Maxwell-Boltzmann Distribution of M^{2+}: Vacancy Pairs in Compensated fcc Lattice*

FRANCIS K. FONG
Department of Chemistry Purdue University, Lafayette, Indiana 47907
(Received 7 April 1969; revised manuscript received 2 June 1969)

Coulomb interactions in the face-centered cubic (fcc) lattice are exemplified by the interactions of M^{2+} impurity ions with their charge compensation vacancies in alkali halides. At low temperatures and high dilution, the canonical ensemble partition function leads to a Maxwell-Boltzmann distribution in the distance of separations of the M^{2+}: vacancy pairs, which can be calculated in terms of the geometric restrictions of the fcc lattice. The most predominant pairs, in the order of their relative importance, are C_{4v} (2,0,0), C_s (2,1,1,), C_{2v} (1,1,0), C_{2v} (2,2,0), C_s (3,1,0), C_1 (3,2,1), C_{3v} (2,2,2), and C_{4v} (4,0,0). The calculated distribution is compared with optical Zeeman and spin-resonance spectroscopic observations in the KCl:Sm^{2+} and KCl:Mn^{2+} systems.

INTRODUCTION

FOR a given temperature, there exists in alkali-halide crystals an equilibrium law which governs the presence of cationic and anionic vacancies. The introduction of M^{2+} impurity ions into the cation sublattice increases the number of the cationic vacancies, such that electroneutrality is maintained. If the concentration of the M^{2+} ions, N_i, is much greater than the equilibrium concentration of the intrinsic lattice defects, one can assume equal numbers of vacancies and M^{2+} ions. The assumption that the vacancies and M^{2+} ions undergo long-range Coulombic interactions leads to apparent divergences.[1] In reality, the effective interaction between charges is actually limited in its range because of the screening arising from the polarization of the ionic atmosphere in the vicinity of a given charge.[2] The number of neighbors with which a central charge interacts is thus finite. In general, we write for the configuration energy

$$U(\hat{R}_1,\hat{R}_2,\ldots\hat{R}_{2N_i})=\sum_{1\leq i<j\leq N}\nu(R_{ij})=\sum_{k=1}^{N_i}\sum_{l=N_i+1}^{2N_i}-e\phi(R_{kl})2\sum_{1\leq m<n\leq N_i}e\phi(R_{mn}),\quad(1)$$

where $\nu(R_{ij})$ is the pairwise interaction between the ith and jth charges, $\phi(R_{kl})$ and $\phi(R_{mn})$ are the potentials between the interacting charges k,l and m,n, respectively, and $\hat{R}_1$, $\hat{R}_2\cdots\hat{R}_{2N_i}$ are position vectors of the $2N_i$ charges.

The present work was prompted by a recent investigation[3] in which we observed, by means of the fluorescence Zeeman effect, that Sm^{2+} ions in KCl exist in a multiplicity of site symmetries. A large number of the lines arising from transition between the ^5D and ^7F multiplets of the $4f^6$ ground configuration show no observable Zeeman shifts,[3] suggestive of their origin in the nearest-neighbor (nn) $C_{2v}(1,1,0)$ sites with the charge compensation K^+ vacancy in the nn (1,1,0) lattice point. From fluorescence lines which exhibit anisotropy Zeeman patterns, two different C_{4v} sites and a distant C_{2v} site were observed.[4] In addition, other Zeeman patterns were found which arise from still other unidentified site symmetries.[3]

