3(c). In this regime the extrinsic photocurrent is the sum of that shown in Figs. 3(b) and 3(c) and is shown in Fig. 3(d).

Summarizing, we conclude that the shape of the spectrum of extrinsic photocurrent at 4 K and the change of this spectrum in going to 77 K support the donor-acceptor pair recombination model of PW rather than that of RS.

ACKNOWLEDGMENT

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PHYSICAL REVIEW B VOLUME 4, NUMBER 4 15 AUGUST 1971

"Off-Center" Effect in the Relaxed Excited State of Cu^+ Substitutional in Alkali Halides

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Lifetime data on the $3d^9 4s \rightarrow 3d^{10}$ forbidden transition of the substitutional Cu^+ ion in several alkali halides are reported. From a detailed study of the temperature dependence of τ and the comparison with the known data on the temperature variation of the oscillator strength, $f(T)$, it is concluded that the position in the lattice of Cu^+ in the relaxed excited state and in the ground state may or may not be the same. In particular, it should be the same in the alkali iodides and NaCl, but different in the alkali bromides and KCl and RbCl.

I. INTRODUCTION

In recent years there has been considerable attention given to the change in ionic and electronic properties in crystals in which substitutional impurity ions occupy "off-center" positions. A quite comprehensive review, with complete references, has been written by Smoluchowski.[1]

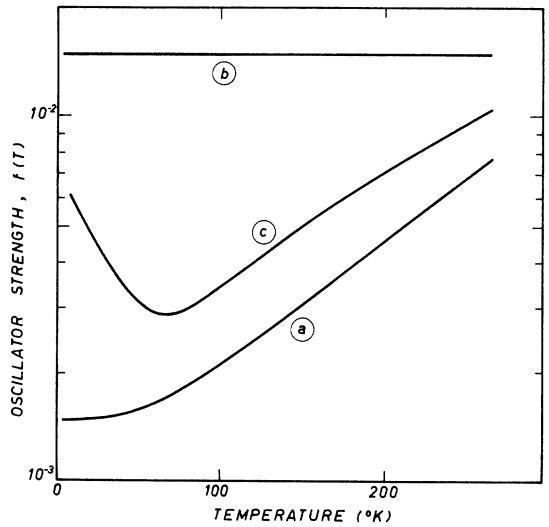

FIG. 1. Possible types of temperature dependence of the oscillator strength (schematic).

At present, we are interested in the electronic properties and, in particular, in the $3d^{10} \rightarrow 3d^9 4s$ dipole forbidden transition of Cu^+ in alkali halides. This transition, and the analogous one in Ag^+, has already been studied extensively by absorption, and several interesting conclusions have been reached. When the substitutional ion sits in the regular lattice position, as Ag^+ usually does, the dipole forbidden transition is made possible by odd lattice vibrations which dynamically mix the initial and final wave functions with different-parity wave functions. The oscillator strength f is of the order of 10^{-3} and has a strong temperature dependence essentially of the type $f(T) = f(0)\coth(\hbar\omega/2kT)$, as shown in Fig. 1(a). When the substitutional ion sits in an off-center position, there is still the dynamical effect but the static mixing is much stronger because of the lack of inversion symmetry. In these cases, typically in Cu^+ in K and Rb halides, the oscillator strength is of the order of 10^{-2} and essentially temperature independent as in Fig. 1(b). A third interesting case occurs in RbCl : Ag and RbBr : Ag. In these crystals, f (at high temperatures) has a temperature dependence of the hyperbolic cotangent type, but below a critical temperature (60 °K in RbCl : Ag) it increases again. It has been demonstrated[2] that at low temperatures Ag^+ is off center, and so the increase in f would be explained. Deviations from these behaviors have been discussed,[3] but the curves we draw schematically in Fig. 1 refer to the typical cases.

