TABLE III. Parameters used in the modified Gaussian decays of Figs. 5 and 6 for bcc symmetry.

	$M_2(X^{-2})$ [a]	$M_4(X^{-4})$ [a]	$a^2(X^{-2})$	$b(X^{-1})$
$I=\frac{1}{2}$	7.76	133.45	1.49	4.34
$I=1$	7.76	135.40	1.62	4.29

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$I=\frac{1}{2}$ powder decays.

The modified Gaussian expression $[e^{-a^2t^2/2} \times \sin bt/bt]$ for the decays is plotted in Figs. 5 and 6 for bcc symmetry along with the powder decays of Fig. 1, obtained from the Lowe-Norberg decay formula. The parameters a and b and the second (M_2) and fourth (M_4) moments used in the evaluation are given in Table III. Figures 5 and 6 show that the modified Gaussian decay is fairly similar to the Lowe-Norberg decay for $I=\frac{1}{2}$ but that the agreement is considerably poorer for $I=1$. The modified Gaussian powder decays were also calculated for fcc symmetry, and their agreement with the Lowe-Norberg decays was very similar to the bcc case, good for $I=\frac{1}{2}$ but considerably poorer for $I=1$.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 11 1 DECEMBER 1971

Study of the Thermal Kinetics of the F'-to-F Conversion in KCl by Electron Spin Resonance*

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The temperature dependence of the F'-to-F conversion has been studied in additively colored KCl, at a number of temperatures at which the F' center is thermally unstable. The conversion was monitored by observing the increase of the ESR signal of the F center. The data were analyzed in terms of a kinetics which allowed the electron on leaving the F' center to go to a vacancy to form an F center or to an F center to form another F' center. The results of the analysis indicate that the half-life of the F'center is dependent on the concentration of the F' centers. An activation energy of 0.53 ± 0.05 eV was deduced for low concentrations of F' centers, where it is indicated that the half-life is independent of the concentration of the F' centers.

I. INTRODUCTION

A broad optical absorption on the red side of the F band at about 1.6 eV in KCl has been attributed to two electrons trapped at an anion vacancy. This model of the F' center is supported by Pick's study of the F-to-F' and F'-to-F quantum yields.[1,2] He found that the conversion reaction could be described by $2F \rightleftharpoons F'$ and that the F' optical band could be bleached optically at very low temperatures with a quantum yield of two, indicating that the F' center has no bound excited state. The broadness of the F' optical absorption is attributed to the fact that excitations of the center are to states in the conduction-band continuum. Little attention has been paid to the thermal stability of the center. The broadness of the F' band, which results in it overlapping into the F band, complicates optical studies of the thermal annealing process. However, some studies have been reported and activation energies measured on the assumption that the thermal kinetics is first order.[1,3] More detailed studies have indicated the possibility that the decay is not first order. A simultaneous measurement of the decrease of the F'-band optical absorption and the increase of the F paramagnetic resonance

absorption at – 90 °C in additively colored KCl indicated that the thermal decay of the F' center followed a more complicated kinetics.[4] No activation energy was determined from this work, as the decay was only studied at one temperature.

In order to determine the activation energy taking into account the more complicated kinetics, the increase of the ESR signal of the F center owing to the thermal annealing of the F' center in additively colored KCl has been measured at a number of different temperatures. The data have been analyzed in terms of a more complicated kinetics and an activation energy deduced.

II. EXPERIMENTAL METHOD

Cleaved single crystals of potassium chloride were obtained from the Harshaw Chemical Company. The F centers were produced in the crystals by additive coloration. The experimental arrangement used was similar to the one devised by Van Doorn.[5] It consisted of a stainless-steel bomb which was vacuum sealed so that it could be pumped down to a pressure of about a micron. The crystals were suspended over a piece of potassium metal by a nickel wire from the lid of the bomb. The bomb was then placed in a vertical tubular furnace which was maintained at a temperature of 580 °C. The crystals on being removed from the furnace were immediately quenched in an oil bath which was at room temperature. Measurements of the optical absorption and ESR of these crystals showed only the presence of the F center. The ESR measurements were made on a Varian E-3 spectrometer equipped with apparatus enabling the temperature of the sample to be controlled. Optical measurements were made on Carey 14-R spectrometer. Typically, the number of F centers produced by additive coloration was estimated to be on the order of $10^{17}/\text{cm}^3$. The estimates were made from optical-absorption measurements and the use of Smakula's equation. The oscillator strength of the F band was taken to be 0.85.

