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Temperature Dependence of Phonon-Induced Electronic Transitions in Insulating Solids*

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The temperature dependence of the oscillator strength of a forbidden electronic transition at an impurity in an insulating solid is calculated, assuming that the transition is induced by a local linear electron-phonon interaction. The electronic states are allowed to couple, not merely to one configuration coordinate, but to all the modes of vibration of the imperfect crystal. The frequencies of these modes and their relative contributions to the oscillator strength are calculated using Green's-function techniques. In particular, the $4d^{10}$ to $4d^9 5s$ transition of Ag^+ in NaCl is considered. A model which represents the host ions as point charges is shown to be inconsistent with the experimentally determined temperature-dependent oscillator strength. Good agreement with experiment is obtained if one assumes that the short-range interaction between the Ag^+ impurity and the host ions is important.

I. INTRODUCTION

Electronic transitions forbidden in a free atom may occur when the atom is inserted into a crystal. One mechanism for such a transition is based on phonon mixing of electronic states.[1] A thermal displacement of the atoms near the impurity mixes a state of similar energy and of symmetry appropriate for a dipole transition into the ground or excited states of the transition. In this paper we assume that such a mixing can take place through a local linear electron-phonon interaction. This simple form of the interaction allows us to calculate the temperature dependence of the oscillator strength of a forbidden transition. The problem conveniently divides into three topics which can be treated independently: (i) the electronic states of the impurity in a stationary lattice, (ii) the modes of vibration of the imperfect crystal, and (iii) the electron-phonon interaction.

The first topic will not be considered here. The electronic states of the impurity in a stationary lattice are assumed to be either known or the same as the states of a free ion.

The second topic will be treated more carefully than has been done in the past. Kubo and Toyozawa[2] and Liehr and Ballhausen[3] have shown that if phonons of only one frequency ω are involved, the oscillator strength for the transition should have the form

$$f = f_0 \coth(\hbar\omega/2kT). \tag{1}$$

We will not represent all the modes of vibration of an imperfect crystal by one configuration coordinate. Such a simplification is not necessary since the dynamics of an imperfect crystal can be solved quite precisely using Green's functions.[4,5] Mulazzi *et al.*[6] have formulated a wide variety of electron-phonon problems using Green's-function techniques. In order to make a calculation using such techniques it is necessary to choose a localized model for the defect. This can be done by studying experiments independent of the linear electron-phonon interaction, for example, infrared absorption.

As for topic (iii), calculations of the electron-phonon coupling parameters themselves have often involved the point-ion approximation. In that model the electronic states localized at the impurity are assumed to interact with a point-ion potential representing the neighboring atoms. If the electronic states are localized around the impurity, however, it does not seem plausible that the short-range interaction between the impurity and host ions is small. This paper is in part a test of the point-ion approximation in electron-phonon interactions.

Fussgänger *et al.*[7] have measured the temperature dependence of the absorption spectra of Ag^+-doped NaCl. Several strongly temperature-dependent absorption bands were observed in the region of 6.8 to 4.4 eV. The position and temperature dependence of these bands indicated that they corresponded to the parity-forbidden electronic transition $4d^{10}$ to $4d^9\,5s$ in free Ag^+. They analyzed their low-temperature data making use of the two parameters characteristic of a configuration coordinate model, Eq. (1). In this paper their results are reexamined using the Green's-function formulation of the problem. There is only one independent parameter in this approach, the oscillator strength at zero temperature. In addition, the temperature dependence is not necessarily a hyperbolic cotangent function.

II. FORMULATION

The oscillator strength of a transition from a ground electronic state with energy E_a to an excited state with energy E_b is given by the expression[8]

$$f_{ba} = (2m^*/3\hbar^2)(E_b - E_a)\mathrm{Av}_\alpha \textstyle\sum_\beta |\vec{r}_{ba\beta\alpha}|^2, \tag{2}$$

where

$$\vec{r}_{ba\beta\alpha} = \int\int \Phi^*_{b\vec{u}}(\vec{r})\chi^*_{b\beta}(\vec{u})\,\vec{r}\,\Phi_{a\vec{u}}(\vec{r})\chi_{a\alpha}(\vec{u})\,d\vec{r}\,d\vec{u}\,. \tag{3}$$