Theoretically, the reasons for the instability of the substitutional impurity ions in the regular lattice position have been investigated by several authors.[4–6] What we know is that there are stabilizing and destabilizing contributions to the energy of the ion, the ion's polarizability being the main member of the second species and the repulsive energy the principal factor for maintaining the "status quo."

Due to these considerations and to earlier measurements performed in our laboratory[7] we thought that in the excited state, since the ionic radius and the ion polarizability of Cu^+ are modified, the energy balance should be modified as well, and the minimum energy position could be different from that of the ion in its electronic ground state. Parallel to an effort directed to the detailed analysis of $f(T)$ and the spectrum of Cu^+ in Rb and Na halides,[8] we have measured the excited-relaxed-state lifetime τ of several alkali halides in the temperature range 4.2–300 °K. The physical quantity of interest, $1/\tau(T)$ (the total decay probability of the excited state), is for the emission process, as it is well known, analogous to $f(T)$ for the absorption, and so the same type of discussion can be made. Here we want to report on the data we obtained since, to our knowledge, they are the first off-center effects on the excited-relaxed state known. Further, the results are interesting and confirm our assumption that in the excited-relaxed state the ion position can be different from that of the ion in its electronic ground state.

II. EXPERIMENTAL

A. Techniques

The technique with which the $\tau(T)$ measurements were performed has been described before.[7] In excitation a Baird atomic interferential filter centered at 2600 Å was used, and in emission, a combination of glass filters whose transmission was centered at 3900 Å, was used. Measurements were taken while the crystal holder was slowly warming up (2–3 h from 4.2 to 80 °K). Crystals were doped by a diffusion technique and quenched from 600 °C before each run. Absorption was controlled with a Cary 14 spectrophotometer.

Due to the fact that, particularly at low temperatures, the lifetime turned out to be very long and comparable to the preamplifier clipping time, we found it essential to analyze with a computer and with a best-fitting program the decay curves we photographed from the oscilloscope screen. We first analyzed the signal obtained when the light from the flashlamp hit the photocathode of the photomultiplier directly. This signal $V_1(t)$, which is given by the superposition of two exponential curves, has the following form:

$$V_1(t) = [A_1/(\tau_1 - \tau_2)](\tau_1 e^{-t/\tau_2} - \tau_2 e^{-t/\tau_1})$$

in which A_1 is an amplitude factor and the time constants τ_1 and τ_2 depend from the circuital pa-

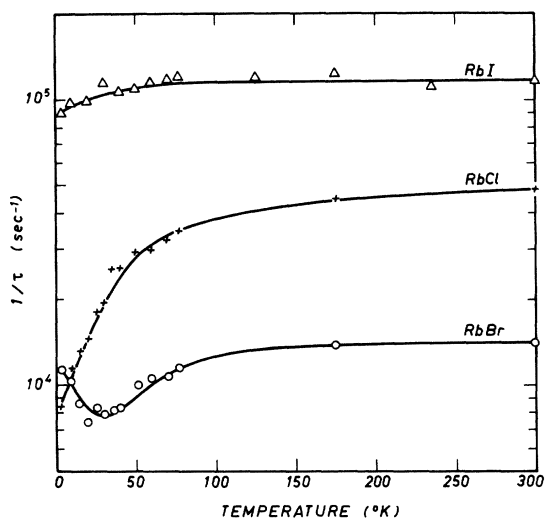

FIG. 2. Temperature dependence of $1/\tau(T)$ for the $3d^9 4s \rightarrow 3d^{10}$ transition in substitutional Cu^+ in RbCl, RbBr, and RbI.

rameters. After obtaining τ_1 and τ_2 we studied the luminescent decay at several temperatures. The curves we analyzed can be written as

$$V_2(t) = A_2\tau_1\tau_2\tau\left(\frac{e^{-t/\tau_1}}{(\tau_2-\tau_1)(\tau_1-\tau)} + \frac{e^{-t/\tau_2}}{(\tau_1-\tau_2)(\tau_2-\tau)} + \frac{e^{-t/\tau}}{(\tau_1-\tau)(\tau-\tau_2)}\right),$$

where τ is the constant in which we were interested.

