here. Application of the theory will be limited to the case of very low concentrations of F centers in pure KCl.

Electron-Crystal Hamiltonian

For a paramagnetic center, the Hamiltonian of the electron-lattice system may be written in the form

$$\mathcal{3C}=\mathcal{3C}_e+\mathcal{3C}_p+\mathcal{3C}_i, \tag{1}$$

where $\mathcal{3C}_e$ is that part of the Hamiltonian which contains the static interaction of the electron with the external magnetic field and with the lattice, $\mathcal{3C}_p$ is the Hamiltonian of the lattice, and $\mathcal{3C}_i$ contains the interactions between the center and the lattice vibrations.

$\mathcal{3C}_e$ is given[2] approximately by

$$\mathcal{3C}_e=p^2/2m+e\phi(\mathbf{r})+\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})+\lambda\mathbf{L}\cdot\mathbf{S}$$

$$+\sum_k A_k\mathbf{I}_k\cdot\mathbf{S}+\sum_k \frac{B_k}{r_k{}^3}\left[3\frac{(\mathbf{I}_k\cdot\mathbf{r}_k)(\mathbf{S}\cdot\mathbf{r}_k)}{r_k{}^2}-\mathbf{I}_k\cdot\mathbf{S}\right]$$

$$+\sum_l \frac{C_l}{r_l{}^3}\left[3\frac{(\mathbf{S}_l\cdot\mathbf{r}_l)(\mathbf{S}\cdot\mathbf{r}_l)}{r_l{}^2}-(\mathbf{S}_l\cdot\mathbf{S})\right], \tag{2}$$

where $\phi(\mathbf{r})$ is the electrostatic potential produced by the lattice, $\mathbf{H}$ is the external magnetic field, λ is the spin-orbit coupling coefficient for the electron, A_k is the isotropic hyperfine coupling coefficient for the kth nucleus, B_k is the anisotropic hyperfine coupling coefficient for the kth nucleus, the hyperfine interactions are summed over the nearby nuclei, and the last term represents the dipolar interaction of the electron with the other (identical) centers. The observed electron spin-resonance absorption spectra correspond to transitions among the lowest lying eigenstates of $\mathcal{3C}_e$. $\mathcal{3C}_p$ in the usual way[27] leads to a description of the thermally excited lattice in terms of phonons.

$\mathcal{3C}_i$ results from the dependence on the lattice coordinates of terms appearing in $\mathcal{3C}_e$, namely $\phi(\mathbf{r})$, λ, A_k, B_k, and C_l. Changes in the lattice coordinates from their equilibrium values can be expressed as a linear combination of the strains produced at the F center by the phonons. Expanding $\mathcal{3C}_i$ in a power series in ϵ_m, the

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strain produced by a phonon in the mth mode, one can write

$$\mathcal{3C}_i=\sum_m V_m\epsilon_m+\sum_{m,n} V_{mn}\epsilon_m\epsilon_n+\cdots, \tag{3}$$

where

$$V_m=\frac{\partial\mathcal{3C}e}{\partial\epsilon_m} \quad\text{and}\quad V_{mn}=\frac{\partial^2\mathcal{3C}e}{\partial\epsilon_m\partial\epsilon_n}.$$

Because of the time dependence of ϵ_m and therefore of $\mathcal{3C}_i$, transitions can occur among the eigenstates of $\mathcal{3C}_e$ and $\mathcal{3C}_p$. The electron system will then come into thermal equilibrium with the lattice with a characteristic relaxation time T_1. All of the processes for relaxation to be discussed are independent of each other and therefore $1/T_1=\sum_i 1/T_{1i}$ where T_{1i} is the characteristic time for the ith process.

Relaxation Mechanisms

The mechanisms causing spin-lattice relaxation may be considered to be of two classes. The first arises from the modulation of the crystalline electric field, represented in $\mathcal{3C}_i$ by the terms containing derivatives of $\phi(\mathbf{r})$ and λ. This class of mechanisms usually causes the spin relaxation in centers containing transition-metal ions or rare-earth ions. The other class arises from the modulation of the magnetic dipole interaction, represented by the terms containing derivatives of A_k, B_k, and C_l.

Crystal Field Interaction

If the ground states of the center being considered were members of a pure spin multiplet, the crystal field interaction would produce no transitions among them since it does not couple to a spin. However, the presence in $\mathcal{3C}_e$ of the term $\lambda\mathbf{L}\cdot\mathbf{S}$ adds to the pure spin states a small admixture of the excited states in such a way that the ground states have a nonzero orbital moment. The time-dependent crystal field now couples to this orbital moment and causes transitions between the members of the ground-state multiplet.

Magnetic Dipole Interactions

The hyperfine interactions are described by the terms in $\mathcal{3C}_i$ containing derivatives of A_k and B_k; the electron-electron interactions, by the terms containing derivatives of C_l. Of the electron-electron terms, the one containing $\mathbf{S}_l\cdot\mathbf{S}$ leads to mutual flips of a pair of spins, conserves the magnetic energy and the net moment of the spin system, and therefore does not lead to spin-lattice relaxation. In some cases, these mutual spin flips occur much more frequently than transitions involved in spin-lattice relaxation. The other electron-electron terms give rise to spin-lattice relaxation,[3] but their contribution can be made insignificant by a sufficient dilution of the paramagnetic centers.

Some caution must be used in evaluating the hyper-

fine interaction in $\mathcal{K}_i$. The hyperfine terms are of the forms $I_{zk}S^+ + I_{zk}S^-$ and $I_k^+S^- + I_k^-S^+$, both of which cause transitions between states of differing M_s with transition probabilities depending on m_{Ik}. In cases for which the spin-resonance spectrum of the electron center contains resolved hyperfine lines, each resolved line is due to centers with a given $M_I = \sum_k m_{Ik}$ for each set of equivalent neighboring nuclei that have sufficiently large couplings [A_k and B_k in Eq. (2)]. Each of the resolved lines will relax with its characteristic time constant arising from all of the above terms. For each term the appropriate sum over m_{Ik} gives time constants which are almost independent of M_I, and thus almost the same for each line. In cases of unresolved hyperfine structure such as the F center in KCl, there are additional reasons for expecting relaxation to occur uniformly over the whole spectrum.