The approximations made in deriving this expression are discussed in detail by Dexter.[8] The electronic wave function, coordinate, initial quantum number, and final quantum number have been denoted by Φ, $\vec{r}$, a, and b, respectively. The vibrational wave function, coordinate, initial quantum number, and final quantum number are χ, $\vec{u}$, α, and β. Notice that for this particular electronic transition we have summed over all final vibrational states and performed a thermal average over the occupied initial vibrational states. We will assume that the excited electronic state $\Phi_{bu}(r)$ is a mixture of two free-ion states $b0$ and $b1$. The ground electronic state remains pure:

$$\begin{aligned}\Phi_{bu}(\vec{r}) &= [1 - A^2(\vec{u})]^{1/2}\Phi_{b0}(\vec{r}) + A(\vec{u})\Phi_{b1}(\vec{r}) ,\\ \Phi_{au}(\vec{r}) &= \Phi_{a0}(\vec{r}) .\end{aligned} \tag{4}$$

Notice that $A(u)$, the admixture of state $b1$ into $b0$, contains all the u dependence in $\Phi_{bu}(r)$. Substitute Eq. (4) into Eq. (3):

$$\begin{aligned}\vec{r}_{ba\beta\alpha} &= \int \Phi^*_{b1}(\vec{r})\, \vec{r}\,\Phi_{a0}(\vec{r})\, d\vec{r} \int \chi_{b\beta}(\vec{u})A(\vec{u})\chi_{a\alpha}(\vec{u})d\vec{u},\\ \vec{r}_{ba\beta\alpha} &= \langle b1 | \vec{r} | a0 \rangle \langle \beta | A | \alpha \rangle .\end{aligned} \tag{5}$$

Here we have made use of the fact that the $a0$ to $b0$ transition is dipole forbidden. If we sum the square of the matrix element defined by Eq. (5) over all vibrational states of all normal modes of the excited electronic state, we obtain

$$\textstyle\sum_\beta |\vec{r}_{ba\beta\alpha}|^2 = |\langle b1 | \vec{r} | a0\rangle|^2 \sum_\beta \langle \alpha | A^* | \beta\rangle \langle \beta | A | \alpha \rangle .$$

Using the closure relation this simplifies to

$$\textstyle\sum_\beta |\vec{r}_{ba\beta\alpha}|^2 = |\langle b1 | \vec{r} | a0 \rangle|^2 \langle \alpha | A^*A | \alpha\rangle . \tag{6}$$

At low temperatures the amplitude of vibration of the atoms is small and a Taylor expansion of $A(\vec{u})$ becomes appropriate. We have already assumed that the constant term in such an expansion is zero, that is that $b0$ and $b1$ are mixed only by lattice vibrations. Quadratic and higher-order terms have been shown to be important at relatively high temperatures.[7] However, we will assume the temperature is low enough so that the linear term predominates,

$$A(\vec{u}) = \sum_{l\kappa\alpha} A(l\kappa\alpha)u_\alpha(l\kappa) . \tag{7}$$

The displacement of ion κ in the lth unit cell in the α direction has been denoted by $u_\alpha(l\kappa)$. Expand $\vec{u}$ in terms of the normal modes of the imperfect crystal,

$$u_\alpha(l\kappa) = \textstyle\sum_d Y(l\kappa\alpha, d)Q_d, \tag{8}$$

where the amplitude of normal mode d is Q_d. Using Eqs. (7) and (8), the matrix element in Eq. (6) can be written

$$\begin{aligned}\langle \alpha | A^*A | \alpha\rangle &= \sum_{l\kappa\alpha} \sum_{l'\kappa'\alpha'} A^*(l\kappa\alpha)A(l'\kappa'\alpha')\\ &\times \sum_{dd'} Y^*(l\kappa\alpha, d)Y(l'\kappa'\alpha', d') \langle \alpha | Q^*_d Q_{d'} | \alpha\rangle .\end{aligned} \tag{9}$$

The matrix element on the right-hand side of Eq. (9) is

$$\langle \alpha | Q^*_d Q_{d'} | \alpha\rangle = \delta_{dd'}(2N_d + 1)\hbar/2\omega_d, \tag{10}$$

where ω_d is the frequency of mode d and N_d is the number of phonons in mode d. If Eqs. (10), (9), and (6) are substituted into Eq. (2) and the indicated thermal average is made, we obtain

$$\begin{aligned}f_{ba} &= (m^*/3\hbar)(E_b - E_a)|\langle b1 | \vec{r} | a0\rangle|^2\\ &\times \sum_{l\kappa\alpha} \sum_{l'\kappa'\alpha'} A^*(l\kappa\alpha)A(l'\kappa'\alpha')\\ &\times \left[\sum_d \frac{Y^*(l\kappa\alpha, d)Y(l'\kappa'\alpha', d)}{\omega_d} \coth\left(\frac{\hbar\omega_d}{2kT}\right)\right] .\end{aligned} \tag{11}$$

