

Aggregation of Divalent Impurities in Sodium Chloride Doped with Cadmium*†

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The occurrence of remarkable precipitation phenomena of Cd additions in NaCl single crystals is studied by means of ionic thermoconductivity. An excess of impurity-cation vacancy dipoles anneals following monomolecular third-order kinetics, at temperatures ranging from 275 to 324°K. The motion parameters have been determined and are discussed. A careful investigation shows that the kinetics is more complicated during the first stage of the precipitation process.

1. INTRODUCTION

THE results of Rabin¹ show that the NaCl:CdCl₂ system has an atypical behavior in comparison with NaCl doped with other divalent metallic impurities. The relative linear expansion of x-irradiated NaCl:CdCl₂ versus *F*-center concentration resembles very closely that of the pure crystals; moreover, Cd impurities are ineffective in enhancing crystal colorability. These phenomena are probably due to the fact that Cd does not enter as a dissolved impurity into the host lattice: In fact, the CdCl₂ solubility at low temperatures is very low² and the mobility of Cd ions is high^{3,4}; these results indicate the existence of remarkable precipitation phenomena. This has been shown by x-ray diffraction measurements performed by Suzuki⁵ in the solid solution NaCl:CdCl₂ with impurity contents greater than 1 mole %.

In the present work we study the precipitation process in the impurity range usually covered in doped alkali halides (10⁻²–10⁻¹ mole %). It is well known that in these materials the foreign cations can be present either as single substitutional ions or as impurity-vacancy (IV) dipoles. The standard methods employed to observe the precipitation of impurities are: (1) EPR for paramagnetic impurities like Mn in NaCl^{6,7}: This technique is particularly useful because it allows one to follow the behavior of associated and free impurities at the same time. (2) Dielectric losses: These are as a rule useful for all divalent impurities.⁸ However, in the case of NaCl:CdCl₂, the peak which appears in the dielectric-loss plot versus the frequency and which is due to dipolar relaxation is not well resolved. It is doubtful

that it can be identified with a simple Debye peak,² i.e., the relaxation process is not characterized by a single relaxation time. Moreover, the Debye peak of Cd complexes can be observed only at relatively high temperatures, but under these conditions the precipitation process takes place at too high a rate.

We have studied the variations of dipole concentration for NaCl doped with Cd (Cd²⁺ is not paramagnetic) by means of the ionic thermoconductivity (ITC).⁹

2. EXPERIMENTAL PROCEDURE

The samples used were grown in our laboratory by means of the Kyropoulos method in controlled atmosphere (dry nitrogen) in order to minimize contamination by OH, H₂O, and oxygen, which are present in air and affect the precipitation phenomena.¹⁰ CdCl₂ salt was added to the molten NaCl in percentages ranging from 2×10⁻⁴ to 2×10⁻² in weight. Colorimetric analysis was employed to determine the concentration of Cd impurity in crystals. The aqueous solution of the salt was brought to pH 8.5 by addition of NH₄OH and extracted with 5 cc of dithizone 0.01% in chloroform. The optical density of the extract was then measured with the spectrophotometer at 5200 and 5400 Å. This simplified procedure was possible because it was ascertained by previous measurements¹¹ that the total content of Co, Cu, Mn, Ni, Zn, and Pb was less than 0.3 ppm.

The ITC measurements were performed by the usual technique.⁹ The samples (about 15×15×0.5 mm³) were polarized in a static field of 10⁴ V/cm for 3 min at 226°K, and then cooled down to 120°K, after which the field was switched off. During these steps the dipoles become polarized at saturation, and remain orientated in the same configuration obtained at the polarization temperature, because at low temperature the relaxation time is practically infinite. The crystal was then warmed up at the constant rate of 0.1°K/sec: The dipole relaxation time for orientation gets shorter and the dipoles lose their preferred orientation, giving rise to a depolarization current. This was detected at linearly increasing temperature by a vibrating reed electrometer

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¹ H. Rabin, *Phys. Rev.* **116**, 1381 (1959).

² Y. Haven, in *Reports of the Conference on Defects in Crystalline Solids, Bristol, 1954* (The Physical Society, London, 1955), p. 261.

³ H. W. Etzel and R. J. Maurer, *J. Chem. Phys.* **18**, 1003 (1959).

⁴ D. Mapother, H. N. Crooks, and R. J. Maurer, *J. Chem. Phys.* **18**, 1231 (1950).

⁵ K. Suzuki, *J. Phys. Soc. Japan* **16**, 67 (1961).