In continuation of the initial effort,[3] we have made a detailed analysis[4] of the 4.2°K fluorescence Zeeman spectra of the KCl:Sm^{2+} system, in which no field lines ($^5D_0\rightarrow{}^7F_4$) have been attributed to C_s sites for the Zeeman patterns arising from the 8122.2 and 8126.6 Å. Before details of this fairly complicated spectroscopic analysis can be given, we must first set down the basic principles which underlie the interpretations of our experiments. A more pertinent incentive for the present study, however, lies in the apparent lack of agreement in the literature. In earlier studies,[5] the broadening of the Debye loss curve observed for the dielectric relaxation of the M^{2+}: vacancy pairs suggests the presence of inequivalent dipolar pairs. Current theories[6] on the conductivity of alkali-halide: M^{2+} crystals, however, are formulated on the assumption that only the nn pairs are bound. The ESR (electron-spin-resonance) studies of Schnieder *et al.*[7] and Watkins,[8] give convincing evidence for the predominance of the next-nearest neighbors rather than the nn pairs in the KCl:Mn^{2+} system, in agreement with the theoretical calculations of Bassani and Fumi.[9] In addition, a large signal corresponding to Mn^{2+} in distant compensation was observed. Nevertheless, the vibronic structure of the $Sm^{2+}4f^6\rightarrow 4f^55d^1$ absorption bands in alkali halides have been interpreted

* Work supported under the Advanced Research Projects Agency Institutional Grant No. SD102.

[1] D. Pines and Philippe Nozieres, *The Theory of Quantum Liquids* (W. A. Benjamin, Inc., New York, 1966), Vol. 1, p. 149.
[2] P. P. Debye and F. Hückel, Z. Physik **24**, 185 (1923).
[3] F. K. Fong and E. Y. Wong, Phys. Rev. **162**, 348 (1967).
[4] F. K. Fong and J. C. Bellows, Phys. Rev. (to be published).
[5] R. G. Breckenridge, J. Chem. Phys. **16**, 959 (1948); **18**, 913 (1959); *Imperfections in Nearly Perfect Crystals* (John Wiley & Sons, Inc., New York, 1952), p. 219.
[6] A. B. Lidiard, Phys. Rev. **94**, 29 (1954); *Handbuch der Physik* edited by S. Flügge (Springer-Verlag, Berlin, 1957),Vol. 20, p. 246.
[7] E. E. Schneider and J. E. Caffyn, *Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 74; P. A. Forrester and E. E. Schneider, Proc. Phys. Soc. (London) **B69**, 833 (1956).
[8] G. D. Watkins, Phys. Rev. **113**, 79 (1959); **113**, 91 (1959).
[9] F. Bassani and F. G. Fumi, Nuovo Cimento **11**, 274 (1954); M. P. Tosi and G. Airokli, *ibid.* **8**, 584 (1958).

TABLE I. Values of g_l, R_l, and ϵ_l where $l \geqq 32$ and the point-group symmetry of possible M^{2+}:K^+ vacancy pairs in KCl.

