

Effects of Random Fields on Radiative Decay of Color Centers

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Transitions which are normally forbidden have been observed in a variety of defects in solids because of the electric fields associated with lattice vibrations or with random impurities. The radiative decay of an F center is a good example of this. We ask in this paper: When will the contribution of random impurities be important, and when will the decay be intrinsic? Several qualitatively distinct examples are analyzed, and tables for the transition probabilities in terms of dimensionless parameters characteristic of the host and the defects are given. Random fields should dominate in III-V and group-IV hosts, but they should prove less important in the alkali halides. Effects of random fields on related phenomena are also discussed.

I. INTRODUCTION

Recent experiments have analyzed the effects of applied electric fields on color centers. The results have included important effects which are interpreted in terms of nearly degenerate s -like and p -like states of the center.

Here, we examine the following two questions: To what extent are the observed properties of the centers intrinsic (i. e., characteristic of a single defect in an otherwise perfect crystal), and how much are they affected by the random defects in real crystals? These questions are not academic, even for the rather pure crystals usually studied, because internal electric fields can be substantial when charged-defect concentrations are only a few parts per million.

Most experiments have been performed on the F center in the alkali halides¹⁻⁴ although analogous effects may occur in silicon. Thus Kleiner and Krag⁵ have argued that internal fields from charged defects may be responsible for the presence of parity-forbidden transitions. In pure ionic crystals, the major contribution to internal fields comes from lattice vibrations, and we shall attempt to compare this dynamic contribution with the static-defect terms.

For simplicity, we shall concentrate on the F center, and we shall discuss the above effects by using a simple model of the type used to analyze experiments. Thus, we assume a $2s$ -like excited state and three degenerate $2p$ -like excited states which are separated from the $2s$ -like state by an energy Δ . We choose Δ positive when the p states are higher in energy than the s state. This model is a gross oversimplification, since we shall not attempt a full discussion of vibronic effects. An exact solution to a vibronic model with strong

coupling to T_{1u} vibrational modes has been reported.⁶ These calculations⁶ suggest that the strong-coupling limit is not likely to account for the observed lifetime of the relaxed excited state of the F center. In addition, a proper treatment of the Jahn-Teller effect might, in any case, obscure the specific problem which we wish to consider.

The model we consider has orbital electronic degeneracy (principally associated with $2p$ states, although accidental degeneracy with the $2s$ state is possible). The Jahn-Teller theorem requires that there will be a distortion which lowers both the energy and the symmetry. Different internal field distributions are relevant, depending upon the strength of the Jahn-Teller coupling. We consider in Sec. II these distributions of internal fields. In Sec. III, we examine their effects on defects. The results are valid for a variety of systems, such as the silicon system of Ref. 5 or the F center. For this reason, we tabulate a number of results which may prove useful elsewhere. In Sec. IV, we discuss those systems for which extrinsic effects are likely to be most important and make comparisons with experiment. We also present in the Appendix asymptotic expansions for the distributions of internal fields.

II. DISTRIBUTIONS OF INTERNAL FIELDS

We are interested in two main cases. First, if there is no Jahn-Teller effect or if it is weak, then we are concerned with the distribution in magnitude of the field, irrespective of its direction. The field not only mixes the states, but determines which p components are mixed. The distribution of electric fields \vec{E} appropriate in this case is written $P_1(E/E_0)$, where E_0 is a characteristic electric field to be defined and where E is the

magnitude of the field \bar{E} .

The second case arises when there is a strong static Jahn-Teller effect. Then we need the distribution of the projection of the internal field along a given direction which we denote by $P_{II}(E/E_0)$. For example, if there is a strong tetragonal distortion, then we should require the projection of the internal field \bar{E} along the tetragonal axis.

For completeness, we include a third case, namely, a Gaussian distribution $P_G(E/E_G)$ of internal fields. Contrary to popular belief, random impurities never give a Gaussian distribution.⁷ However, because the Gaussian form is a limiting case of some distributions which do occur in practice, we also include results for this situation.