⁶ G. D. Watkins, *Phys. Rev.* **113**, 79 (1959).

⁷ G. Alzetta, P. R. Crippa, and S. Santucci, *Nuovo Cimento* **42**, 100 (1966).

⁸ R. G. Breckenridge, *J. Chem. Phys.* **16**, 959 (1948).

⁹ C. A. Bucci, R. Fieschi, *Phys. Rev. Letters* **12**, 16 (1964).

¹⁰ R. W. Dreyfus, *Appl. Phys. Letters* **3**, 175 (1963).

¹¹ M. Beltrami, G. Massarani, and M. Scalvini, *Japan. J. Appl. Phys.* **4**, 203 (1965).

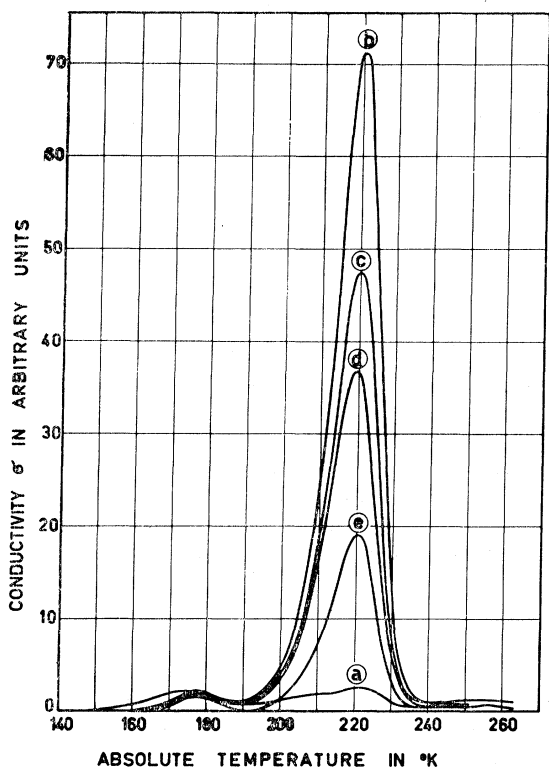


FIG. 1. Ionic thermocurrents of NaCl: CdCl₂ (impurity contents: $1.2 \times 10^{18} \text{ cm}^{-3}$ from chemical analysis). Curve (a): sample not previously treated; curve (b): sample heated at 230°C for 45 min and quenched at room temperature; curve (c): after an annealing of 85 min at room temperature; curve (d): after an annealing of 225 min at room temperature; curve (e): after an annealing of 1090 min at room temperature.

(Vibron 33C) and recorded by a Speedomax. The apparatus can measure currents as low as 10^{-16} A. The contacts between samples and silver electrodes were improved with colloidal graphite. The reproducibility of measurements was within 2%.

The samples were heated in vacuum in the cryostat; the cryostat was then filled with dry N₂ and cooled down to 273°K in 4 min.

3. RESULTS

Direct evidence of the precipitation of Cd, which occurs in NaCl, can be obtained comparing the ITC of a sample immediately after a fast cooling from 503°K [Fig. 1, curve (b)] with the ITC of a sample not subjected to this thermal treatment [Fig. 1, curve (a)]. The main peak at 220°K is due to IV dipoles; the dipole concentration before quenching is about 4% of that observed immediately after it. The other curves of Fig. 1 represent ITC from samples kept for longer times at room temperature. Since the area under the curves is proportional to the concentration of IV dipoles, the above results show that the excess of atomically dispersed impurities induced by the thermal treatment

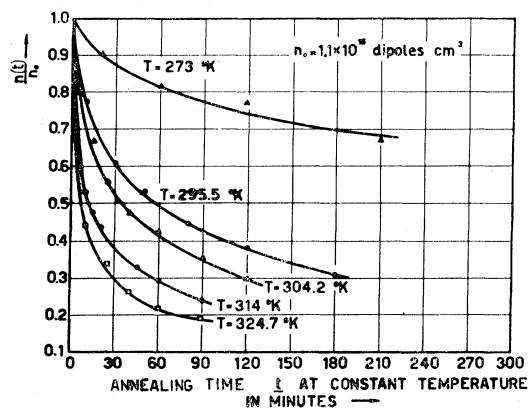


FIG. 2. Precipitation of Cd dipoles in NaCl at different temperatures. The concentration of dipoles $n(t)$ at time t normalized to initial concentration of dipoles n_0 ($n_0 = 1, 1 \times 10^{18} \text{ cm}^{-3}$) is plotted versus annealing time (in minutes) at constant temperature T . —△—, precipitation at $T = 273^\circ\text{K}$. —○—, precipitation at $T = 295^\circ\text{K}$. —▲—, precipitation at $T = 304.2^\circ\text{K}$. —●—, precipitation at $T = 314^\circ\text{K}$. —□—, precipitation at $T = 324.7^\circ\text{K}$.