The relative contribution to the time constant from the several terms can be determined in principle from observations of the recovery of the system from known initial perturbations. For example, for the F center, if the $I_k^+S^- + I_k^-S^+$ term dominates the relaxation, and if all parts of the line are uniformly perturbed from thermal equilibrium, the line would become somewhat skewed during recovery. The $I_{zk}S^+ + I_{zk}S^-$ term would not cause such a skewed line. For F centers the maximum skewness is estimated to be too small to be observable.

Dependence of Relaxation Time on H and T

As is usually done,[4,9] we will distinguish two modes of spin-lattice relaxation. In the direct or resonant process, an electron spin flip is accompanied by the absorption or emission of a resonant phonon. In the indirect or Raman process, a spin flip is accompanied by the inelastic scattering of a phonon.

Direct Process

The direct process occurs when first-order, time-dependent perturbation theory is applied to all of the terms in $\mathcal{K}_i$ which are linear in the strain produced at a spin site by a phonon.

We make the following assumptions: (1) The spin-lattice Hamiltonian is given by $\mathcal{K}_i = \bar{V} \sum_m \epsilon_m$, where $\sum_m \epsilon_m$ is the local strain and $\bar{V}$ is an average value of V_m. (2) The number of phonons in a mode of frequency ν is given by $N = [\exp(h\nu/kT) - 1]^{-1} \approx kT/h\nu$, i.e., the lattice is in equilibrium and $kT \gg h\nu$. (3) The density of phonon modes is given by a Debye spectrum $\rho(\nu) \propto \nu^2$. (4) The local strain at the F-center site due to a phonon is the same as that at a normal lattice site (or at least depends in the same manner on phonon frequency). (5) H, the external field, is large compared to the width of the resonance. (6) The Zeeman splitting is proportional to H. One then finds, after some manipulation,[9] that

$$1/T_{1D} = AH^2T, \tag{4}$$

where the subscript D indicates a direct process, and A is evaluated from the matrix element of the appropriate spin-lattice interaction.

For a one-electron (Kramers) system, in which the crystal field interaction is being considered, one can show from symmetry arguments that A is zero when H is zero. In the presence of a field, however, $A = A'H^2$ because excited states are mixed into the ground multiplet. For this situation, therefore

$$1/T_{1DH} = A'H^4T, \tag{5}$$

where the subscript H indicates a field-assisted process.

Symmetry considerations do not cause such a cancellation in those circumstances for which relaxation is caused by magnetic interactions. In these cases T_{1DM} will vary with H^2T, as in Eq. (4).

Therefore, one can in principle determine from the measured field dependence of the direct process whether a magnetic hyperfine coupling or a crystal field interaction is the dominant relaxation mechanism.

Raman Process

Relaxation by Raman processes results from nonlinear terms in $\mathcal{K}_i$ taken to first order and from the linear terms in $\mathcal{K}_i$ taken to second order in perturbation theory. In either case a double integration over the phonons in the Debye spectrum[4,9,25] must be made. Specializing the resultant expression to the case of magnetic hyperfine interactions, both the linear and nonlinear terms give

$$1/T_{1RM} = B_M(T/\theta_M)^7 J_6(\theta_M/T), \tag{6}$$

where[28] $J_n(Z) = \int_0^z X^n \exp X[\exp(X) - 1]^{-2} dX$, and θ is the Debye temperature.

For $\theta/T > 10$, $J_n(\theta/T)$ is independent of T. Thus for sufficiently low temperatures, Eq. (6) gives $1/T_{1RM} \propto T^7$.

On the other hand, for higher temperatures where $\theta/T < 1$, $1/T_{1RM} \propto T^2$. This is a general property of any two-phonon process at temperatures above the Debye temperature, since all modes then have occupation numbers proportional to T. For an n-phonon process, $1/T_{1R} \propto T^n$ when $\theta/T < 1$.

For a Kramers system and a crystal field interaction, one can show, as for the direct process, that the relevant matrix elements are zero in the absence of a magnetic field. If one introduces an additional mixing of the Kramers states due to the magnetic field, one obtains[9]

$$1/T_{1RH} = B_H H^2 (T/\theta_H)^7 J_6(\theta_H/T). \tag{7}$$

Equation (7) holds whether the magnetic field mixes excited states into the ground state or among themselves.

Phonons can be used instead of a magnetic field to mix the states giving[8]

$$1/T_{1RP} = B_P(T/\theta_P)^9 J_8(\theta_P/T). \tag{8}$$

[28] W. M. Rogers and R. L. Powell, Natl. Bur. Std. (U. S.) Circ. 595 (1958).

Again, a comparison of the field and temperature dependence of the observed relaxation time with that of the above equations allows one to determine which is the dominant relaxation mechanism for the Raman process.

Exponentially Activated Processes

For the sake of completeness it should be noted that there are at least two special cases which could give a temperature dependence of $1/T_1 \propto \exp(-\Delta/kT)$. If the paramagnetic center has an excited state which lies within the lattice phonon spectrum (say at an energy Δ), then, as shown by Orbach,[9,25] the phonons for which $h\nu = \Delta$ will have matrix elements for relaxation which are greatly enhanced over those for other phonons. For $kT \ll \Delta$, this can lead to a relaxation time of the form $\exp(-\Delta/kT)$. Such a process has been identified in rare-earth salts,[29] for donors in silicon,[10] for $V(+4)$ in TiO_2,[30,31] and for $Ti(+3)$ in Al_2O_3[26,32–34]. Since the F center in KCl apparently has no such low-lying excited state,[12] we may presumably ignore this case.