Expressions of the distributions $P_I(E/E_0)$ and $P_{II}(E/E_0)$ are available in the literature.⁷⁻⁹ The assumptions involved in these calculations are (i) that the defects which produce the internal fields are distributed randomly, (ii) that nonlinear effects may be ignored, and (iii) that the host lattice can be regarded as an isotropic dielectric continuum. These assumptions should be valid for the systems under consideration. The assumption which usually causes the most difficulty is that of randomness. The results do not include the constraint that no two charged defects can occupy the same site. Hence, the results will be in error at high concentrations; in practice this means at concentrations of more than a few atomic percent—much larger than necessary for the systems of interest in this paper, but an experimentally accessible regime.

The distribution of the magnitude of the field, irrespective of direction, is given by Chandrasekhar⁸:

$$P_I(y) = (2/\pi y) \int_0^\infty dx x \sin x e^{-(x/y)^{3/2}},$$

where $y = E/E_0$ and E_0 is the characteristic field,

$$E_0 = (2\pi/\epsilon_0) \left(\sum_\alpha \frac{4}{15} \rho_\alpha |Z_\alpha e|^{3/2} \right)^{2/3}.$$

In this expression ϵ_0 is the static dielectric constant and ρ_α is the number of defects of species α per unit volume with charge $Z_\alpha |e|$ relative to the perfect lattice. The distribution $P_I(y)$ has a maximum value at $y = 1.61$.

The distribution in the magnitude of the projection of \bar{E} along a specific direction is given by Mims and Gillen⁹:

$$P_{II}(y) = (1/\pi y) \int_0^\infty dx \cos x e^{-(x/y)^{3/2}}.$$

The symbols have the same meanings as before. Both P_I and P_{II} are known as Holtsmark functions. The function $P_{II}(y)$ is symmetrical about $y = 0$ and has a full width at half-intensity of about $\Delta y_{1/2} = 2.88$.

The characteristic field E_0 is the important

parameter. Its value for an alkali halide with nearest-neighbor distance $a \times 10^{-8}$ cm and for a fractional concentration of f parts per million of defects with Z equal to 1 is

$$E_0 = (f^{2/3}/\epsilon_0 a^2) 2.36 \times 10^5 \text{ V/cm}.$$

For KCl, where $a = 3.14$ and $\epsilon_0 = 4.67$, this characteristic field is $f^{2/3} \times 0.513 \times 10^4$ V/cm. Substantial fields can occur with modest defect concentrations.

The distribution of fields for those cases in which a Gaussian distribution is appropriate has the form

$$P_G(y) = \pi^{-1/2} e^{-y^2/4},$$

where $y = E/E_G$ and E_G is a characteristic field of the phenomenon giving rise to the distribution P_G .

Static strains and field gradients from all defects may be important for closely spaced energy levels. But if the $2s$ and $2p$ states have a similar radial extent, then it seems likely that these effects will shift both levels by similar amounts and that this will not have a significant effect on the observed properties.

We emphasize that these internal fields vary appreciably over distances comparable with the separations of the charged defects which produce them. Thus, the internal field can be assumed constant over each individual center of interest, e. g., an F center.

III. EFFECTS OF RANDOM FIELDS

A. Radiative Decay

The observable properties of immediate interest involve the radiative decay of an excited F center to a $1s$ -like state and the thermal excitation of the center to higher excited states or the conduction band. The effects on these properties include (a) the change of the radiative lifetime for the $2s \rightarrow 1s$ transition due to the admixture of $2p$ states into the $2s$ state and (b) the change of the measured activation energies due to three main effects: the shift of energy levels due to the $2s$ - $2p$ admixture, the interference between the static electric field and the intrinsic phonon field in the matrix element causing a transition, and the fact that all F centers are not equivalent. When random fields are present, a distribution of characteristic decay times and activation energies will occur to complicate the kinetics.

The change in the lifetime of a $2s$ state due to the admixture of a $2p$ state is determined by the ratio of the matrix element $\langle 2s | eEz | 2p \rangle$ to the energy separation Δ . We define

$$\Lambda = E_0 \langle 2s | eEz | 2p \rangle / \Delta \quad (1)$$

as a dimensionless parameter which characterizes

the admixture. When the 2s state is lowest, its decay rate to the ground 1s state becomes the factor