l	Symmetry (i,j,k)	g_l	R_l(Å)	E_l(eV)
1	$C_{2v}(1,1,0)$	12	$\sqrt{2}a=4.44$	-0.65
2	$C_{4v}(2,0,0)$	6	$(\sqrt{4})a=6.28$	-0.46
3	C_s (2,1,1)	24	$(\sqrt{6})a=7.69$	-0.38
4	$C_{2v}(2,2,0)$	12	$(\sqrt{8})a=8.88$	-0.32
5	C_s (3,1,0)	24	$(\sqrt{10})a=9.92$	-0.29
6	$C_{3v}(2,2,2)$	8	$(\sqrt{12})a=10.88$	-0.26
7	C_1 (3,2,1)	48	$(\sqrt{14})a=11.75$	-0.24_6
8	$C_{4v}(4,0,0)$	6	$(\sqrt{16})a=12.56$	-0.23_0
9	C_s (4,1,1)	24	$(\sqrt{18})a=13.32$	-0.21_7
	$C_{2v}(3,3,0)$	12		
10	C_s (4,2,0)	24	$(\sqrt{20})a=14.04$	-0.20_6
11	C_s (2,3,3)	24	$(\sqrt{22})a=14.75$	-0.19_6
12	C_s (4,2,2)	24	$(\sqrt{24})a=15.38$	-0.18_8
13	C_1 (3,1,4)	48	$(\sqrt{26})a=16.01$	-0.18_0
	C_s (5,1,0)	24		
14		0		
15	C_1 (5,1,2)	48	$(\sqrt{30})a=17.19$	-0.16_8
16	$C_{2v}(4,4,0)$	12	$(\sqrt{32})a=17.16$	-0.16_3
17	C_s (4,3,3)	24	$(\sqrt{34})a=18.31$	-0.15_8
	C_s (5,3,0)	24		
18	C_s (2,4,4)	24	$(\sqrt{36})a=18.84$	-0.15_3
	$C_{4v}(6,0,0)$	6		
19	C_1 (5,3,2)	48	$(\sqrt{38})a=19.35$	-0.14_9
	C_s (6,1,1)	24		
20	C_s (6,2,0)	24	$(\sqrt{40})a=19.86$	-0.14_5
21	C_1 (5,1,4)	48	$(\sqrt{42})a=20.35$	-0.14_2
22	C_s (6,2,2)	24	$(\sqrt{44})a=20.83$	-0.13_9
23	C_1 (6,3,1)	48	$(\sqrt{46})a=21.29$	-0.13_6
24	$C_{3v}(4,4,4)$	8	$(\sqrt{48})a=21.75$	-0.13_3
25	$C_{2v}(5,5,0)$	12	$(\sqrt{50})a=22.20$	-0.13_0
	C_s (7,1,0)	24		
	C_1 (5,3,4)	48		
26	C_s (6,4,0)	24	$(\sqrt{52})a=22.64$	-0.12_8
27	C_s (2,5,5)	24	$(\sqrt{54})a=23.07$	-0.12_5
	C_s (6,3,3)	24		
	C_1 (7,1,2)	48		
28	C_1 (6,4,2)	48	$(\sqrt{56})a=23.49$	-0.12_3
29	C_s (7,3,0)	24	$(\sqrt{58})a=23.91$	-0.12_1
30		0		
31	C_1 (7,3,2)	48	$(\sqrt{62})a=24.72$	-0.11_7
	C_1 (6,5,1)	48		
32	$C_{4v}(8,0,0)$	6	$(\sqrt{64})a=25.12$	-0.11_5

in terms of the unique existence of the nn $C_{2v}(1,1,0)$ sites.[10] While our own spectroscopic work appears to agree with Watkins's, the mystery of site distribution which has given rise to apparent contradictions remains to be unraveled.

In the present paper, we shall provide a critical evaluation of the many site symmetries by means of the canonical partition function, which leads to a Maxwell-Boltzmann distribution consistent with the geometrical restrictions of the discrete fcc lattice. A meaningful calculation of the distribution is possible in view of the numerous spectroscopic observations.

DISTRIBUTION OF SITE SYMMETRIES IN ALKALI HALIDE: M^{2+} SYSTEM

The interaction potential $\phi(R)$ in Eq. (1) for charged particles in a dielectric medium is

$$\phi(R)=(e/\epsilon R)e^{(-bR)}, \tag{2}$$

where $b=(8\pi N_i e^2/\epsilon\Omega kT)^{1/2}$, Ω being the volume of the system and ϵ the dielectric constant of the medium. Due to this screened potential, the effective number of interacting neighbors is finite. The *total* pairwise interaction energy of a given configuration can thus be expressed

$$U(\hat{R}_1,\hat{R}_2,\cdots\hat{R}_{2N_i})=\sum_{1\leq j<j\leq N}\nu(R_{ij})$$
$$=\tfrac{1}{2}\sum_{i=1}^{2N_i}\sum_{j=1}^{z_i}\pm e\phi(R_{ij}), \tag{3}$$

where z_i is the actual effective number of interacting neighbors of the ith charge. The factor $\frac{1}{2}$ corrects for the over-counting incurred in the double sum. The configuration partition function is

$$Z_{\text{configuration}}=\sum_n e^{-U_n(\hat{R}_1,\hat{R}_2,\cdots\hat{R}_{2N_i})/kT}$$
$$=\sum_n \exp\left[-\frac{1}{2kT}\sum_{i=1}^{2N_i}\sum_{j=1}^{z_i}\pm e\phi(R_{ij})\right]_n, \tag{4}$$

where the sum is carried over all the n possible configurations. At sufficiently low temperatures, the attractive terms will predominate as opposite charges tend to pair formation, in which case Eq. (4) can be rewritten

$$Z_{\text{configuration}}=\sum_{Ril}\exp\left[-\frac{1}{kT}\sum_{i=1}^{N_i}-e\phi(R_{il})\right]$$
$$=\left(\sum_{Rl} g_l e^{-e\phi(Rl)/kT}\right)^{N_i}. \tag{5}$$