Klemens[27] has suggested that a paramagnetic defect center which has a localized vibrational state above the Debye limit could exhibit an exponential temperature dependence with an activation energy equal to the energy of the local mode. Little is known about possible localized modes of the F center. We shall see that no evidence of an exponential temperature dependence of T_1 is found.

Extrinsic Relaxation Mechanisms

Other relaxation mechanisms exist which are distinguishable from the spin-lattice processes discussed above. They usually involve some intermediate defect or impurity to which the spin energy can be transferred. If these extrinsic mechanisms are effective, they may cause a nonexponential recovery, a distorted line shape during recovery, or a field and temperature dependence other than that predicted for the above models.

Summary

Each spin-lattice interaction leads one to expect a specific dependence of T_1 on temperature and on magnetic field. A calculation of the absolute magnitude of T_1 is difficult and uncertain. However, it should be possible in the absence of extrinsic relaxation to determine the dominant relaxation mechanisms for both the direct
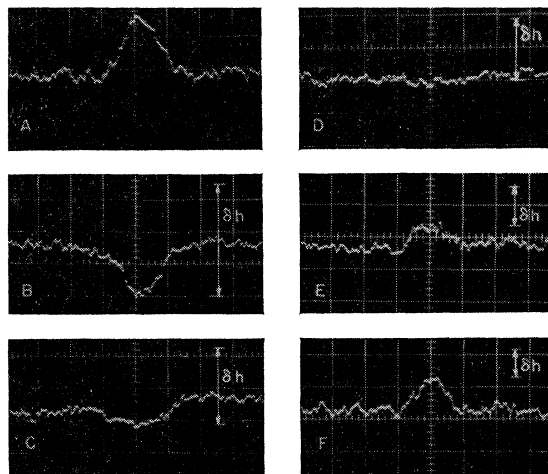
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[30] G. M. Zveryev, Zh. Eksperim. i Teor Fiz. **44**, 1859 (1963) [English transl.: Soviet Phys.—JETP **17**, 1251 (1963)].

[31] H. J. Gerritsen (private communication).

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[33] L. S. Kornienko and A. M. Prokhorov, *Paramagnetic Resonance* (Academic Press Inc., New York, 1963), Vol. I, p. 126.

[34] A. A. Manenkov and A. M. Prokhorov, *Paramagnetic Resonance* (Academic Press Inc., New York, 1963), Vol. II, p. 425.

FIG. 1. Oscilloscope display of F-center absorption signal during recovery. A is the equilibrium signal and B, the signal immediately after inversion. C, D, E, and F photographed with increasing delay after inversion illustrate the gradual recovery of δh to zero. The sample was prepared by gamma irradiation and the measurements were taken at 4.2°K and 3.2 kOe. The F-center concentration was about 4×10^{16} cm^{-3}.

and Raman processes by comparing the dependence on T and H of the observed relaxation time with that of the various models.

The F center has large hyperfine coupling and relatively little spin-orbit coupling as shown by the large linewidth and the very small g shift of the F center resonance. We might therefore expect that relaxation due to the hyperfine interaction would be more effective than relaxation due to the crystalline field. As we shall see, this expectation appears to be confirmed.

EXPERIMENTAL TECHNIQUES

Spin Resonance

Spin relaxation times were measured by the inversion recovery technique, which has been described in detail previously.[35] This method consists of perturbing the spin system from its equilibrium configuration and observing its relaxation back to equilibrium. The perturbation normally used was the inversion of the net magnetization and thus the spin resonance signal by adiabatic rapid passage.[1] The resonance line was then observed periodically after inversion. Both inversion and observation were accomplished by a fast field-sweep technique. The static field from a 12-in. Varian magnet was adjusted to be several linewidths away from the resonant value, and the total field was then swept rapidly through its resonant value by a current pulse applied to a pair of Helmholtz coils mounted on the microwave cavity. The spin resonance was detected with a sensitive superheterodyne detection system and displayed on an

[35] J. G. Castle, Jr., D. W. Feldman, P. G. Klemens, and R. A. Weeks, Phys. Rev. **130**, 577 (1963).

oscilloscope as shown in Fig. 1. The fast field-sweep technique has an advantage over pulse saturation measurements in that the line shape of the resonance is observed during recovery, and shape changes indicative of spin diffusion effects, etc., can be detected.

If the shape of the resonance line remains constant during relaxation, its height h is proportional to the total magnetization at any given time. The logarithm of the deviation δh of this height from its equilibrium value is then plotted against time. If the result is a straight line, the slope defines a unique spin-relaxation-time constant τ. Normally values of δh over at least one decade are required to decide whether the relaxation can be described by a single time constant and to measure its value to within $\pm 10\%$. Because of the very long time constants encountered at low temperatures in these experiments, it was impractical in some cases to make measurements over a complete decade; this limitation resulted in a larger uncertainty in τ.

Sometimes rather than inverting all of the spins, only those in a small section of the line were inverted. The time for this "hole" to "heal" was a measure of spin diffusion in the line, a process discussed in more detail in the subsequent paper.[24]

The microwave spectrometer operated at a fixed frequency of about 9 Gc. Thus the observing field H_0, and usually the field in which the spins relaxed H_R, were fixed near a value of 3200 Oe. In some cases, however, very long relaxation times allowed the adjustment of H_R during relaxation to any desired value. Thus if τ were long compared to the time constant of the electromagnet (about 20 sec), the field could be held at the desired value of H_R, being periodically brought to H_0 for short intervals to monitor the magnetization. When H_R differed from H_0, the observed relaxation times were corrected for the intervals that the spins were at H_0. Whenever this technique was practicable, the samples were also kept in the highest available field (≈ 10kOe) for many minutes before the beginning of a measurement. This enhanced the polarization of the spins and made it possible to obtain usable signals from samples which would otherwise have contained too few F centers.