B. Results

In Fig. 2 we see $1/\tau(T)$ for Cu^+ in RbCl, RbBr, and RbI. Absorption data[8] tell us that $f(T)$, in all the cases considered here, behaves as curve (b) in Fig. 1; in other words it appears that in all these crystals Cu^+ is off center in its electronic ground state. $1/\tau(T)$ in RbI seems to suggest that Cu^+ is probably off center also in the excited-relaxed state. The curve, in fact, is comparable with curve (b) of Fig. 1 because it is essentially temperature independent: A small decrease of $\simeq 25\%$ is observed below 50 °K. We further observe that the absolute value of $1/\tau$ is the highest with respect to the other two crystals. In RbCl there is a strong temperature dependence of $1/\tau$ (a factor of 6 from 4.2 to 300 °K): In this respect there is a relationship to curve (a) in Fig. 1. On the other hand, $1/\tau$ in RbCl apparently does not behave as an hyperbolic cotangent: The tangent at 0 °K to the curve with which we interpolate the experimental data does not seem to be parallel to the abscissa. In RbBr two facts are worthy of notice. First, the value of $1/\tau$ in the high-temperature range (100 °K) is very low compared with RbI and RbCl, and second, in the low-temperature range there is a well-defined behavior of the type in Fig. 1(c) with a minimum at $\simeq 30$ °K.

The data of Figs. 3 and 4 on the K and Na halides, respectively, are very similar to those shown in Fig. 2. We note again the independence of $1/\tau$ from temperature in the iodides, the strong temperature dependence near 0 °K in the chlorides, the minimum in the $1/\tau$ curve for KBr at $\simeq 20$ °K, and that NaBr and KBr have the lowest $1/\tau$ values in the respective series. The values of $1/\tau$ at 300 and 4.2 °K in all nine alkali halides we studied are collected in Table I. We remember that in all of the potassium halides,[3] and in NaI,[8] $f(T)$ is very weakly temperature dependent [essentially behaving as curve (b) of Fig. 1]. In NaCl, $f(T)$ has a fairly strong temperature variation from 4.2 to 300 °K.[3] In NaBr,[2] below 80 °K, $f(T)$ increases considerably, being constant in the upper temperature range, from 80 up to 300 °K; this behavior is different from all others shown in Fig. 1.

III. DISCUSSION

The main features of our $1/\tau(T)$ data are the following: (a) At $T > 100$ °K in all the crystals studied $1/\tau(T)$ is very weakly temperature dependent (in the iodides also below 100 °K); (b) in the chlorides at $T < 100$ °K, $1/\tau(T)$ has a strong temperature dependence; (c) in RbBr and KBr, at low temperatures, $1/\tau(T)$ shows the typical behavior due to an

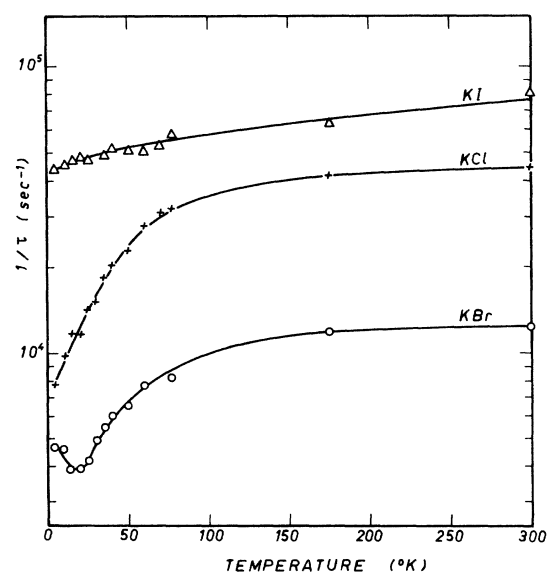

FIG. 3. Temperature dependence of $1/\tau(T)$ for the $3d^9 4s \rightarrow 3d^{10}$ transition in substitutional Cu^+ in KCl, KBr, and KI.