The sum after the first equal sign is carried over all possible values of R_{il}, the distance of separation of the ith charge from its nearest opposite charge. Only the attractive terms are retained in Eq. (5). The sum over j of Eq. (4) is set equal to $-e\phi(R_{il})$, the attractive energy of the ith charge with its close-by opposite charge. In effect, these simplifications are equivalent to neglecting the weak dipolar interactions between the charge pairs. The second equal sign in Eq. (5) reduces the configuration-partition function to a product of "molecular" partition functions of N_i *pairs* of opposite charges. Here, R_l is the distance of separation of a specified pair, and g_l is the number of equivalent ways in which such a pair can be formed.

A typical alkali halide is KCl. The cation sublattice is fcc. The K^+-Cl^- separation a is 3.14 Å. When a divalent cation M^{2+} enters the lattice substitutionally, a K^+ vacancy is created so that charge neutrality is main-

[10] M. Wagner and W. E. Bron, Phys. Rev. **139**, 223 (1965).

tained. Neglecting the dipolar interactions between the M^{2+}: vacancy pairs, as in Eq. (5), we assume that at sufficiently low temperatures and concentrations, each M^{2+} ion is associated with a K^+ vacancy with an energy which varies as R^{-1}. Since the vacancy can only occupy discrete positions, R can assume only discrete values, with the consequence that the Coulomb energy of association, ϵ_l, is also discrete:

$$\epsilon_l = -e^2/\epsilon R_l,$$

where $\epsilon = 5.03$. Here, we have assumed that the quantity b in Eq. (2) is vanishingly small at high dilution.

Taking the structural properties of the fcc lattice into consideration, one observes that R_1 for the nn pair is $\sqrt{2}a$, and that there are 12 distinguishable but equivalent nn sites whose C_2 symmetry axes point in the directions of the [110], [101], [011], [$\bar{1}$10], [$\bar{1}$01], [0$\bar{1}$1], [1$\bar{1}$0], [10$\bar{1}$], [01$\bar{1}$], [$\bar{1}\bar{1}$0], [$\bar{1}$0$\bar{1}$], and [0$\bar{1}\bar{1}$] crystal axes. For the nnn pair, R_2 is $(\sqrt{4})a$ with six possible equivalent sites with the vacancy occupying one of the six equivalent (2,0,0) lattice points. Proceeding in this manner, it is possible to enumerate for the lth nn M^{2+}:K^+ vacancy pairs, the quantities R_l, ϵ_l, and the number g_l of distinguishable but equivalent lattice points. The results of this enumeration for $l \leqq 32$ along with the point-group symmetry of each type of pair are listed in Table I. If the M^{2+} ion is taken as the origin and the lattice point occupied by the associated vacancy is given by (i,j,k), $(i+j+k)$ must be even, in order for the vacancy to be in the K^+ sublattice. The value for R_l is simply $(i^2+j^2+k^2)^{1/2}a$. R_l can be written as $\sqrt{(2l)}a$, where $l = 1, 2, 3, \ldots$, except that for $l = 14$ and 30, $g_l = 0$. The various site symmetries (and corresponding values of the g_l number of distinguishable but equivalent lattice points in parenthesis) are C_{2v}(12) when $i = j \neq 0$, $k = 0$; C_{4v} (6) when $i \neq 0$, $j = k = 0$; C_s (24) when $i \neq j = k$, $(i, j, k \neq 0)$; C_s (24) when $i \neq j$, $k = 0$ and $i, j \neq 0$; C_1 (48) when all i, j, and k are unequal and not equal to zero; and C_{3v} (8) when $i = j = k \neq 0$. At $l = 9$, 13, 17, 18, 19, 25, 27, and 31, more than one site symmetry can occur (see Table I).