anneals if the sample is stored at room temperature: IV dipoles migrate into the lattice thereby building up microprecipitates, and no longer contribute to the ITC glow peak at 220°K. The small band with a peak at 177°K does not play any role in the precipitation kinetics; its nature, however, is not clear.

The precipitation of dipoles has been measured at different temperatures, ranging from 0 to 51.7°C, in the same way as reported above for room temperature. In Fig. 2 the concentration of dipoles $n(t)$ normalized to the initial value n_0 is drawn versus time t of aging at a given temperature T .

Precipitation rates strongly depend on the initial concentration of dipoles, in agreement with the similar measurements carried out by Cook and Dryden¹² in KCl: SrCl₂, as is seen from Fig. 3, where the normalized

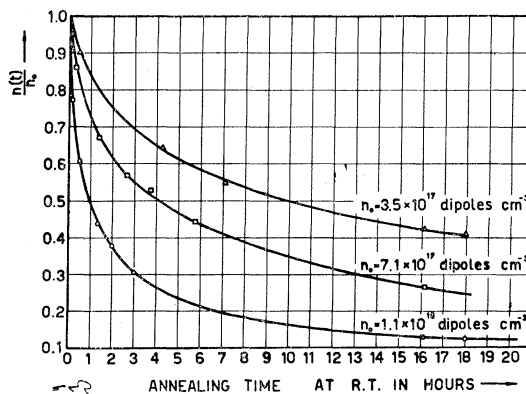


FIG. 3. Precipitation of Cd dipoles in NaCl for different initial concentrations of dipoles n_0 . The concentration of dipoles $n(t)$ at time t , normalized to initial concentration n_0 versus annealing time (in hours) at room temperature. —△—, $n_0 = 3.5 \times 10^{17} \text{ cm}^{-3}$. —□—, $n_0 = 7.1 \times 10^{17} \text{ cm}^{-3}$. —○—, $n_0 = 1.1 \times 10^{18} \text{ cm}^{-3}$.

¹² J. S. Cook and J. S. Dryden, Proc. Phys. Soc. (London) 80, 479 (1962).

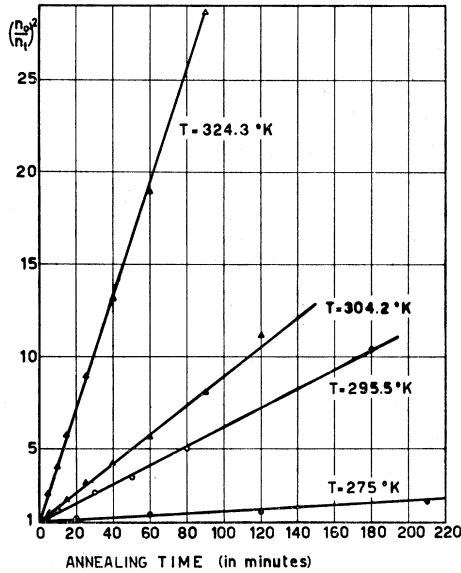


FIG. 4. Fitting of third-order kinetics for dipole decay at different temperatures. $(n_0/n)^3$ is plotted versus annealing time (in minutes) at a given temperature.

concentration of dipoles (n/n_0) is plotted versus time of annealing at room temperature for different concentrations.

4. DISCUSSION

A. Precipitation Kinetics and Trimer Formation of Cd- and Sr-Doped NaCl

On the hypothesis that precipitation of dipoles is monomolecular, one can attempt a fitting of the experimental data of ITC with a chemical rate equation in the form

$$dn/dt = -\nu_0 n^\alpha \exp(-E/kT). \tag{1}$$

Hence, under boundary condition $t=0, n=n_0$:

$$(n_0/n)^{\alpha-1} = (\alpha-1)n_0^{\alpha-1}\nu_0 t \exp(-E/kT) + 1. \tag{2}$$