While the ESR signal of the F center was being observed at – 90 °C, the crystal was exposed to F-band light through slots on the ESR cavity. The ESR signal of the F center typically decreased by 62%. The observation of the optical absorption at this temperature showed the presence of the F' band. Crystals in which the F' centers were produced were then held at constant temperatures at which the F' center is thermally unstable, and the increase of the ESR of the F center was monitored. It was possible to control the temperature to within ± 2 °C.

III. RESULTS AND ANALYSIS

A plot of the ratio of the number of F' centers to the initial number of F' centers vs time for a number of different temperatures is shown in Fig. 1. The fraction F'/F'_{max} is measured by observing the increase in the ESR of the F center as the F' center is undergoing thermal annealing, and by using the fact that when an F' center is destroyed two F centers are produced. A plot of the logarithm of the number of F' centers vs time at a fixed temperature is not a straight line, indicating that the kinetics is not first order. Similarly a plot of $1/F'$ vs time is also not a straight line, showing that the kinetics is not second order.

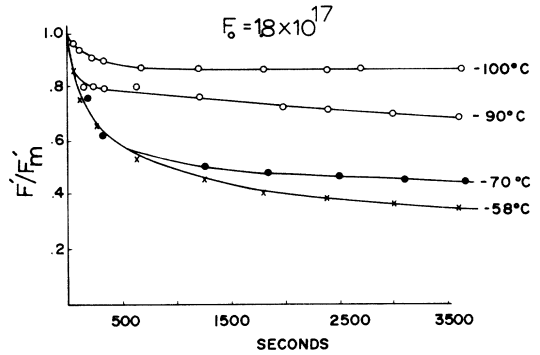

FIG. 1. Plot of the number of F' centers over the initial number of F' centers vs time at a number of different temperatures at which the F' center is unstable.

In order to determine the activation energy of the F' center, the kinetics of the decay must be known. A model for the decay kinetics of the F' center has been proposed by Schmidt and Wolf.[4] They simultaneously measured the decrease in the optical absorption of the F' center and the increase of the ESR of the F center at – 90 °C. They found that at any time after the start of the decay of the F' center, the increase of the ESR of the F center, ΔF, divided by ΔF_{max}, was equal to the decrease of the F' band, $\Delta F'$, divided by the initial height of the F' band. This suggests that the electron on leaving the F' center in additively colored KCl can only do two things. It may go to an F center to form an F' center or it may go to a vacancy to form an F center. It appears that in additively colored KCl other traps are not playing a role in the F'-to-F conversion. Our data will be analyzed in terms of a kinetic model which takes into account this fact. If V denotes the number of vacancies, we have

$$e + V \rightarrow F \,, \tag{1a}$$

$$e + F \rightarrow F' \,. \tag{1b}$$

The rate of decrease of F' centers is given by

$$\frac{dF'}{dt} = -\frac{F'}{\tau}\left(1 - \frac{\beta F}{\alpha V + \beta F}\right), \tag{2}$$

where β is the probability for an F center to capture an electron and α is the probability for an elec-

tron to be captured in the ground state of the vacancy. The half-life of the F' center is denoted by τ. The F' centers are produced by optically bleaching an F center, creating a vacancy. Thus we have

$$F' = V \tag{3a}$$

and

$$F(t) = F_0 - 2F'(t)\,, \tag{3b}$$

where F_0 is the number of F centers before conversion to F' centers. The solution of Eq. (2) is

$$\frac{t}{\tau} = \left(\frac{2\beta}{\alpha} - 1\right) \ln \frac{F'(t)}{F'(0)} + \frac{\beta}{\alpha} F_0 \left(\frac{1}{F'(t)} - \frac{1}{F'(0)}\right), \tag{4}$$