The energy of pairing can now be written as

$$\begin{aligned} &\epsilon_1 = -0.39 \text{ eV}, \\ &\epsilon_l = -e^2/\epsilon\sqrt{(2l)}a = -k\Theta_p l^{-1/2}, \quad l = 2, 3, 4, \ldots. \end{aligned} \tag{6}$$

The value ϵ_1 for the nn M^{2+}:K^+ vacancy is assumed to be the same as that for the nn pair energy in KCl:Sr^{2+}, as calculated by Bassani and Fumi,[9] namely, -0.39 eV. This has been confirmed experimentally by Watkins in the KCl:Mn^{2+} system.[8] The pairing energies for $l > 1$ are estimated by using the simple homogeneous dielectric shielding model. This is a fairly good approximation. The calculated value for ϵ_2 is -0.50 eV (KCl:Sr^{2+}).[9] The experimental value ~ -0.42 eV (KCl:Mn^{2+}) was obtained by Watkins.[8] The Coulombic value -0.46 eV (Table I) lies in between the two values quoted above. Further confidence in the assumptions for Eq. (6) is gained from Watkins's convincing interpretation of his dielectric loss and EPR linewidth measurements in terms of these assumptions. For KCl, $\Theta_p = e^2/\epsilon\sqrt{2}ak = 7497$°K.

TABLE II. Some typical calculations for $q_p = \sum_{l=1}^{l=l'} g_l e^{-\epsilon_l/kT}$.

T°K	$q_p(l'=13)$	$q_p(l'=21)$	$q_p(l'=32)$
300	3.878×10^8	3.879×10^8	3.879×10^8
500	6.123×10^5	6.229×10^5	6.316×10^5
700	4.117×10^4	4.467×10^4	4.830×10^4
900	1.241×10^4	1.452×10^4	1.684×10^4

Assuming the conditions for the canonical ensemble configuration-partition function of Eq. (5), we now write the distribution numbers n_l^* associated with the energy level ϵ_l:

$$n_l^* = \frac{N_i g_l e^{-\epsilon_l/kT}}{\sum_{l'} g_{l'} e^{-\epsilon_{l'}/kT}} = N_i q_p^{-1} g_l e^{-\epsilon_l/kT}, \tag{7}$$

where the crystal contains N_i impurity atoms/cm^3, and q_p is the molecular partition function for the pair formation. Equation (7) holds subject to the restrictive conditions

$$\epsilon_p = \sum_l n_l^* \epsilon_l, \quad \text{and} \quad N_i = \sum_l n_l^*,$$

where ϵ_p is the total energy of the crystal due to pairing, and is actually the most probable configuration energy $U^*(R_{ij})$ if Eq. (5) is valid. To obtain n_l^*, we substitute the appropriate values for g_l and ϵ_l from Table I into Eq. (7). In our calculations, q_p is summed over $l = 1, 2, \cdots, 32$ for $T = 0$, 100, 150, 300, 400, 500, 700, and 900°K. When $\epsilon_l \gg kT$, only the ground level ϵ_2 is populated, and $q_p = g_2 e^{-\epsilon_2/kT}$ leading to the result that $n_2^* = N_i$, i.e., all the M^{2+} ions and K^+ vacancies are associated as nnn pairs. As T increases, the excited levels become populated. The partition function must now be summed over successively increasing values of l to obtain accurate results. For example, some typical calculations are shown in Table II, in which q_p is summed over $l = 1$ to $l = l'$. At 300 and 500°K, the value for q_p does not change significantly when the sum is carried beyond $l' = 13$, whereas at 700 and 900°K, the terms in q_p beyond $l' = 13$ become increasingly significant, and q_p apparently does not converge readily. There are several reasons for this difficulty. First of all, as the distant sites become populated, the Coulombic interaction tends to be screened, and Eq. (6) is no longer valid. More significantly, the assumptions underlying Eq. (5) are no longer valid at high temperatures, since the repulsive terms and the terms other than the first in the sum over j in Eq. (4) can no longer be neglected. To do justice to the problem, we must employ the configuration energy of Eq. (4) in our calculations, which is a somewhat more difficult problem. Thus, in using the molecular approach, we have meaningful values of q_p at temperatures less than 500°K. At higher tempera-