Sample temperatures at and below 4.2°K were determined from the vapor pressure of the liquid helium in contact with the sample. Temperatures from 8 to 20°K were determined from the vapor pressure of the liquid or solid hydrogen which was used as a bath. Above 20°K the temperature was measured by a copper-constantan thermocouple which was clamped to the sample. Since the cryostat was not designed to maintain the sample at stable temperatures other than that of a cryogenic fluid in contact with the sample, temperatures above 20°K were obtained by allowing the sample temperature to drift slowly up or down to the temperature of the liquid nitrogen in the outer jacket of the double Dewar. Good agreement was found between the 20°K data taken using a hydrogen bath and using the "drift" technique.

Sample Preparation

Early in the measurement of relaxation times at low temperatures it was found necessary to use crystals which had low concentrations of F centers, low concentrations of aggregate centers (M, R, etc.), and extremely low concentrations of OH ions in order to observe the very long times intrinsic to isolated F centers. The importance of the first two of these conditions was recently reported by Ohlsen and Holcomb.[22] To satisfy these requirements we grew "OH-free" crystals, used techniques of sample preparation which were designed to reduce both the OH and the aggregate-center concentrations as much as possible, and kept the F-center concentration very low. Samples prepared with the most rigorous application of these precautions are referred to in the discussions that follow as samples prepared in our "best way."

Crystal Growth

Preliminary measurements were made with Harshaw crystals and home-grown crystals doped, in some cases, with impurities such as KOH or $SrCl_2$. The majority of the crystals, however, and all of those giving long relaxation times, were prepared in a zone-refining apparatus[36] constructed of quartz and operated on an atmosphere of dry HCl. The resulting boules were usually single crystals, but the cleavage faces showed more substructure than Harshaw crystals. The existence of optical absorption bands due to defects or impurities was investigated at 300°K over the wavelength range 200–2600 mμ. A band was found at 247 mμ (due perhaps to a monovalent impurity like Tl), with a peak absorption coefficient of 5×10^{-2} cm^{-1}; no other band (including that at 204 mμ due to OH) was observed. The limit of detectability was 5×10^{-3} cm^{-1}, which corresponds to an impurity concentration of about 2×10^{13}/cm^3, or about one part per billion. It is estimated, therefore, that the crystals contained at least 10 parts per billion of an unknown impurity giving the absorption band at 247 mμ, but less than 1 ppb of OH. The concentration of divalent impurities as determined by electrical-conductivity measurements[37] was about 10 parts per billion. No resonant microwave-absorption signals were observed in uncolored crystals that had been grown in our "best way."

Coloring

Three coloring techniques have been successfully employed to produce F centers with long relaxation times: gamma irradiation, additive coloring,[38] and electrolytic coloring[39] (abbreviated by Γ, A, and E). A minimum

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[37] H. Kelting and H. Witt, Z. Physik **126**, 697 (1949).

[38] R. W. Pohl, Proc. Roy. Soc. (London) **49** (extra part), 3 (1937).

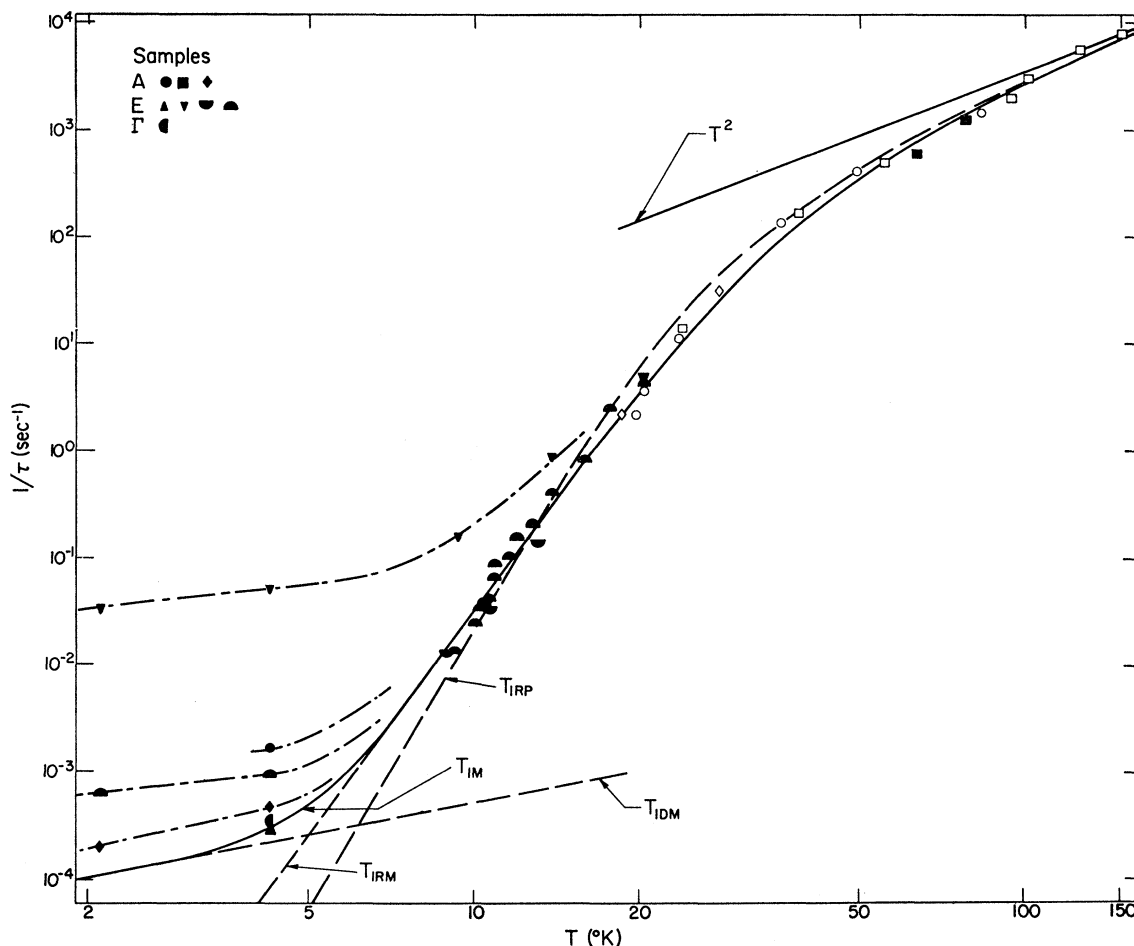[39] G. Heiland, Z. Physik **127**, 144 (1950).