Using a convenient representation of the δ function, the quantity in brackets can be written

$$\begin{aligned}&\int \sum_d Y^*(l\kappa\alpha, d)Y(l'\kappa'\alpha', d)\delta(\omega - \omega_d) \coth\left(\frac{\hbar\omega}{2kT}\right) d\omega_d\\ &= \frac{2}{\pi}\int \lim_{\epsilon\to 0}\left(\sum_d \frac{Y^*(l\kappa\alpha, d)Y(l'\kappa'\alpha', d)}{\omega^2 - \omega_d^2 - i\epsilon}\right)\coth\left(\frac{\hbar\omega}{2kT}\right) d\omega .\end{aligned} \tag{12}$$

The quantity in square brackets is the Green's function of the imperfect crystal, $G(l\kappa\alpha, l'\kappa'\alpha', \omega^2 - i\epsilon)$. Substituting Eq. (12) into Eq. (11) we have the final result

$$\begin{aligned}f_{ba} &= (2m^*/3\hbar\pi)(E_b - E_a)|\langle b1 | r | a0\rangle|^2\\ &\times \sum_{l\kappa\alpha}\sum_{l'\kappa'\alpha'} A^*(l\kappa\alpha)A(l'\kappa'\alpha')\\ &\times \int_0^{\omega_L} \lim_{\epsilon\to 0} \operatorname{Im}G(l\kappa\alpha, l'\kappa'\alpha', \omega^2 - i\epsilon)\\ &\times \coth(\hbar\omega/2kT)\, d\omega.\end{aligned} \tag{13}$$

The maximum vibrational frequency of the imperfect crystal has been denoted by ω_L. If there are no localized modes, ω_L is just the maximum phonon frequency of the perfect crystal. ω_L can be used as an upper limit of integration since ImG is zero for all higher frequencies. Remember $A(l\kappa\alpha)$ is the amount of Φ_{b1} mixed into Φ_{b0} when atom l, κ is displaced a unit distance in the α direction. We will assume that the electron-phonon interaction is local. Therefore, only nearest neighbors to the impurity will be allowed to have nonzero A's. The space defined by the displacement coordinates of the impurity and its nearest neighbors will hereafter be called the defect space. It is convenient that we need only those elements of the Green's-function matrix in the defect space, because the submatrix G_0 corresponding to the space of the defect can be written in terms of similar submatrices of the Green's function of the perfect crystal g and the defect matrix δ:

$$G_0 = (1 - g\delta)^{-1}g . \tag{14}$$

The defect matrix has nonzero elements only in the space of the defect. These elements indicate the changes in masses and force constants necessary to define the imperfection. More specifically, the dynamical matrix of an imperfect crystal is obtained by adding the defect matrix to the dynamical matrix of the perfect crystal.[4,5]

III. CALCULATION

There exist several absorption bands in NaCl:Ag that seem to correspond to parity-forbidden transitions between the $4d^{10}$ and $4d^9\,5s$ configurations of Ag^+. Their oscillator strength shows a strong temperature dependence, indicating they are phonon induced. Equation (13) should be applicable to such a transition with some modification. The modification is necessary since $4d^9$ $5p$ states are probably mixed into both the excited and ground states of the transition. In this case the oscillator strength can be written

$$f_{ba}=(2m^*/3\hbar\pi)\,(E_b-E_a)\sum_{l\kappa\alpha}\;\sum_{l'\kappa'\alpha'}C(l\kappa\alpha)C^*(l'\kappa'\alpha')\times\int_0^{\omega_L}\lim_{\epsilon\to 0}\mathrm{Im}G_0(l\kappa\alpha,\,l'\kappa'\alpha',\,\omega^2-i\epsilon)\times\coth(\hbar\omega/2kT)\,d\omega,\tag{15}$$

where

$$C(l\kappa\alpha)=\sum_{\gamma 1,\gamma 2,\gamma 3}\left[A_1(l\kappa\alpha)\,\langle 5p_{\gamma 1}|\,r_{\gamma 2}|\,5s\rangle+A_2(l\kappa\alpha)\,\langle 5p_{\gamma 1}|\,r_{\gamma 2}|\,4d_{\gamma 3}\rangle\right],$$

where A_1 determines the amount of $4d^9 5p$ mixed into the ground state and A_2 determines the amount of $4d^9 5p$ mixed into the excited state. The sum is over all partners γ of the appropriate representation.