$$\phi(y, \Lambda) = \frac{1}{2} \{1 - [1 + (2y\Lambda)^2]^{-1/2}\}, \quad (2)$$

times the decay rate for the pure p state. Here $y = E/E_0$, as given earlier. We assume here that the field does not affect the details of the $|2s\rangle$ or $|2p\rangle$ states. This should be a valid first approximation. The result when the $2p$ state is lowest is trivial to derive. The minus sign in Eq. (2) becomes a plus sign. Absorption experiments suggest that for the F center in KCl the 2s state lies above the $2p$ state.¹⁰ Emission experiments¹⁻⁴ for the F center indicate that the 2s state is lower than the $2p$ state. Most theories confirm this,¹¹⁻¹³ although the accuracy of even the best of these is less than the observed splittings. Sak¹¹ has shown that, for the weakly coupled bound polaron, the 2s state is lower than the $2p$ state. However, for other systems to which these results apply, the s state may be higher in energy. An example might be a system for which the 3s state is about one longitudinal-optic phonon energy above the $2p$ state. The resonant interaction could push the $|3s\rangle$ above the $|3p\rangle$ to give a p state below the corresponding s state. Similar resonances have been discussed by Larsen.¹⁴

The s - p admixtures can occur also in absorption. One of the earliest models for the K band associated with an F center concerned transitions to s states which are rendered allowed by a p -state admixture. This model is now thought improbable,¹⁵ so we shall not consider it further.

Two points stand out immediately about Eq. (2). First, it is nonlinear. Hence, we should average it over the various distributions of internal fields. Second, because it is nonlinear, the effects of static internal fields and the phonon fields are not simply additive.

B. Averages for Radiative Decay

In calculating radiative lifetimes we need to average $\phi(y, \Lambda)$ over the distributions of internal fields. We express the averages of $\phi(y, \Lambda)$ in the form

$$\phi(y_{\text{eff}}, \Lambda) = \langle P(y)\phi(y, \Lambda) \rangle. \quad (3)$$

Thus, the effective internal field, which is the unique field chosen to give the same decay rate, is

$$E_{\text{eff}} = y_{\text{eff}} E_0. \quad (4)$$

Table I shows the values of y_{eff} for the three distributions defined in Sec. II. The distributions $P(y)$ are given by infinite integrals, so the averages over y in Eq. (3) present some problems. Parts of the integrals can be performed analytically in terms of modified Bessel functions. Near $y = 1$,

they can be integrated directly by Gaussian quadratures. Asymptotic expansions are needed for very small or large y and these are listed in the Appendix. Such expansions are likely to be useful outside the context of this section.

IV. EXPERIMENT AND INTERNAL FIELDS

Here we try to assess the importance of internal electric fields and the cases in which their effects should be apparent. The standard for comparison usually is the internal field from lattice vibrations in ionic crystals. This is absent in the covalent crystals for which the radiative decay of 2s-like states to lower s -like states has been observed.

The lattice vibration term differs from the defect contribution in two major ways. First, it is a dynamic term, rather than a static term. It also depends upon temperature. A proper treatment of the vibronic problem is still needed. Second, the static defect field is essentially constant over the color center of interest. But the phonon field contains terms from all wave vectors. The phonons with wavelengths much less than the effective radius of the electronic states give a negligible contribution to the matrix element. This distinction may be made as follows: We assume 2s and 2p functions whose radial dependence is of the form $re^{-\beta r}$. If the field varies slowly over the wave function, then

$$|\langle 2s | e E(r) z | 2p_z \rangle|^2 \sim \langle e^2 E^2 \rangle / 4\beta; \quad (5)$$

i. e., the matrix element factorizes. But, if one evaluates the corresponding term using the Fröhlich interaction, one obtains [Ref. 16, Eq. (17)]

$$\{0.044 (\hbar\omega)^2 (\hbar/2m\omega)^{1/2} \alpha\} \beta, \quad (6)$$

where ω is the radial frequency of the longitudinal optic phonon, α is the Fröhlich coupling constant, and m is the effective mass for the conduction band. The dependence on β is most significant. It

TABLE I. Values of y_{eff} , for which $\phi(y_{\text{eff}}, \Lambda) = \langle P(y)\phi(y, \Lambda) \rangle$. The Λ parameter is $E_0 \langle 2s | ez | 2p \rangle / \Delta$ in case 1 [small Jahn-Teller effect and static field, $P(y) = P_I(y)$] and in case 2 [large Jahn-Teller effect and static field, $P(y) = P_{II}(y)$]; Λ is $E_G \langle 2s | ez | 2p \rangle / \Delta$ in case 3 for Gaussian distributions, $P(y) = P_G(y)$.