FIG. 2. Temperature dependence of $1/\tau$ at 3.2 kOe. The experimental points correspond to various samples colored in different ways as indicated. The labels on the curves have the following meanings: T_{1D}—Relaxation by a direct process, Eq. (4). T_{1RP}—Raman relaxation involving the crystal field and phonon mixing of states, Eq. (8). T_{1RM}—Raman relaxation involving the magnetic hyperfine field, Eq. (6). T_{1M}—Relaxation involving T_{1RM} and T_{1D}, Eq. (9).

usable *F*-center concentration of about $10^{16}/cm^3$ was set by the sensitivity of the microwave apparatus and the maximum usable size (about 0.2 cm³) of the samples.

The Γ crystals were irradiated at 77 or 300°K by a 0.667-MeV Cs [137] source and then held at room temperature for several hours.

The *A* crystals were prepared in an apparatus (designed to reduce OH contamination) which in its final form consisted of a high-vacuum gas-handling system and a sealed quartz bomb containing the crystals to be colored, triply distilled potassium, and an HCl atmosphere. The coloring process itself was carried out in the standard way,[38] by heating the bomb for many hours and finally quenching it rapidly in water.

The *E* crystals were prepared in a much simpler way. Two opposite faces of each crystal were coated with Alkydag[40] and connected to a voltage source of about

[40] "dag" dispersion No. 154, Acheson Colloids Company, Port Huron, Michigan.

500 V. The crystal was then heated in dry N_2 until an appropriate temperature (about 600°C) was reached at which the current passing through the crystal was about 1 mA and color started to enter from the negative electrode. After the crystal was uniformly colored (usually in a few minutes) the current was stopped and the crystal cooled.

Because of the complexity of preparation and the possibility of contamination during the long heating cycle, additive coloring was not the preferred technique. It was, however, the only one that gave high enough *F*-center concentrations for the highest temperature-relaxation measurements. The *E* crystals and the Γ crystals irradiated at 77°K appeared to give equally good results in relaxation measurements. The Γ crystals irradiated at 300°K were inferior to these. Because of the expected presence of other defect centers in Γ crystals, and because of the long time needed for the irradiation of the Γ crystals, *E* crystals were most commonly employed.
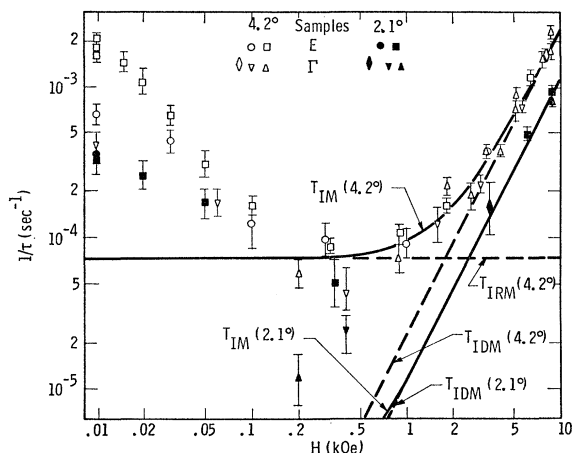
FIG. 3. Field dependence of $1/\tau$ at 4.2°K and 2.1°K. The experimental points correspond to various samples colored in different ways and measured at 4.2 or 2.1°K as indicated. The labels on the curves have the following meanings: T_{1D} (4.2°)—Relaxation by a direct process at 4.2°K, Eq. (4). T_{1D} (2.1°)—Relaxation by a direct process at 2.1°K, Eq. (4). T_{1M} (4.2°)—Relaxation involving T_{1D} (4.2°) and T_{1RM} (4.2°). T_{1M} (2.1°)—Relaxation involving T_{1D} (2.1°) and T_{1RM} (2.1°).

Handling

The Γ crystals were handled in the dark from the beginning of irradiation until the completion of the relaxation measurements to avoid the generation of aggregate centers. They were stored in liquid N_2, and were discarded if exposed to light. The A crystals were stored in liquid N_2, and handled in the dark. The E crystals, having been exposed to some light during the coloring process, were stored at room temperature without excluding light. Just before a relaxation measurement, the E crystals were annealed at a high temperature, quenched and handled thereafter in the dark. If at any time A or E (not Γ) crystals were adversely effected by light exposure, they could be returned to their original state by a reanneal and requench. The quench process consisted of heating the crystal to about 400°C for 2 min in dry N_2 followed by rapid cooling in a blast of dry N_2—all in the dark. It was found that this relatively gentle quench achieved an M-center concentration as low as more violent quenching processes, and did not crack the crystals. F-center concentrations were determined from optical absorption measurements[41] only after the completion of all relaxation measurements.

RELAXATION RESULTS

All of the samples discussed in this paper exhibited exponential recoveries from inversion and undistorted line shapes within the precision of our measuring techniques. The relaxation-time constant τ was measured at 4.2°K and 3.2 kOe for more than 60 different samples. Especially interesting samples were measured over a

[41] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1950), p. 115.

wide range of temperature and field. τ was found to be independent of the orientation of the sample with respect to the magnetic field.

As shown in Figs. 2 and 3, every sample gave the same relaxation time for given values of T and H_R whenever the values of these parameters were sufficiently high. This relaxation time appears to be an intrinsic property of F centers in KCl. We judge τ to be intrinsic when it is the longest time measured at a given T and H_R, and when it can be consistently observed with crystals having the "best" sample preparation.