Here n is the concentration of dipoles at time t , n_0 is

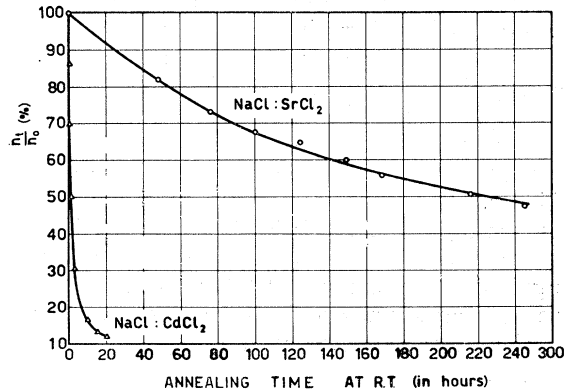


FIG. 5. Precipitation of IV dipoles in NaCl doped with different impurities at room temperature. Curve (a): precipitation of dipoles in NaCl:CdCl₂; Curve (b): precipitation of dipoles in NaCl:SrCl₂.

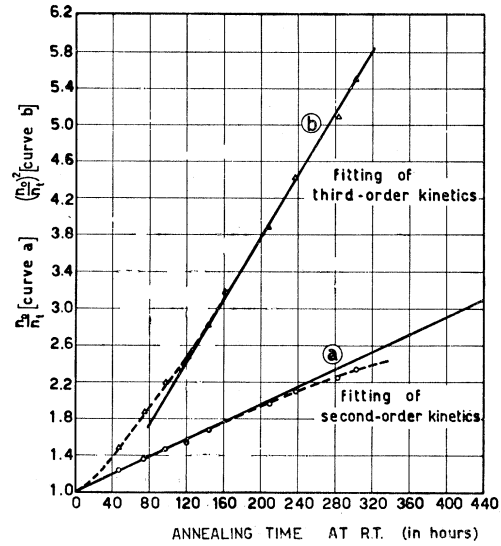


FIG. 6. Fitting of second and third-order kinetics for precipitation of IV dipoles in NaCl:SrCl₂ at room temperature. (n_0/n) and $(n_0/n)^2$ are plotted versus time (in hours) [curves (a) and (b), respectively].

the concentration at $t=0$, α is a coefficient which determines the order of the kinetics, E is the activation energy for the process, and ν_0 is the frequency factor. From (2) the kinetics order α can easily be obtained, since a plot of $(n_0/n)^{\alpha-1}$ versus time has to be a straight line.

From our results, $\alpha=3$ for temperatures ranging from 275.5 to 324°K and for dipole fractions between 85 and 30% of initial concentration (see Fig. 4). Following Cook and Dryden,^{12,13} this would mean that trimers, i.e., clusters of three dipoles, are built up by the simultaneous concurrence of three dipoles. However, it seems more likely that such a mechanism takes place by steps, i.e., a dipole joins the initial seed built up by two dipoles. The first stage in which dimers are created may be very fast so that the whole mechanism is likely to be masked by third-order kinetics.

This hypothesis is supported by a tentative study on precipitation of Sr dipoles at room temperature, performed by us in NaCl, where dipoles leave the solid solution very slowly in comparison with the Cd dipoles in NaCl (see Fig. 5). (That is, Sr dipole concentration reaches 50% in about ten days.) We noticed that in the first stage the precipitation follows approximately second-order kinetics, and gradually approaches third-order kinetics. This can be appreciated from Fig. 6, where n_0/n [curve (a)] and $(n_0/n)^2$ [curve (b)] are plotted versus time. The two plots should be straight lines when the precipitation process is ruled by second- or third-order kinetics, respectively.

¹³ H. F. Symmons and R. C. Kemp, Brit. J. Appl. Phys. 17, 607 (1966).

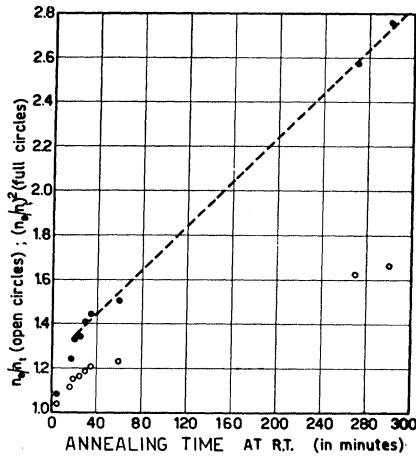


FIG. 7. First-stage precipitation of IV dipoles in NaCl:CdCl₂ at room temperature: n_0/n_1 (open circles) and $(n_0/n_1)^2$ (full circles) are plotted versus annealing time.