$ \Lambda $	Case 1	Case 2	Case 3
100	0.86	0.26	0.26
25	0.87	0.26	0.26
10	0.88	0.28	0.28
2.5	0.91	0.39	0.38
1.0	1.02	0.54	0.51
0.25	1.36	0.83	0.66
0.10	1.70	1.07	0.70
Values of y for comparison	$y = 1.61$ at peak of $P_I(y)$	Full width at half-intensity, $\Delta y_{1/2} = 2.88$	Full width at half-intensity, $\Delta y_{1/2} = 3.33$

is as if the mean square phonon field is reduced by a factor proportional to β^3 . For a diffuse wave function, the phonon contribution for shorter wavelengths diminishes rapidly compared with that for phonons whose variation over the color center is small. Thus for the numerical wave functions obtained by Bennett,¹⁷ the reduction in the effective phonon field is about three orders of magnitude. Unfortunately, wave functions are not available for some of the best current calculations (e. g., Wood and Öpik¹²). However, quoted parameters suggest a substantial effect is probable. Values of the effective phonon fields E_{ph} in absorption lie between 10^5 and 4×10^5 V/cm in KCl for the various systems we have considered. Rather lower results are appropriate in emission. These results are theoretical in some cases (Bogan and Fitchen,¹ Fowler,¹⁶ and present work using Bennett's wave functions,¹⁷), or they are obtained from the analysis of experiments (Bogan and Fitchen¹ from the Stark effect in emission, and Loader¹⁸ from the temperature dependence of the moments in absorption). The differences depend on the detailed assumptions about the coupling, the wave functions and the $2s$ - $2p$ separation.

The third parameter which we need is $E_M \equiv \Delta / \langle 2s | e z | 2p \rangle$. When E_M is much larger than the defect field or the phonon field, then the admixture is small. Values vary from a few times 10^5 V/cm to more than 10^6 V/cm. Most of the uncertainty comes from the energy difference Δ . Theory can give both the $2s$ and $2p$ energies separately with fair accuracy, but it is grossly unrealistic to expect the energy differences of order 0.01 eV to be given with high relative accuracy. Indeed, we doubt if any available theory is accurate to better than 0.05 eV in each level separately and 0.1 eV in the difference. Even the sign of the difference should not be considered certain when it is determined by theory alone. The relative errors in the wave functions are probably less because no cancellation of large parts is involved. Probably the best solution is to use the experimental value of Δ with theoretical matrix elements. This approach leads to values of E_M in the same range as E_{ph} , i. e., 1×10^5 to 5×10^5 V/cm when the matrix elements due to Wood and Öpik,¹² Fowler,¹⁶ and Bennett¹⁷ are used.

The following criteria must be satisfied in order for the internal defect fields to be important. First, the defect field should be significant in magnitude compared with the phonon field. Hence, we need $E_0 \geq 0.25 E_{ph}$, for example. The factor 0.25 is arbitrary but is chosen to ensure that the effects can be observed. Second, in order to observe the decay rates, we need E_M to be much larger than E_{ph} .

If this condition is violated, then the mixing is

already large and the extra fields will have little effect. When we are interested in the energy shifts, we should require $E_0 \sim E_M \gg E_{ph}$.

Examining our results in the light of these criteria, we note the following: (i) In KCl, the field values for the F center in emission are in the ranges

$$E_0 \sim 2 \times 10^4 \text{ V/cm},$$

$$E_{ph} \sim 10^5 - 4 \times 10^5 \text{ V/cm},$$

$$E_M \sim 10^5 - 5 \times 10^5 \text{ V/cm},$$

for about 5 ppm charged impurities. Thus, we do not expect defect fields to be important in the very pure crystals used in these experiments.

(ii) It is likely that defect fields are important in other systems for which the wave function is more extensive (i. e., ϵ_0 and ϵ_∞ are larger) and for which the phonon contribution is less (i. e., a smaller Fröhlich coupling constant). Thus, the valence crystals III-V and II-VII semiconductors and the silver halides are possible hosts. Indeed, Kleiner and Krag⁵ appear to have observed these phenomena already in silicon.