For temperatures below 20°K, and especially at low fields, τ was sometimes found to be shorter than the intrinsic value and to vary from sample to sample. We refer to this as extrinsic behavior. Every sample apparently displayed extrinsic behavior at the lowest T and H. The range of T and H for which extrinsic behavior was observed in each sample was related to its preparation and treatment. These extrinsic effects are the subject of the subsequent paper.[24]

Temperature Dependence

Figure 2 shows values of $1/\tau$ versus temperature measured at 3.2 kOe on eight crystals colored in the three different ways. The F-center concentrations of these crystals varied from $10^{16}/cm^3$ to $10^{18}/cm^3$. The solid points represent data taken for crystals immersed in a cryogenic medium (He, H_2, or N_2) for which the uncertainty in temperature and τ is less than the size of the symbols. The hollow points represent data taken while the sample temperature was drifting up or down. The absolute temperature error was greater in these cases, but since the temperature was also greater, the relative uncertainty was small, being indicated by the size of the symbol.

The data can be divided into three regions: for $T \geq 50°K$, where τ is approximately $\propto T^{-2}$; for $T \leq 5°K$, where $\tau \propto T^{-1}$; and in between, where τ varies much more rapidly with temperature. The two higher temperature parts will be grouped in the discussion of the Raman processes; the low-temperature part will be discussed below as the direct process.

Magnetic Field Dependence

The magnetic field dependence of the intrinsic relaxation time was observed to be quite strong at 2.1 and 4.2°K. At 8°K, however, the intrinsic τ was found to be constant (within a factor of 2) between 100 and 9000 Oe. Measurements were not made of the field dependence of τ at higher temperatures.

Figure 3 is a plot of the low-temperature data for five Γ and E crystals in which $1/\tau$ is shown as a function of H_R with T as a parameter. The solid points represent 2.1°K data; the hollow points 4.2°K data. The temperature uncertainty was insignificant; the uncertainty in τ is shown by the vertical line through each point. At low fields the data show a large scatter between samples,

indicating that here none of the samples gave an intrinsic relaxation time. It should be emphasized that of necessity these crystals all had the "best" handling and lowest F-center concentrations of the samples investigated.

Inhomogeneity of F-Center Resonance

The inhomogeneity of the F-center resonance line was observed by inverting a "hole" in the line, usually near its center, and observing the recovery toward thermal equilibrium of the parts of the line affected. Typically a "hole" that covered the central tenth of the line spread into the rest of the line in a few seconds for F-center concentrations of 10^{17} cm^{-3}. The disappearance of the hole was dependent on the F-center concentration, taking longer in the more dilute samples. The disappearance was found to be field dependent but to take the same time at 2.1 and at 4.2°K. Above 15°K, τ was shorter than this time, and therefore in this temperature range, a hole disappeared by spin-lattice relaxation without spreading out.

DISCUSSION

Intrinsic behavior was observed for several different methods of sample preparation and widely different F-center concentrations. We assume that the intrinsic relaxation-time constant is characteristic of an isolated F center in pure KCl, label it T_1, and compare the field and temperature dependence of T_1 with that of the models discussed above.

Raman Processes

Of all the relaxation mechanisms discussed in the theory section, three predict relaxation times with temperature dependences that approximately fit the measured points of Fig. 2 above about 8°K. Two, given by Eqs. (6) and (8), have no field dependence; the third, given by Eq. (7), has an H^2 field dependence. The last must be a relatively unimportant mechanism since no difference (within a factor of 2) was observed in the relaxation times measured between 100 and 9000 Oe at 8°K. Of the field-independent mechanisms, the one due to crystalline field coupling, predicts a relaxation-time constant given by

$$1/T_{1RP} = B_P(T/\theta_P)^9 J_8(\theta_P/T).$$

The other, due to magnetic hyperfine coupling, predicts a relaxation-time constant given by

$$1/T_{1RM} = B_M(T/\theta_M)^7 J_6(\theta_M/T).$$

The following values for the undetermined constants have been chosen to give the best fit of each of these expressions to the experimental points:

$$\theta_P = 170°K, \quad B_P = 6.9 \times 10^4 \text{ sec}^{-1}$$

for phonon mixing and crystal field modulation, and

$$\theta_M = 210°K, \quad B_M = 7.8 \times 10^4 \text{ sec}^{-1}$$

for magnetic hyperfine modulation.

The solid and dashed lines in Fig. 2 show these expressions. For temperatures higher than those shown on the graph, both expressions predict essentially the same times, proportional to T^{-2}. Within the experimental scatter, either curve is an acceptable fit to the experimental points for temperatures above 8°K. Any normalized sum of these terms will also be an acceptable fit above 8°K.

For temperatures below 8°K, these expressions predict quite different times, but the direct relaxation process contributes significantly to the total relaxation, making a clear choice between the Raman processes difficult. At 4.2°K, for instance, the two Raman expressions give $T_{1RP} = 1.1 \times 10^5$ sec and $T_{1RM} = 1.4 \times 10^4$ sec, while the measured time constant at 3.2 kOe, due largely to the direct process, is 3×10^3 sec. As will be discussed later, the detailed measurements made at 4.2°K suggest that the hyperfine process giving T_{1RM} is the strongest Raman process.

A more convincing way, however, to determine which, if either, of the Raman mechanisms is dominant is to consider the magnitudes of the cutoffs θ_P and θ_M. Various evidence points to the fact that even though the true phonon spectrum of a material may seem to be far from a Debye spectrum, most events that involve thermal phonons average over enough of the spectrum to smooth its details and give results in remarkably good agreement[42] with that calculated from a Debye spectrum with a unique Debye temperature characteristic of that material. As an illustration, Blackman in a review article[16] lists θ values for KCl determined over a wide temperature range and in several different ways. These values all are within 10% of 225°K. As an example directly related to this study, Weber[43] has investigated the Raman relaxation of nuclei in various alkali halides (KCl not among them) and concludes that a Debye phonon spectrum using the θ determined from specific heat measurements describes the nuclear relaxation fairly well in all cases, and does so quite well for cases (like KCl) where all the ions have about the same mass and where (like KCl) the actual vibrational spectrum is expected to be reasonably close to a Debye spectrum. An acceptable relaxation theory then should involve a Debye temperature for KCl of approximately 225°K. θ_M of 210°K$\pm$5% (where the uncertainty in θ is esti-