B. First Stage of Precipitation in NaCl:CdCl₂

Since the precipitation is fast, it is necessary to slow down the process in order to analyze it with good accuracy. This is achieved either by using samples with a low concentration of impurities (10^{-4}) or by following the precipitation at relatively low temperature (room temperature). The precipitation rate in the first stage is faster than that expected if the phenomenon is ruled by either second- or third-order kinetics. In Fig. 7, $(n_0/n_1)^2$ are plotted versus time. At least in the first stage, the experimental points cannot be fitted by straight lines; moreover, the concavity of plots is downwards, outlining the occurrence of higher-order kinetics. This feature is possibly due to a complicated kinetics connected to the existence of many kinds of Cd imperfections, as suggested by the absorption measurements.^{13a}

C. Activation Energy for Trimer Formation

From decay curves in the range in which the third-order law is satisfied, we have obtained the value of the activation energy $E=0.5\pm 0.04$ eV which appears in Eq. (1). This result is compared in Table I with the

TABLE I. Energy and frequency factor for the formation of trimers in different systems obtained from the equation $dn/dt = -\nu_0 n^3 \exp(-E/KT)$.

Salt	Divalent impurity	E (eV)	ν_0 (sec ⁻¹)
KCl	Sr ^a	0.73	4×10^{13}
KCl	Ba ^a	0.74	8×10^{15}
NaCl	Mn ^a	0.83	8×10^{17}
NaCl	Cd ^b	0.5	2.8×10^{16}

^a Reference 12.
^b Present work.

^{13a} R. Cappelletti, Nuovo Cimento (to be published).

analogous values obtained for other salts and impurities.^{7,12}

By analyzing the Cd ionic thermoconductivity¹⁴ bands, one finds $E_r=0.67\pm 0.01$ eV for the activation energy of rotation of cation vacancy around the impurity, in agreement with the data of Dreyfus.¹⁵

Since precipitation is essentially a diffusion process involving both vacancy rotation and impurity-vacancy exchange, the activation energy for the formation of a trimer should be the higher of the activation energies of the two mechanisms. Generally the activation energy for the exchange is larger than that for a jump of the cation vacancy around the impurity, as one can appreciate from Table II, so that a diffusion mechanism should be chiefly driven by the energy necessary for the exchange. In most cases, this energy is slightly lower than the activation energy for the formation of a trimer (see Tables I and II). In NaCl:CdCl₂, the experimentally determined energy required for the migration of dipoles to build up trimers is less than the experi-

TABLE II. Exchange and rotation energies for IV dipoles in different systems.

	Divalent impurity	Radius of impurity (Å)	Energy for exchange (eV)	Energy for rotation (eV)
NaCl	Mg	0.65		0.65 ± 0.03^d
NaCl	Zn	0.74	0.49 ^a	0.66 ± 0.03^d
NaCl	Mn	0.80	0.71 ^b	0.69 ± 0.03^d
NaCl	Cd	0.97		0.67 ± 0.03^d
NaCl	Ca	0.99	0.96 ^b	0.67 ± 0.03^d
NaCl	Sr	1.13	0.91 ^a	0.73 ± 0.03^d
KCl	Cd	0.97	0.54 ^c	
KCl	Pb	1.20	1.18 ^c	
KCl	Ba	1.35		0.7 ^e

^a M. Chemla, Ann. Chim. Phys. **1**, 959 (1956).

^b B. G. Lur'e, A. N. Murin, and R. F. Brigevid, Fiz. Tverd. Tela **4**, 1957 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1432 (1963)].

^c F. J. Keneshea and W. J. Fredericks, J. Phys. Chem. Solids **26**, 501 (1965).

^d Reference 15.

^e Reference 12.

mentally determined rotation energy of dipoles. As suggested by Dreyfus,^{15,16} the probability of exchange between divalent impurity and cation vacancy increases with decreasing impurity radius: It is likely that the jump of Cd²⁺ ions into the cation vacancy requires an energy smaller than E_r . This is supported by comparing the exchange energy and the rotation energy in NaCl for Zn²⁺, which is a quite small impurity (see Table II).

On the other hand, it is hard to explain why ITC measurements give such a high value for orientation energy. It is noteworthy that this value has been obtained at temperatures far from the ones at which precipitation energy was evaluated.

¹⁴ C. A. Bucci, R. Fieschi, and G. Guidi, Phys. Rev. **148**, 816 (1966).