The space of the defect is defined by 21 coordinates, the degrees of freedom of the impurity and its nearest neighbors. This number can be considerably decreased if a transformation is made from atomic displacement coordinates $\mu_\alpha(l\kappa)$ to symmetry coordinates $S(m)$. We will not write out the transformation explicitly since formally it requires only a change of notation from $l\kappa\alpha$ to m in Eq. (15). Many of the $A(m)$ and $C(m)$ will be zero through symmetry considerations.

Only symmetry coordinates that transform like Γ_{15} and Γ_{25} will mix the $4d^9 5p$ states into the ground and excited states of the transition. The Γ_{25} symmetry coordinates correspond to the displacements of the four nearest-neighbor atoms perpendicular to the line joining them to the impurity. A typical Γ_{25} symmetry coordinate is shown in Fig. 1. It is plausible that such symmetry coordinates will have relatively small coupling to the electronic states of the impurity because of the noncentral character of the linear interaction. In fact, we will assume that only the p-like Γ_{15} symmetry coordinates contribute appreciably to the phonon-induced absorption. There are three p-like symmetry coordinates (Fig. 1) each of which is threefold degenerate. Since there is some arbitrariness in defining the symmetry coordinates, we will define them to have particular signficance to electron-phonon models. Symmetry coordinate 3 is the only one which will have a nonzero C for the point-ion model. Symmetry coordinate 2 will be the most important if short-range forces predominate in the electron-phonon coupling. Symmetry coordinate 1 will be important only in models where long-range forces play an important role in the coupling.

Since we do not calculate the various C's in Eq. (15) explicitly, we must treat them as free parameters. It is, therefore, advantageous to work with a system where only one symmetry coordinate contributes to the electron-phonon coupling. The single C can then be determined from the oscillator strength at zero temperature. We have already indicated the appropriate single symmetry coordinate for two models.

If we denote the one important symmetry coordinate by I, Eq. (15) can be written

$$f(T)=B\int_0^{\omega_L}\coth(\hbar\omega/2kT)\lim_{\epsilon\to 0}\mathrm{Im}G_I(\omega^2-i\epsilon)\,d\omega\;.\tag{16}$$

B is independent of both frequency and temperature. In the low-temperature limit, Eq. (16) becomes

$$f(T)\to f_0=B\int_0^{\omega_L}\lim_{\epsilon\to 0}\mathrm{Im}G_I(\omega^2-i\epsilon)\,d\omega\;.\tag{17}$$

In the high-temperature limit of small $\hbar\omega_L/2kT$, Eq. (16) becomes

$$f(T)\to B(2kT/\hbar)\int_0^{\omega_L}\left[\lim_{\epsilon\to 0}\mathrm{Im}G_I(\omega^2-i\epsilon)/\omega\right]d\omega,$$

or, using Eq. (17),

$$f(T)\to\frac{2kf_0T}{\hbar}\left(\int_0^{\omega_L}\left[\lim_{\epsilon\to 0}\mathrm{Im}G_I(\omega^2-i\epsilon)/\omega\right]d\omega\Big/\int_0^{\omega_L}\left[\lim_{\epsilon\to 0}\mathrm{Im}G_I(\omega^2-i\epsilon)\right]d\omega\right).\tag{18}$$

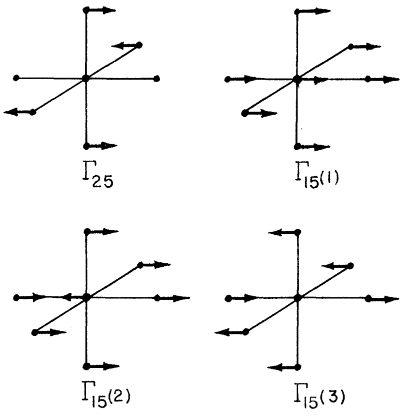

FIG. 1. Symmetry coordinates. Γ_{15} (1) is important only for long-range models. Only Γ_{15} (3) contributes to a point-ion model. Γ_{15} (2) is the most important in an extended-ion model.