where $F'(0)$ is the concentration of F' centers before conversion to F centers by thermal annealing. The ratio β/α is temperature dependent and can be calculated from photoconductivity measurements. When the electron is captured by the vacancy it is captured in the excited state of the F center. There then exists a temperature-dependent probability η that the electron can be thermally ionized to the conduction band. It has been shown from photoconductivity measurements in KCl that[6]

$$\frac{\beta}{\alpha} = \frac{1}{6(1-\eta)}\,. \tag{5a}$$

From the temperature dependence of photoconductivity induced by F-band light η was determined to have the temperature dependence[6]

$$\eta = \frac{1}{1 + Ce^{U/KT}}\,, \tag{5b}$$

where $C = 2.3 \times 10^{-7}$ and $U = 0.16$ eV. Using Eqs. (5a) and (5b) the values of β/α at the temperatures of the measurement of the F'-to-F conversion can be calculated. The values are listed in Table I. These values can then be inserted into Eq. (4) and one can then attempt to fit the decay curves for a constant value of τ at each temperature. When this is done it is found that it is not possible to fit the data by Eq. (4) for a constant value of the half-life τ.

Schmidt and Wolf's work suggests that the proposed mechanism which allows the electron on leaving the F' center to go only to a vacancy or F center is the correct mechanism. The inability to fit the data for a constant value τ at a given temperature may not necessarily lie in the incorrectness of the kinetic model. A possible source of the difficulty is suggested from the data displayed in Fig. 2. In the figure F'/F'_m is plotted vs time at a constant temperature but for two different initial concentrations of F' centers. The data indicate that the rate of decay of the F' center depends on the concentration of F' centers. Thus a possible correction to the kinetics described by Eq. (2) is to incorporate a time dependence for the half-life of the F' centers. A reasonable form for the time dependence that takes into account the fact that the half-life increases as the concentration decreases is

$$\tau_0 + (\tau_\infty - \tau_0)(1 - e^{-\rho t})\,, \tag{6}$$

where τ_∞ is the half-life of the center at low concentrations, τ_0 is the half-life at the beginning of the decay, and ρ is a constant. The solution of Eq. (2) becomes

$$g(t) = \left(\frac{2\beta}{\alpha} - 1\right) \ln \frac{F'(t)}{F'(0)} + \frac{\beta}{\alpha} F_0 \left(\frac{1}{F'(t)} - \frac{1}{F'(0)}\right), \tag{7}$$

where $g(t)$ is given by

$$\frac{t}{\tau_\infty} + \frac{1}{\rho\tau_\infty} \ln\left(\frac{\tau_\infty - (\tau_\infty - \tau_0)e^{-\rho t}}{\tau_0}\right). \tag{8}$$

The function $g(t)$ can be calculated as a function of time for a constant temperature from the data using the right side of Eq. (7). A plot of $g(t)$ calculated in this manner is shown in Fig. 3 for $-70\,^\circ$C. Note that, for long times, Eq. (8) indicates that $g(t)$ becomes linear with a slope of $1/\tau_\infty$. The $g(t)$ can be calculated from the data for different temperatures and fitted to Eq. (8) by appropriate choices for τ_0, τ_∞, and ρ. In Fig. 4 the $\ln(1/\tau_\infty)$ abstracted from

TABLE I. Values of the ratio of the F-center capture probability to the vacancy capture probability for an electron in KCl calculated from photoconductivity measurements.