[42] Recent measurements of the optical sharp-line spectra of the R_2 center in KCl have been analyzed and reported by D. B. Fitchen, R. H. Silsbee, T. A. Fulton, and E. L. Wolf, Phys. Rev. Letters **11**, 275 (1963). Using a method usually applied to the Mossbauer effect they get a value of 170°K for the lattice Debye temperature in disagreement with the other results (Ref. 15). It is not uncommon [c.f. M. Yaqub and C. Hohenemser, Phys. Rev. **127**, 2028 (1962)] and it is even expected [J. L. Feldman and G. K. Horton, Phys. Rev. **132**, 644 (1963)] that Mossbauer experiments give Debye temperatures that are quite low, and so this value is disregarded here.

mated by fitting our experimental points), is in remarkably good agreement; θ of 170°K±5% is less acceptable.

Direct Processes

At a sufficiently low temperature, direct (one-phonon) processes will dominate Raman (multiphonon) processes. Both theories for the direct relaxation process predict a linear temperature dependence, while the predicted field dependences differ, being H^4 for the crystal field interaction given by Eq. (5) and H^2 for the hyperfine interactions given by Eq. (4). The low-temperature data shown in Fig. 3 have a linear temperature dependence. They cannot be fitted by an H^4 field dependence but can be well fitted by an H^2 dependence. To illustrate this agreement, the dashed lines in Fig. 3 are plots at 2.1 and 4.2°K of $1/T_{1DM}=AH^2T$, the form for relaxation by the direct hyperfine interaction alone. $A=5.1 \times 10^{-12}$ sec^{-1} Oe^{-2}°K^{-1} is chosen to fit the high-field points. The solid lines are plots of $1/T_{1M}$ at 2.1 and 4.2°K giving the total relaxation-time constant predicted for all hyperfine interactions. T_{1M} is given by

$$1/T_{1M}=B_M(T/\theta_M)^7 J_6(\theta_M/T)+AH^2T,$$

where the constants B_M and θ_M are not chosen to fit these data but are the Raman constants given in the last section. It can be seen that the fit of the solid curves to the experimental points is good at high and intermediate fields (300 Oe$<H<$10 kOe for 4.2°K and 3 kOe$<H<$10 kOe for 2.1°K).

The contribution of the Raman processes to the 2.1°K data shown in Fig. 3 is small. Relaxation at 2.1°K is completely dominated by the direct processes above 3 kOe and by extrinsic behavior below 3 kOe; this is not true for the 4.2°K data. The inclusion of the relaxation predicted for the Raman processes gives a significantly better fit of the 4.2°K data (for 300 Oe$<H<$3 kOe), but only if the T^7 process is employed. The better fit with the T^7 term is supporting evidence for the determination of the dominant Raman process made in the previous section. Below 300 Oe, apparently unavoidable extrinsic effects dominate the relaxation.

Summary

The F-center resonance line is found, in agreement with the theoretical discussions, to relax with a single time constant and without distortion. There is, therefore, no experimental way of distinguishing between relaxation by isotropic and anisotropic hyperfine interactions.

The direct process is clearly due to a magnetic hyperfine interaction. This same interaction dominates the Raman relaxation below about 20°K, where T is much less than θ, since the data including the field dependence at 4.2°K can be fitted only by an H^0T^7 term.

This interaction alone will also fit the data at higher temperatures, by the selection of $\theta_M=210$°K. Such a choice of θ is in agreement with the specific heat θ and is consistent with the findings of Weber.[43] It is possible that some other Raman relaxation process may contribute at higher temperatures, but this would require an unusually low θ_M in the hyperfine term.

Comparison with Other Work

T_1 for F centers in KCl has been calculated by Deigen and Zevin[21] for the direct process and the magnetic hyperfine interaction.[44] They obtained a value of 120 to 1300 sec at 4°K and 3 kOe. The observed relaxation time at this temperature and field is caused by both the direct and Raman processes. The contribution from the direct process alone, with which Deigen and Zevin's calculation should be compared, can be determined from $T_{1DM}=(AH^2T)^{-1}$. It is 5500 sec±10%, as is evident from Fig. 2 or 3. The difference between this value and that of Deigen and Zevin is not surprising considering the number of simplifying assumptions made in their calculations.

The values of τ measured by us in the helium range are more than an order of magnitude greater than those reported by Ohlsen and Holcomb. Their results were presumably dominated by extrinsic effects similar to those which will be discussed in the subsequent paper.[24]

Note added in proof. T_1 for F centers in KCl has been calculated by V. Ya. Zevin (Fiz. Tverd. Tela **3**, 599 (1961) [English transl.: Soviet Phys.—Solid State **3**, 439 (1961)]) for the Raman process and the magnetic hyperfine interaction. He finds a value of 2.5×10^{-4} sec at 300°K.

T_1 for F centers in KCl was measured at 300°K and 3 kOe by Portis[17] using the cw saturation method. He obtained a value of 2.5×10^{-5} sec, in excellent agreement with that given by the function which we have fitted to our data. The relaxation time, therefore, has approximately a T^{-2} dependence from 100°K up to at least room temperature. Thus there is no evidence for the existence of a three- (or more) phonon process below 300°K.

Note added in proof. A subsequent investigation [H. Seidel, Z. Physik **165**, 239 (1961)] casts doubt on Portis' T_1 determination. P. R. Moran (private communication) has measured T_1 by a different technique and finds $T_1=3\times10^{-5}$ sec.

CONCLUSIONS

F centers which exhibit intrinsic spin-lattice relaxation over a considerable range of temperature and magnetic field have been produced in KCl crystals in three completely different ways and in concentrations covering a range of about one hundred. The intrinsic spin-lattice relaxation-time constant T_1 for F centers can be

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[43] M. J. Weber, Phys. Rev. **130**, 1 (1963).