Notice that at high temperatures $f(T)$ approaches asymptotically a straight line through the origin. The oscillator strength would have the same high-temperature behavior if we had assumed coupling to one mode of vibration with frequency ω_{eff}. At high temperatures Eq. (1) becomes

$$f(T) \to f_0 2kT/\hbar\omega_{\text{eff}} . \tag{19}$$

Although we see from Eq. (16) that $f(T)$ will not be a hyperbolic cotangent of temperature, such an assumption is often made in fitting experimental data. The effective frequency is used as a parameter in the fitting procedure. If the data clearly shows a high-temperature asymptote, then ω_{eff} is unambiguously defined in terms of the slope of the asymptote. It is useful to obtain an expression for the experimental parameter ω_{eff} in terms of Green's functions. A comparison of the high-temperature result of the exact calculation, Eq. (18), with the high-temperature result for the one-mode approximation, Eq. (19), shows that

$$\omega_{\text{eff}} = \int_0^{\omega_L} \lim_{\epsilon \to 0} \operatorname{Im} G_I(\omega^2 - i\epsilon)\, d\omega \Big/ \int_0^{\omega_L} [\lim_{\epsilon \to 0} \operatorname{Im} G_I(\omega^2 - i\epsilon)/\omega]\, d\omega . \tag{20}$$

The final part of this paper will be a calculation of ω_{eff} using Eq. (20) for two different models and a comparison of the results with experiment for the system NaCl:Ag.

The Green's functions of the imperfect crystal can be found using Eq. (14). In order to use this equation we must have perfect crystal Green's functions and parameters for a realistic lattice defect model. The perfect crystal Green's functions have been calculated using shell model of NaCl. The defect-model parameters have been determined by fitting infrared absorption data.[9] In this model the mass and nearest-neighbor force constant of the Ag^+ impurity were changed. The technique and model are discussed in Ref. 9, which also discusses refinements to this model. The force constant was decreased by approximately 50% in order to fit the infrared resonance at a frequency of 1×10^{13} rad/sec. The inversion of the complex matrix indicated in Eq. (14) and the integrations indicated in Eq. (20) were performed numerically on a computer.

Equation (20) was derived assuming only one of the three p-like symmetry coordinates is important in inducing a transition. We have evaluated the effective frequency for the point-ion symmetry coordinate and for the extended-ion symmetry coordinate. Two very different numbers were obtained. The point-ion ω_{eff} was found to be 2.22×10^{13} rad/sec. The extended-ion ω_{eff} was found to be 1.25×10^{13} rad/sec.

It would be of interest to know how closely the calculated temperature-dependent oscillator strength follows a hyperbolic cotangent curve. We have, therefore, calculated the ratio of Eqs. (16) and (1) for the extended-ion model,

$$R = \frac{f_0 \coth(\hbar\omega_{\text{eff}}/2kT)}{B \int_0^{\omega_L} \lim_{\epsilon \to 0} \operatorname{Im} G_I(\omega^2 - i\epsilon) \coth(\hbar\omega/2kT)\, d\omega} , \tag{21}$$

where B is evaluated using Eq. (17). Clearly this ratio should be equal to one at zero temperature and at very high temperature. For the intermediate region, R is shown in Fig. 2. Apparently $f(T)$ will deviate from a hyperbolic cotangent function by only 2% for the extended-ion model. This would be an unobservable effect in even a carefully performed experiment.

IV. DISCUSSION

The temperature dependence of the oscillator strength for the $4d^{10}$ to $4d^9 5s$ transition in NaCl:Ag has been measured by Fussgänger *et al.*[7] They have observed that the curve does not asymptotically approach a straight line through the origin. They have attributed this high-temperature effect to two-phonon processes. Because of this complication, it was necessary for them to obtain an effective frequency for one-phonon processes from low-temperature data. Such a procedure is meaningful only if $f(T)$ closely approximates a hyperbolic cotangent function. The results shown in Fig. 2 indicate that the procedure was valid and that the effective frequency they obtained can be compared with our calculations.