T (°C)	$\frac{\beta}{\alpha}$
−100	16.0
−90	28.7
−70	75.7
−58	128.2

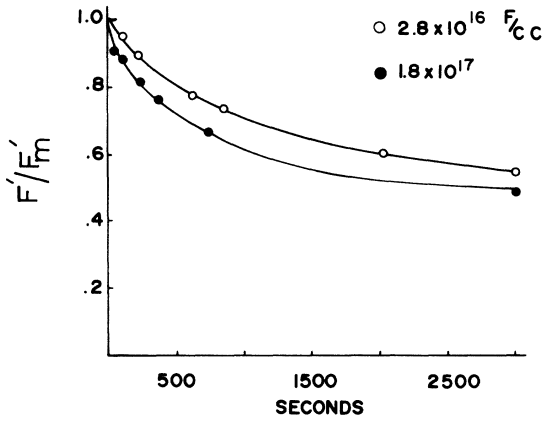

FIG. 2. Plot of the number of F' centers over the initial number vs time for two different initial concentrations of F' centers. The graphs are labeled by the F-center concentration before conversion to F' centers. In both cases the same fraction of F centers was converted.

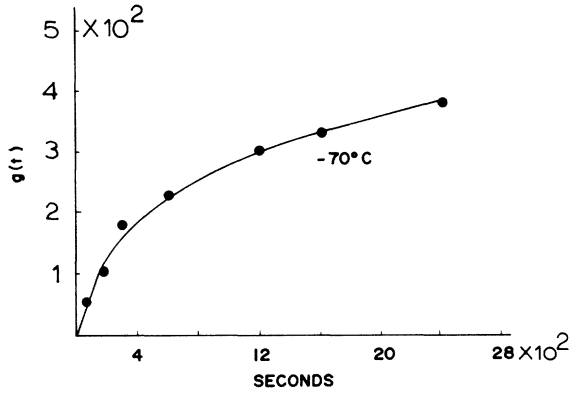

FIG. 3. Plot of $g(t)$ vs time at one temperature. The $g(t)$ was calculated from the data and the right side of Eq. (7).

the data in this manner is plotted against the reciprocal of the absolute temperature. Since

$$\tau_\infty = e^{E/KT}/S \,, \tag{9}$$

the slope of this straight line determines the activation energy. This is determined to be 0.53 ± 0.05 eV, and the frequency factor S, is calculated to be 1.4×10^{12} sec^{-1}.

IV. DISCUSSION

The object of the experiment has been to investigate the nature of the kinetics of the F'-to-F conversion and to study the temperature dependence of the reaction in order to determine the activation energy of the F' center. The kinetics of the F'-to-F conversion was analyzed in terms of a kinetic model proposed by Schmidt and Wolf. The half-life of the F' center was observed to depend on the concentration of F' centers. This was built into the model by assuming that the half-life was time dependent and had the form given in Eq. (6). By fitting the decay kinetics to Eq. (7) it was possible to determine τ_∞ at each temperature. The assumed form of the half-life indicates that τ_∞ is the half-life for sufficiently long times after the start of the decay, where the half-life becomes independent of concentration. The fact that $g(t)$ calculated from the right-hand side of Eq. (7) became linear in time indicates that the half-life eventually does become independent of the concentration of F' centers. If the half-life were constant and independent of concentration, $g(t)$ would be linear in time and have a slope of $1/\tau_\infty$.

That τ_∞ is a concentration-independent half-life can be argued from the data of Fig. 2, where the decay of the F' center is monitored for two different initial F-center concentrations at $-90\,^\circ$C. A calculation of $g(t)$ for both curves shows that $g(t)$ eventually becomes linear, and the slope in the linear region is the same for both sets of data, indicating that τ_∞ is the same.

Although the kinetics described by Eq. (7) is a most plausible possibility and does fit the data for the appropriate choice of parameters, it is not proven unambiguously that this is the correct model for the kinetics. Therefore the uniqueness of the τ_∞ determined from the analysis may be questioned. For example, one might possibly construct a different equation for the time dependence with τ_∞ as a parameter, which could lead to a fit of the data for a different value of τ_∞. However, it is possible to determine the value of τ_∞ without specifying the detailed form of the time dependence of the half-life. This is possible because $g(t)$ eventually becomes linear in time and therefore the slope must be $1/\tau_\infty$.

Other kinetic models which allow for the two-trap possibility have also been investigated. For example, solutions of

$$\frac{dF'}{dt} = -\frac{F'^N}{\tau}\left(1 - \frac{\beta F}{\alpha V + \beta F}\right) \tag{10}$$

were investigated for values of N ranging from 2 to 5, and were found not to fit the data.