[44] A similar calculation was made, prior to the report by Deigen and Zevin, by B. Gourary (unpublished). This calculation also gave about 10^3 sec at 4°K and 3 kOe.

accurately expressed for all of these crystals by

$$1/T_1 = 5.1 \times 10^{-12} H^2 T$$
$$+ 7.8 \times 10^4 (T/210)^7 J_6(210/T), \quad (9)$$

where H is in Oe, T in °K, and T_1 in sec. The two terms in this expression, identified with the direct and Raman processes, are consistent with the model in which the only effective relaxation is by means of the hyperfine interaction of an isolated F center with the surrounding nuclei and in which the lattice phonons are described by a Debye distribution with the same cutoff as has been determined from measurements of specific heat.

Concentration-Dependent Electron Spin Resonance*

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A number of workers have studied the decrease of the intensity of a nuclear magnetic resonance (NMR) line as one adds impurities to the specimen. Usually the intensity of the line is $\propto (1-c)^n$, where $c =$ the concentration of the impurities and n is the so-called wipe-out number, i.e., if the impurity is within a sphere containing n neighboring positions its effect is large enough so as to cause a nuclear quadrupole splitting of the host nuclei so that they no longer contribute to the NMR line. Experimentally one can determine n. The extension of this type of experiment into the domain of electron spin resonance (ESR), in a very simple way, is described. Also, the wipe-out number for Mn^{2+} in two systems, $(Zn_{1-c}+Cd_c)S$ and $Zn(S_{1-c}+Se_c)$, is measured. One finds $n = 157$ and 270, respectively.

INTRODUCTION

In the early studies of the nuclear magnetic resonance (NMR) of metals and alloys, Bloembergen and Rowland[1] measured the decrease of intensity of the Cu NMR in the cubic system $Cu_{1-c}+Zn_c$ as c increased. They found that the intensity, I, of the Cu NMR decreased with the concentration c of Zn according to

$$I = I_0(1-c)^n, \quad (1)$$

where n is the so-called wipe-out number or dead-site number. Equation (1) comes from the assumption that if a given Cu nucleus has a Zn atom in any one of n neighboring positions, the resultant nuclear quadrupole resonance (NQR) splitting will be large enough so that the Cu nucleus no longer contributes to the NMR line. By measuring I versus c, one can determine n for the system in question. Cu has a nuclear spin of $\frac{3}{2}$ which in a magnetic field splits into four equally spaced levels. The transitions between the $\pm\frac{1}{2}$ and $\mp\frac{1}{2}$ levels will be unaffected to first order by quadrupole effects.[2] On the other hand, the transitions from the $\pm\frac{3}{2}$ to $\pm\frac{1}{2}$ levels will be affected by first-order quadrupole effects. Thus, one can measure the wipe-out number for either the first- or second-order effects.[1,3] A number of these experiments have been performed in metals.[4] The major contribution to n in metals appears to arise from long-range oscillations in the electron charge density around the solute atom.[5]

This type of experiment has also been carried out in a number of cubic alkali-halide systems.[6] For example, the wipe-out number for either the Na or Cl in the system $Na(Cl_{1-c}+Br_c)$ can be studied. It appears that one can do a reasonable job in calculating the wipe-out numbers by focusing one's attention on the dipole moments, direct and induced, that occur due to the strain in the lattice set up by the solute atom.[7,8]

An experiment similar to the above type has been performed on[9] single crystals of $(Na_{1-c}+Ag_c)NO_3$. In this

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1 N. Bloembergen and T. J. Rowland, Acta Met. **1**, 731 (1953).

2 For general references to the field of NQR see: M. C. Cohen and F. Reif, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 5; and T. P. Das and E L. Hahn, *ibid.*, Suppl. 1.
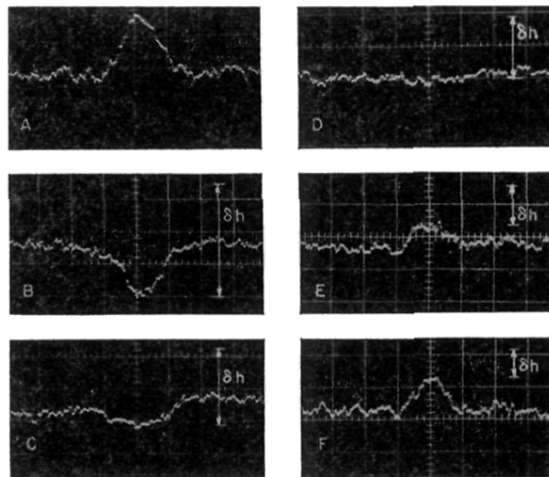
3 T. J. Rowland, Acta Met. **3**, 74 (1955).

4 T. J. Rowland, Phys. Rev. **119**, 900 (1960).

5 W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).

6 H. Kawamura, E. Otsuka, and K. Ishiwatari, J. Phys. Soc. Japan **11**, 1064 (1956); E. Otsuka and H. Kawamura, *ibid.* **12**, 1071 (1957); E. Otsuka, *ibid.* **13**, 1155 (1958); E. Otsuka, Y. Oshio, T. Kobayashi, and H. Kawamura, *ibid.* **14**, 1454 (1959); Y. Fukai, *ibid.* **18**, 1580 (1963).

7 T. P. Das and B. G. Dick, Phys. Rev. **127**, 1063 (1962).

8 Y. Fuksi, J. Phys. Soc. Japan **18**, 1580 (1963).

9 M. I. Kornfeld and V. V. Lemanov, Zh. Eksperim. i Teor. Fiz. **39**, 53 (1960) [English transl.: Soviet Phys.—JETP **12**, 38 (1961)].

FIG. 1. Oscilloscope display of F-center absorption signal during recovery. A is the equilibrium signal and B, the signal immediately after inversion. C, D, E, and F photographed with increasing delay after inversion illustrate the gradual recovery of δh to zero. The sample was prepared by gamma irradiation and the measurements were taken at 4.2°K and 3.2 kOe. The F-center concentration was about 4×10^{16} cm^{-3}.