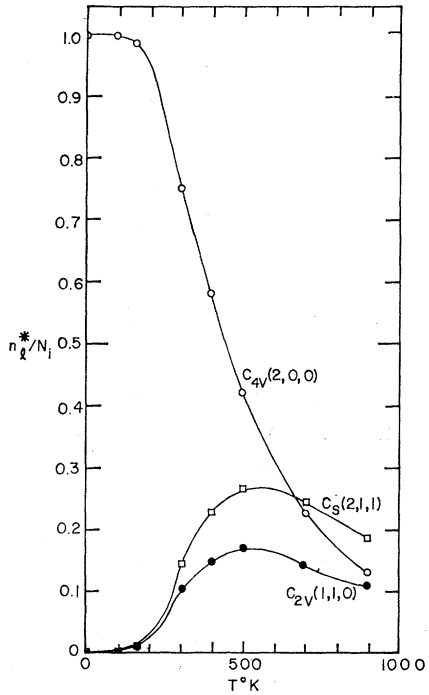

FIG. 1. Probabilities n_i^*/N_i of finding C_{4v} (2,0,0), $C_s(2,1,1)$, and $C_{2v}(1,1,0)$ sites at different temperatures.

tures, population of states corresponding to large separation leads to configuration energies, which are not separable in terms of pair formation. Calculations of q_p at these temperatures are thus subject to serious errors. Nevertheless, even at 900°K, the largest terms in q_p are still those characterized by the smallest l values, i.e., those corresponding to the low-lying bound states.

The calculated values of n_i^*/N_i are plotted against T in Fig. 1 for the first three bound states, and in Fig. 2 for the next five higher bound states. The results are interesting, and are quite unexpected. For temperatures up to 600°K, the $C_{4v}(2,0,0)$ nnn pairs are the predominant species. This result has been known to be the case in view of the fact that $\epsilon_1 > \epsilon_2$ according to the lattice theory.[9] That the C_s (2,1,1) pairs ($l=3$) are more predominant than the $C_{2v}(1,1,0)$ nn pairs at all temperaperatures is indeed unexpected. Upon reflection, however, the result is quite reasonable, for although $\epsilon_1 = -0.39$ eV is slightly lower than $\epsilon_3 = -0.38$ eV, the number of equivalent sites g is 24 for the $C_s(2,1,1)$ pair as compared with 12 for the $C_{2v}(1,1,0)$ pair. At concentrations an order of magnitude lower and at temperatures below 500°K, we find the group of three different types of pairs, namely the $C_{2v}(2,2,0)$, $C_s(3,1,0)$, and $C_1(3,2,1)$ pairs (Fig. 2). At a still lower order of magnitude in concentration, we find the group of two pairs identified as $C_{3v}(2,2,2)$ and $C_{4v}(4,0,0)$.