The experiment clearly shows that the F' center does not decay by first-order kinetics and that therefore previous analysis assuming first-order kinetics is questionable. It is of interest to compare our results with those previously reported. There have been two previous reports of activation-energy measurements for the thermal decay of the F' center in KCl. An early measurement from the thermal annealing of the F' optical band yielded 0.51 eV under the assumption of first-order kinetics.[1] A measurement from thermoluminescence studies yielded 0.54 eV.[3] This measurement also assumed first-order kinetics in the analysis of the

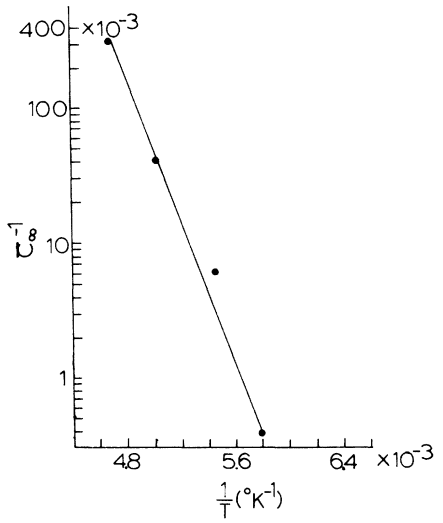

FIG. 4. Plot of $\ln(1/\tau_\infty)$ obtained from the data fit vs the reciprocal of the absolute temperature.

thermoluminescence data. None of the measurements took into account any dependence of the half-life of the F' center on the concentration of F' centers.

The analysis of this work yields an activation energy in essential agreement with those previously reported. At first sight this would appear puzzling, since the early measurements did not consider the concentration dependence of the half-life. Our analysis only deduced an activation energy for low concentrations of F' centers (less than $10^{16}/cm^3$), where the half-life was indicated to be independent of the F' concentration. Pick's measurement of the activation energy of the F' center was for initial F' concentrations of less than $10^{16}/cm^3$. Thus, his measurement was also in the concentration-independent region, and could be expected to agree with our result.

It is of interest to speculate on the reason why the half-life of the F' center is dependent on the concentration of the F' centers. It is possible that for high concentrations of F' centers, other F' centers or vacancies are sufficiently close to a given F' center to polarize it, which in turn might affect the stability of the center. Such an effect would depend on the distance between centers, which would be concentration dependent.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 11 1 DECEMBER 1971

Effects of Temperature on the Magnetic Hyperfine Properties of Beryllium†

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The temperature dependence of the Fermi contact and exchange core-polarization (ECP) contribution to Knight shift K and nuclear-spin relaxation time T_1 in beryllium has been studied. The variation in the spin density shows a similar trend to that in cadmium, namely, the s content of the conduction-electron wave function Ψ_k increases with temperature at the expense of a decrease in the p content. Combining both direct and ECP contributions, K increases by 2.3% and T_1T decreases by 8% from 0 to 300 °K. The results are compared with the available experimental data.

The hyperfine properties of metals that depend upon the wave functions of the conduction electrons on the Fermi surface are of particular interest, because they serve as sensitive indices of the nature of the energy bands constituting the Fermi surface and of the associated electronic wave functions. In the case of alkali metals, the Fermi surface is spherical and is inside the first Brillouin zone. However, for the group-II hcp metals in the extended zone scheme, the Fermi surface intersects the second Brillouin zone substantially and is composed of several bands with varying degrees of angular symmetry. The nuclear-magnetic-resonance properties of the various divalent hcp metals provide very interesting trends.

Recently, the unusual temperature dependence of the Knight shift[1] K in Cd has been explained by changes in the $s(l=0)$ content of the conduction-electron wave functions which are brought about by the temperature variation of the ionic potential produced by electron-phonon interaction. In Be, the lightest of the hcp metals, K has been explained by the combination of direct, exchange core-polarization[2] (ECP), and Landau-type orbital contributions.[3] Since the conduction electrons in Be at 0 °K are very p-like[2] and the ECP contribution of a p