The importance of random fields is very sensitive to the host. We demonstrate this by taking the ratio of Eq. (5), evaluated for random fields, to Eq. (6) for phonon fields. We write $\beta = \beta_0/a_0$ in order to scale reasonably, where a_0 is the effective Bohr radius for $\epsilon = \epsilon_0$ and m is equal to the polaron mass. The ratio of Eq. (5) to Eq. (6) is then of the form $\Phi f^{4/3}/\beta_0^3$, where Φ depends only on the host. The values of Φ for five hosts are as follows: KCl, 2.5×10^{-4} ; AgCl, 1.5×10^{-2} ; AgBr, 6.8×10^{-2} ; GaAs, 136.5; InP, 42.5. The point we emphasize here is that the effects of random defect fields may be rather common; the lifetimes of forbidden transitions are probably not intrinsic properties in a number of cases.

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APPENDIX: ASYMPTOTIC EXPANSIONS FOR THE DISTRIBUTIONS P_I AND P_{II}

The asymptotic forms of $P_I(y)$ are

(i) $y \ll 1$,

$$\frac{4}{3\pi} \left(y^2 - \frac{\Gamma(10/3)}{6} y^4 + \frac{\Gamma(14/3)}{120} y^6 + \dots \right);$$

(ii) $y \gg 1$,

$$\frac{15}{8} \left(\frac{2}{\pi} \right)^{1/2} y^{-5/2} + \frac{24}{\pi} y^{-4} + \frac{10395}{384} \left(\frac{2}{\pi} \right)^{1/2} y^{-11/2} + \dots$$

The first term in each of these series appears also in Ref. 19. Similar results for $P_{II}(y)$ are

(i) $y \ll 1$,

$$\frac{4}{3\pi} \left(\frac{\Gamma(2/3)}{2} \right) - \frac{y^2}{4} + \left(\frac{\Gamma(10/3)}{48} \right) y^4 + \dots,$$

(ii) $y \gg 1$,

$$\frac{3}{8} \left(\frac{2}{\pi} \right)^{1/2} y^{-5/2} + \frac{3}{\pi} y^{-4} + \frac{945}{384} \left(\frac{2}{\pi} \right)^{1/2} y^{-11/2} + \dots$$

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Identification of Optical-Absorption Bands in uv-Irradiated Potassium Azide

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The optical-absorption bands of uv-irradiated potassium azide are correlated with the electron-spin-resonance (ESR) spectra of previously identified defects by comparison of thermal annealing kinetics. The bands which peak at 580, 700, and 780 nm are attributed to the N_4^- defect, since their annealing kinetics are identical, with an activation energy of 0.92 ± 0.09 eV. The thermal conversion of the 565-nm band to the 580-, 700-, and 780-nm bands closely resembles that of the N_2^- defect to the N_4^- defect, and, accordingly, the 565-nm band is tentatively attributed to the N_2^- defect. The activation energy for the thermal conversion of the optical spectrum is 0.70 ± 0.05 eV. No ESR spectrum could be correlated with the 360-nm band, which annealed below 140 K. All of the observed optical transitions are polarized perpendicular to the c axis. Models are proposed for the electronic structure of N_2^- , and of N_4^- in a rectangular conformation, which account qualitatively for the observed optical and ESR spectra.

I. INTRODUCTION

Color centers can be produced in the alkali azides (NaN_3 , KN_3 , RbN_3 , and CsN_3) by uv light and ionizing radiation. The phenomenon has been of interest for some time in that the defects produced are thought to be involved in the process of photochemical decomposition.^{1,2} It is therefore important that the nature of the color centers be understood in order to illuminate the mechanism of photochemical decomposition.

The object of this study is to attempt to identify

the optical-absorption bands in uv-irradiated KN_3 by means of a detailed comparison of the properties of the paramagnetic defects and optical-absorption bands that have been observed. The nature of the thermal annealing kinetics of both the electron-spin-resonance (ESR) and the optical spectra are compared and the optical bleaching properties determined. The characteristics of the growth of the spectra with dosage and intensity of the uv light are investigated. The optical-absorption spectrum is interpreted in terms of the electronic structure of the paramagnetic defects.