¹⁵ R. W. Dreyfus, Phys. Rev. **121**, 1675 (1961).

¹⁶ R. W. Dreyfus, Phys. Rev. **135**, A1413 (1964).

5. CONCLUSIONS

(a) The accurate analysis of the first stage of the precipitation shows that the process is not simply represented by third-order kinetics, as found for Sr and Ba in KCl and Mn in NaCl.^{7,12,13} The situation in NaCl:SrCl₂ suggests a step mechanism in which an aggregation of a couple of dipoles occurs as a first stage (dimer), followed by the addition of an isolated dipole to build up the final product (trimer). However, the results obtained from a simplified mathematical approach to the problem do not supply satisfactory agreement with the experimental data.

(b) The precipitation process has peculiar features depending on the impurity which precipitates: In fact Cook and Dryden¹² found an equilibrium stage between dipoles and trimers in KCl:SrCl₂, while we did not find

this phenomenon in NaCl:CdCl₂ in the temperature range covered by our measurements.

(c) The fact that the activation energy of dipole orientation (measured in the temperature range from 190 to 240°K) is higher than that for aggregation into trimers (measured in the temperature range from 275 to 324°K) shows that the aggregation process is a complicated one and that it requires further analysis. Detailed study of the morphology of precipitates, such as may be given by means of Mössbauer-effect or EPR measurements, would help to clarify the problem.

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Magnetic Circular Dichroism of the R_2 Band in KCl and KF*

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Circular dichroism has been observed in both the zero-phonon line and sidebands of the R_2 transition in KCl and KF. The magnetic field was of magnitude 8 kG and the temperature range was $7^\circ\text{K} > T > 1.3^\circ\text{K}$. The zero-phonon-line dichroism was analyzed by a method of moments. It is shown theoretically that the changes in zeroth moment depend on the strain in the sample, whereas the changes in first moment do not. Experimentally the strain dependence of the zeroth moment is measured by applying a variable external stress simultaneously with the magnetic field. Quite good agreement is found with theory in a non-parameter fit. An estimate of the ground-state splitting in the internal strain field of the crystal is made ($\delta_0 = 1.5 \text{ cm}^{-1}$). The first-moment data yield values of the reduced angular momentum Λb (0.06 ± 0.01 for KCl and 0.11 ± 0.01 for KF) and of the reduced spin-orbit coupling $\Lambda\lambda b$ ($-0.32 \pm 0.03 \text{ cm}^{-1}$ for KCl and $-0.68 \pm 0.07 \text{ cm}^{-1}$ for KF). The strength of the Jahn-Teller interaction as defined by the parameter k^2 is deduced ($k^2 = 3.2$ for KCl and 2.3 for KF). A study of the well-resolved sideband peaks in KF enables a self-consistent assignment of phonon symmetries for the peaks in strain- and magnetic-field-induced dichroism to be made. The good agreement between theory and experiment in all measurements further confirms the Van Doorn F_2 model of the R center and Silsbee's analysis based on a dynamic Jahn-Teller effect in the ground state.

I. INTRODUCTION

THE Van Doorn model of the R center^{1,2} is a triangle of three neighboring F centers (Fig. 1). The ground state has a twofold orbital degeneracy. In principle, it is possible to lift this electronic degeneracy by applying an external perturbation to the crystal such as a stress, a magnetic field, or an electric field. Silsbee³ has carried out experiments on KCl with an applied uniaxial stress and he observed a marked optical dichroism in both the zero-phonon line and in the broad band associated with the R center. These

experiments confirmed the Van Doorn model and also showed that the Jahn-Teller interaction, which results from the coupling of the degenerate electronic levels to the lattice modes, is strong and must be taken into account.

There have been attempts to observe a magnetic splitting of the levels directly by using very high pulsed magnetic fields,⁴ but with no success. The reason for this is that the Jahn-Teller interaction effectively quenches the angular momentum and so reduces the interaction with the magnetic field. It is still possible to observe the effect of a magnetic field by looking for the small dichroism in the absorption of circularly polarized light which is induced by the field. Preliminary measurements, mainly on KCl, have been

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¹ C. Z. Van Doorn, Phillips Res. Repts. **12**, 309 (1957); Suppl. **4** (1962).

² H. Pick, Z. Physik **159**, 69 (1960).

³ R. H. Silsbee, Phys. Rev. **138**, A180 (1965).

⁴ A. E. Hughes, Proc. Phys. Soc. (London) **86**, 615 (1965).