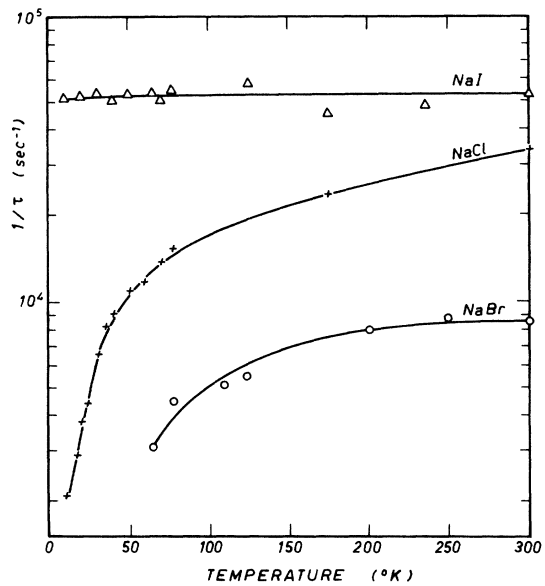

FIG. 4. Temperature dependence of $1/\tau(T)$ for the $3d^9 4s \rightarrow 3d^{10}$ transition in substitutional Cu^+ in NaCl, NaBr, and NaI.

ion moving in an off-center potential well; (d) the bromides have the lowest $1/\tau$ values in the respective series.

From our data and the preceding remarks, we can confidently state that Cu^+ in the iodides is off center in the relaxed-excited state also. However, we cannot say whether or not the displacement from the regular lattice position is the same as in the ground state. Our $1/\tau(T)$ curves for the chlorides bear a strong resemblance to the dipole strength curve for NaCl.[3] In all these cases the experimental points near 0 °K can hardly be interpolated with a hyperbolic cotangent curve such as $\coth(\hbar\omega/2kT)$, unless we choose a very low ω. Weber and Nette[9] measured a resonance frequency at 23.7 cm^{-1} in NaCl : Cu (frequency here measured in wave-number units). Making use of this value and taking into account an off-center effect, a linear electron-phonon interaction, and a quartic anharmonicity of the resonance mode, the dipole-strength data in NaCl could be fit quite well. The physical meaning of such a fitting is that "the Cu^+ ion in NaCl vibrates in a rather flat double-well potential where the first vibrational level lies over the potential barrier."[3] Following the proposal of Füssgaenger we can suggest that in NaCl the position of the ion does not change much from the ground to the relaxed-excited state. In KCl and RbCl, Cu^+ is clearly off-center in the ground state but in the relaxed-excited state the wells of the potential become rather flat and the ion, on the average, occupies a more central position. The role of phonons in making the transition possible becomes, therefore, more important.

TABLE I. Measured values of $1/\tau$ (units of 10^3 sec^{-1}) for the $3d^9 \rightarrow 3d^{10}$ transition of the substitutional Cu^+ ion in several alkali halides.

	Cl	Br	I	°K
Na	33	8.3	53.7	300
	2.1		52	10
K	44.4	12.3	81.2	300
	7.7	4.65	43.6	4.2
Rb	47.7	14.1	115	300
	8.45	11.2	90	4.2

The explanation within this framework is straightforward concerning the bromides. In the bromides the wells of the double-well potential are deeper than in the chlorides; below a certain temperature, Cu^+ remains trapped in one of the wells and $1/\tau(T)$ increases. This is due to the "static" mixing promoted from the lack of center of symmetry or, in other words, from the off-center position.