DISCUSSION

The results shown in Figs. 1 and 2 are in agreement with the spectroscopic observations of site distributions.[3,4,7,8] Prior to the detailed discussion in Sec. II, we were puzzled by the fact that no C_{3v} sites were observed.[3] Visual inspection of the cation sublattice indicates the distinct possible existence of complexes oriented along the ⟨111⟩ axes. From Fig. 2, we observe that the $C_{3v}(2,2,2)$ sites are actually quite improbable in terms of our statistical theory. Watkins' ESR investigations[8] of KCl:Mn^{2+}, indicated a distinct temperature dependence of the site distribution. At low temperatures, the $C_{4v}(2,0,0)$ and the $C_{2v}(1,1,0)$ sites distinctly predominate. At elevated temperatures, a broad signal due to Mn^{2+} in distant compensation becomes prominant. If this broad ESR signal corresponds to the multiplicity of sites [excluding $C_{2v}(1,1,0)$ and $C_{4v}(2,0,0)$] observed in the optical Zeeman studies of KCl:Sm^{2+},[3,4] Watkins' observation lends strong support to the temperature dependence of the distribution curves depicted in Figs. 1 and 2. The lack of resolution of the broad ESR signal into corresponding site symmetries can be readily accounted for. The ground multiplet of Mn^{2+} is ^6S. The relatively weak crystal field splitting of the ground $J=\frac{5}{2}$ level occurs only through admixtures of the excited J levels with $L \neq 0$. Moreover, the compensation crystal field potential varies as $R^{-(k+1)}$ where R is the separation distance of the Mn^{2+} ion and the vacancy, and $k>0$ is the rank of the spherical harmonic in the corresponding crystal-field expansion. The crystal-field effect of the vacancy upon the Mn^{2+} thus rapidly vanishes beyond the detection limit with increasing R. In the optical Zeeman studies of KCl:Sm^{2+}, the transitions involve the $^5D_0$ level and the seven J levels in the ground ^7F

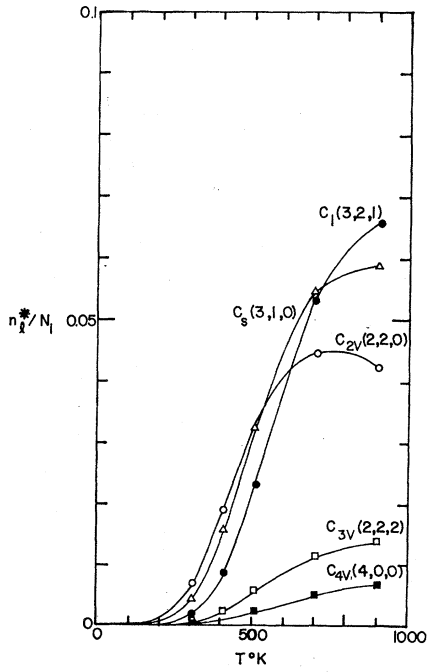

FIG. 2. Probabilities n_i^*/N_i of finding $C_s(3,1,0)$, $C_1(3,2,1)$, $C_{2v}(2,2,0)$, $C_{3v}(2,2,2)$, and $C_{4v}(4,0,0)$ sites at different temperatures.

multiplet. The numerous site symmetries have been observed[3,4] in several *different* $0 \rightarrow J$ transitions. In this connection, the optical Zeeman effect appears to be more versatile than ESR. Not only is the optical Zeeman method not restricted to a paramagnetic ground level, it also has the benefit of information from *several* J-levels, instead of only one as in the case of ESR.

In earlier work[8,11,12] on compensated lattices in KCl:M^{2+} and closely related systems, such as CaF_2:M^{3+} in which the F^- interstitial is the compensation, the prevailing assumption was that the impurity cation was either in close association with the compensation resulting in the removal of the inversion center of the impurity site or that the impurity cation is essentially in a cubic site beyond any significant influence of the distant compensation. On the other hand, the unique existence of the nn $C_{2v}(1,1,0)$ sites was postulated[10] in the interpretation of the $Sm^{2+}4f^6 \rightarrow 4f^45d^1$ absorption bands in alkali halides. In view of the present work, neither of the above two assumptions appears to be valid. According to the predicted distributions, "cubic" sites corresponding to large R_l values are highly improbable. None were observed spectroscopically.[3,4] The unique presence of the $C_{2v}(1,1,0)$ sites is in direct contradiction with the predicted distributions as well as the spectroscopic observation, particularly those of Watkins's in which the $C_{4v}(2,0,0)$ sites are seen to be predominant.