Several frequencies relevant to this discussion are

ω_{eff} (experiment)	1.24×10^{13} rad/sec
ω_{res} (observed infrared resonance peak)	0.97×10^{13} rad/sec
ω_{eff} (extended-ion model)	1.25×10^{13} rad/sec
ω_{eff} (point-ion model)	2.22×10^{13} rad/sec

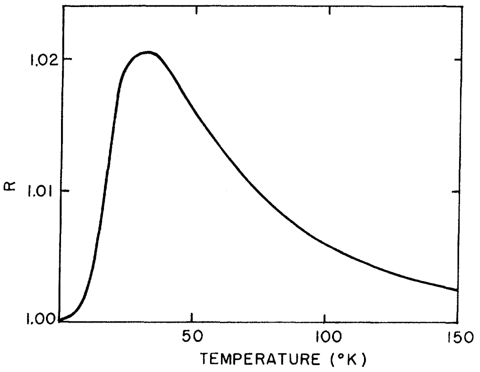

FIG. 2. Deviation of the calculated oscillator strength from a hyperbolic cotangent. R is defined by Eq. (20). An extended-ion model is assumed.

Fussgänger *et al.*[7] compared their experimental value of $\omega_{\rm eff}$, 1.24×10^{13} rad/sec, with the observed frequency of the infrared resonance absorption 0.97×10^{13} rad/sec. This certainly is a logical comparison since the modes of vibration contributing to the infrared resonance have large atomic displacement amplitudes in the vicinity of the impurity. Our calculation shows that a point-ion model will not give an $\omega_{\rm eff}$ in this general frequency region. A calculation consistent with an extended-ion model gives an $\omega_{\rm eff}$ of 1.25×10^{13} rad/sec, in good agreement with the experimental value.

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[1] F. Seitz, Rev. Mod. Phys. 23, 328 (1951).

[2] R. Kubo and Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) 13, 160 (1955).

[3] A. D. Liehr and C. S. Ballhausen, Phys. Rev. 106, 1161 (1957).

[4] A. A. Maradudin, Solid State Phys. 19, 1 (1966).

[5] M. V. Klein, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968).

[6] E. Mulazzi, G. F. Nardelli, and N. Terzi, Phys. Rev. 172, 847 (1968).

[7] K. Fussgänger, W. Martienssen, and H. Bilz, Phys. Status Solidi 12, 383 (1965).

[8] D. L. Dexter, Solid State Phys. 6, 353 (1958).

[9] H. F. Macdonald, Miles V. Klein, and T. P. Martin, Phys. Rev. 177, 1292 (1969).

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Anion-Vacancy Processes Occurring after Room-Temperature *F*-Light Bleaching or Irradiation of NaCl

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The thermally activated processes occurring in the dark after room-temperature F-light bleaching of x- or γ-irradiated NaCl have been investigated. It has been shown that, near room temperature, the concentration of free-anion vacancies decays exponentially with time. The kinetics of the process has been studied by putting the crystal in the dark for a variable time after bleaching and then subjecting it to a short illumination or irradiation pulse which detects the disappearance of the vacancies. It has been observed that the decay in vacancy concentration is closely associated with a decrease in the F'-band intensity and with increases in the F- and M-band intensities. The experimental information has led to the conclusion that vacancies become trapped at F' centers according to a first-order reaction, giving rise to F and M centers through the mechanisms $F' + \text{anion vacancy} \rightarrow 2F$, and $F' + \text{anion vacancy} \rightarrow M$, respectively. The activation energy for the trapping process has been found to be $E = 0.48 \pm 0.06$ eV. These phenomena also occur after an x or γ irradiation, and are shown to provide a coherent picture of the previously reported anomalous coloring behavior appearing at the start of a new irradiation period.

I. INTRODUCTION

It has been shown recently that a thermally activated process takes place in the dark after x or γ irradiation of NaCl.[1–3] This process is responsible for the occurrence of anomalous regions of F coloring upon resumption of the irradiation.[3] It was attributed to the elimination of anion vacancies which remained free at the end of the prior irradiation. The decay in vacancy concentration follows first-order kinetics and was supposed to proceed via trapping at some lattice defects. Although the kinetic parameters for the decay, preexponential factor and activation energy were determined, it was not possible to elucidate the physical nature of the process and identify the defects responsible for the trapping of vacancies.

It is conceivable that the above process could also take place after effective F-light bleaching of the irradiated crystal with the advantage that the number of free-anion vacancies might be higher. Moreover, in this case, the kinetics of the various color centers can be more conveniently investigated in order to try to identify the physical nature of the processes. It is worth noting that although a certain amount of information is available on the evolution of a few color centers after bleaching and irradiation in a variety of alkali halides[4–14] a comprehensive investigation of the simultaneous behavior of all prominent centers (F, F', M, and V)[15] in the dark is lacking for NaCl.

The purpose of this paper is to show the existence of a thermally activated process, after F-light bleaching, whose kinetic behavior is similar to that