In conclusion, we can say that it is most probable that Cu^+ in KCl, RbCl, and the bromides occupies a different position in the lattice whether or not it is in the ground state or in the relaxed-excited state. In the iodides it is very likely that Cu^+ remains off center and in NaCl that it remains in the flat double-well potential both in the ground and in the relaxed-excited state.

A theoretical effort to test our proposals both from the qualitative and quantitative points of view seems very useful. More complicated potentials should be investigated in relation to the possible influence on the temperature behavior and magnitude of $1/\tau(T)$. The possibility of going from an off-center position, say, in the $\langle 111 \rangle$ direction to an off-center position in the $\langle 100 \rangle$ direction, and the stability of these configurations with changing temperature might also give a hint to the interpretation of our data. It would also be interesting to know the reason why the bromides have lower $1/\tau$ values than the chlorides. This problem seems of particular interest in view of the fact that in other cases, also, the bromides behave in a way qualitatively different from the chlorides.[1,2]

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Intermediate Coupling Theory: Padé Approximants for Polarons*

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A general method is presented for obtaining an accurate intermediate-coupling theory from weak- and strong-coupling perturbation theory. The method uses two-point Padé approximants to extrapolate (low-order) expansions about the weak- and the strong-coupling limits into the intermediate-coupling regime. The method is used to evaluate the ground-state energy and effective mass of the polaron with gratifying success. In addition, the weak-coupling perturbation theory of the polaron dispersion relation, ground-state energy, and effective mass are extended to fourth, sixth, and fourth order, respectively. A scheme based on two-point Padé approximants is used to obtain an optimal polaron dispersion relation.

I. INTRODUCTION

A typical problem of theoretical physics is the accurate evaluation of perturbation expansions in the intermediate-coupling regime; that is, for strengths of the perturbation which are not small enough to guarantee either convergence of the series or an accurate asymptotic approximation to it. In some cases it is possible to obtain perturbation expansions about the weak- and strong-coupling limits, but there is no simple scheme for obtaining accurate perturbation expansions for intermediate values of the coupling constant. In this paper we present a systematic procedure for obtaining intermediate-coupling expansions, and we use this procedure to obtain adequate expressions for the ground-state energy and the effective mass of a polaron—an electron interacting with the longitudinal-optical-phonon mode of a polar insulator.[1-3]

The procedure for evaluating intermediate-coupling perturbations consists of obtaining a two-point Padé approximant[4-6] to both the weak-coupling[7] ($\alpha=0$) and the strong-coupling[8] ($\alpha=\infty$) expansions. This procedure is complementary to existing variational theories of intermediate coupling[9-14] in that it provides a simple (albeit unphysical) method for deducing intermediate-coupling results from a knowledge of the weak- and strong-coupling expansions. In principle the two-point Padé method, carried to sufficiently high order, should be capable of attaining the intermediate-coupling results to any degree of accuracy. While the variational methods require physical insight in the choice of trial functions, the Padé method only requires labor in evaluating the power series about $\alpha=0$ and $\alpha=\infty$. Although the variational method can, for example, guarantee that a calculated energy is an upper bound of the true energy; the Padé method makes no such claims,[15] but should be able to locate singularities in the perturbation expansion as a function of coupling constant. In addition, the Padé method is even capable of suggesting the nature of the singularities (i.e., poles, cuts, etc.).

The two-point Padé method is, of course, an extension of the one-point Padé approximant method which has found considerable success in various branches of physics.[16] Such Padé approximants have been used in the study of interacting hard-core bosons,[17] in investigations of Regge-pole trajectories,[18] in phase-transition theories (to predict critical behaviors),[19] and in theories of the anharmonic oscillator,[20] van der Waals interactions in helium,[21] oscillator strengths,[20,22] and exciton migration.[23] In all of these theories the essential role of the Padé approximant is to provide a method for analytically continuing power series; in all cases the Padé approximant seems to provide an almost unbelievably good representation of the