The above calculations apply only in the case of low temperatures ($<500°$) and high dilutions. In KCl:Sm^{2+} samples containing 10^{20} Sm^{2+} ions per cm^{-3}, a group of new lines appear in the $^5D_0 \rightarrow {}^7F_4$ transition energy region.[13] They probably arise from the association of Sm^{2+}: vacancy pairs through attractive dipolar forces. These lines were not observed in samples containing 10^{18} centers per cm^3. Similar problems are involved in the CaF_2:M^{3+} systems for which a number of site symmetries have been well established.[14] Clearly, the procedure outlined above can be readily applied to the CaF_2:M^{3+} systems.

[11] W. Hayes, G. D. Jones, and J. W. Twidell, Proc. Phys. Soc. (London) **81**, 371 (1962).
[12] F. K. Fong and M. A. Hiller, J. Phys. Chem. **71**, 2854 (1967); F. K. Fong, *ibid.* **41**, 2291 (1964).
[13] F. K. Fong, R. H. Heist, C. R. Chilver, J. C. Bellows, and R. L. Ford, J. Luminescence (to be published).
[14] C. W. Rector, B. C. Pandy, and H. W. Moos, J. Chem. Phys. **45**, 171 (1966).

PHYSICAL REVIEW VOLUME 187, NUMBER 3 15 NOVEMBER 1969

ESR and Optical-Absorption Study of the V_1 Center in KCl: NaCl†

CHARLES J. DELBECQ, ELSON HUTCHINSON, DIRK SCHOEMAKER,
EDWARD L. YASAITIS, AND PHILIP H. YUSTER
Argonne National Laboratory, Argonne, Illinois 60439
(Received 19 June 1969)

The results of optical experiments show that the V_1 center in KCl has a strong transition at 357 nm and a weak transition at 560 nm. Both transitions have the same polarization and the transition moments are oriented approximately along ⟨110⟩. The optical measurements show further that the V_1 center disorients in the neighborhood of 17 K, and suggest that it consists of an H center trapped in the immediate vicinity of a substitutional Na^+. These optical measurements have been correlated with the anisotropic ESR spectrum of the V_1 center, which is best observed at 35 K. It is found that the V_1-center ESR spectrum is similar to that of an H center; however, the four nuclei of the Cl_4^{3-} molecule ion are all inequivalent, and the internuclear axis of the two central nuclei lies in a {100} plane and is tipped ($5.7° \pm 0.3°$) away from the ⟨110⟩ direction. Furthermore, the central molecular bond is bent by about 3.5°. The ESR spectra reveal that the V_1 center is an H center trapped by a substitutional Na^+ impurity. The Na^+ lies in the {100} plane containing the Cl_4^{3-} molecule ion and is in a nearest-neighbor position to the central nuclei of the molecule ion. The reorientation of V_1 centers is sufficiently rapid to result in lifetime broadening of the ESR lines above 35 K, and at 50 K the ESR spectrum shows a collapsing of certain four-line groups into single lines, which indicates that a restricted interstitial jump is occurring. At 80 K, the V_1 ESR spectrum averages into an isotropic line at $g=2.020$, with a linewidth of 100 G.

I. INTRODUCTION

THE V_1 absorption band in KCl, situated at about 357 nm, and created at 77 K by x or γ irradiation, was first reported by Casler, Pringsheim, and Yuster.[1] Many models have since been proposed for the corresponding V_1 center. Seitz[2,3] first proposed that it was the antimorph of the F center, a positive hole trapped at a positive ion vacancy. Varley[4] concluded that the V_1 center consisted of an interstitial chlorine atom and four surrounding substitutional chloride ions

† Based on work performed under the auspices of the U. S. Atomic Energy Commission.
[1] R. Casler, P. Pringsheim, and P. Yuster, J. Chem. Phys. **18**, 1564 (1950).
[2] F. Seitz, Rev. Mod. Phys. **18**, 384 (1946).
[3] F. Seitz, Phys. Rev. **79**, 529(L) (1950).
[4] J. H. O. Varley, Atomic Energy Research Establishment, Harwell, England, Report No. AERE-M/R-1508, 1954 (unpublished).