these inflections (see Fig. 7 for a comparison of their spectra with ours) and thus are forced to conclude that these inflections must be due to the higher-impurity content of the Norton crystals they used compared with the Spicer crystals used in our investigation. We are also convinced that the intrinsic shape of the F^+ band is asymmetric and cannot be meaningfully decomposed into a series of Gaussian bands.

In their paper, Henderson *et al.* showed an excellent fit of their data to Eq. (1) using the parameters $H(0) = 0.477$ eV and $\nu = 7.8\times10^{12}$ sec^{-1}. This may have been a fortuitous consequence of the above decomposition of the band. To be valid, $\alpha_m H(T)$ (which is proportional to the area under the absorption curve) should be independent of the temperature. However, their data show $H(T)$ increasing by 45% as the temperature increases from 4 to 372°K. This appears to be excessive compared with the observed decreased of α_m. Our analysis shows $H(T)$ increasing by only 20% in this range, while $\alpha_m H(T)$ remains constant to within 2%.

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Significance of the Third-Nearest-Neighbor Divalent Cation K$^+$ Vacancy Pairs in KCl†

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The identification of the third-nearest-neighbor monoclinic (C_s) site comprised of a Sm^{2+}-K$^+$ vacancy pair with the vacancy at the (2,1,1) lattice point in KCl has been made through a high-resolution Zeeman anisotropy fluorescence spectroscopic investigation of several prominent transitions between the ^5D and ^7F multiplets. The establishment of the dominant presence of the C_s site in KCl:M^{2+}, which constitutes an important feature of the Maxwell-Boltzmann distribution of the M^{2+}-K^+ vacancy pairs, is of fundamental importance in the understanding of numerous phenomena in polar crystals.

I. INTRODUCTION

THAT the introduction of divalent cations (M^{2+}) into the metal-ion sublattice of an alkali halide creates the phenomenon of vacancy compensation is a well-established fact. The manner in which such charge compensation occurs, however, has been a subject of much debate in recent years.[1] Both of the two prevailing views (which are opposite in nature), that the M^{2+}-vacancy pairs are either associated in complex formation or dissociated according to a law of mass action and that (according to the opposite view) the M^{2+}-vacancy pairs are present only in the nearest-neighbor complex form, have been found to be unrealistic on the basis of a statistical mechanical calculation.[1] In this paper, we wish to report the first observation of the dominant presence of the third-nearest-neighbor M^{2+}-K$^+$ vacancy pair in the KCl:M^{2+} system, which was predicted by this statistical mechanical calculation.[1]

Earlier, electron paramagnetic resonance (EPR)[2] and Zeeman anisotropy fluorescence (ZAF)[3] spectroscopic investigations have led to the identification of the nearest-neighbor $C_{2v}(1,1,0)$ site and the next-nearest-neighbor $C_{4v}(2,0,0)$ site in alkali halides doped with divalent cations. In the EPR investigations on the KCl:Mn^{2+} system,[2] a large signal was observed in addition to the signals corresponding to the C_{2v} and the C_{4v} sites. The large signal was attributed to cubic sites corresponding to divalent ions in distant compensation beyond the crystalline fields of the associated cation vacancy. In the ZAF experiments,[3] however, no cubic sites were observed. Since the EPR observation of the cubic sites provided apparently irrefutable grounds for the postulation of the dissociation hypothesis,[2] the identification of the sites responsible for the "cubic" EPR signal in terms of the ZAF experiments thus appears crucial to an understanding of the compensated lattice of the KCl:M^{2+} system.

On the basis of existing spectroscopic evidence, we have shown[1] that 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 face-centered-cubic lattice. The most predominant pairs at $T<500$ K, in the order of relative importance, are $C_{4v}(2,0,0)$, $C_s(2,1,1)$, $C_{2v}(1,1,0)$, and $C_{2v}(2,2,0)$, of which the first three account for approximately 90% of the M^{2+} ions. If this is true, the so-called cubic sites observed in the EPR experiments must be actually low-symmetry sites beyond the second nearest neighbor, the most important of which are the $C_s(2,1,1)$ sites. In order

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[2] 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); G. D. Watkins, Phys. Rev. **113**, 79 (1959); **113**, 91 (1959).

[3] F. K. Fong and E. Y. Wong, Phys. Rev. **162**, 348 (1967).

to give experimental support to the above interpretation, the experimental observation of the $C_s(2,1,1)$ site must be made. The ZAF technique appeared promising in this respect, since in the earlier work on the KCl:Sm^{2+} system we have observed numerous anisotropic Zeeman effects which cannot be readily explained in terms of the C_{4v}- and the C_{2v}-site symmetries.[3] The $C_s(2,1,1)$-site origin of some of these fluorescence lines escaped detection partly because of the fact that in all cases, the Zeeman components of the ZAF patterns were either too weak or not well resolved, but mostly because the importance of the $C_s(2,1,1)$-site symmetry was not suspected.

II. EXPERIMENTAL PROCEDURE

Single crystals of KCl containing 3.6×10^{18} cm^{-3} Sm^{2+} ions were grown[4] by the Czochralski method. The determination of the 4.2 K ZAF patterns at 26.5 kG of the two intense no-field lines at 7694.5 and 7693.5 Å ($^5D_0\rightarrow{}^7F_3$) was achieved through operation of the 2-*M* Bausch & Lomb grating spectrograph at second order. The dispersion was 3.95 Å/mm. The fluorescence lines were calibrated by iron arc spectra, the results in most cases being reproducible to an average deviation of better than 0.1 Å. The ZAF patterns were obtained with the magnetic field rotating in the (001) and the (101) planes.

III. OBSERVATION OF THIRD-NEAREST-NEIGHBOR (C_s) SITE

The perturbation Hamiltonian for the Sm^{2+} ion in an external magnetic field $\hat{H}$ is

$$\mathcal{H}'=g_\lambda\mu_B H_0[\cos\theta_H\, J_Z+\tfrac{1}{2}\sin\theta_H\,(e^{i\phi_H}J_-+e^{-i\phi_H}J_+)], \quad (1)$$

where μ_B is the Bohr magneton, g_λ the Landé g factor, H_0 the effective magnetic field strength, θ_H the angle between the $\hat{H}$ field and the Z axis, and ϕ_H the corresponding azimuthal angle. In C_s symmetry, Z is taken to be the axis $\perp$ to the reflection plane, while ϕ_H is measured from the Sm^{2+}-vacancy axis in the reflection plane. There are altogether 24 equivalent $C_s(2,1,1)$ sites, which are shown in Fig. 1 at the corners of the six squares normal to the [100], [010], [001], [$\bar{1}$00], [0$\bar{1}$0], and [00$\bar{1}$] crystal axes. The 12 sites associated with the [100], [010], and [001] axes are denoted by a, a', b, b'; c, c', d, d'; and e, e', f, f', respectively. Since the magnetic field is invariant upon inversion, the $[l,m,n]$ and $[\bar{l},\bar{m},\bar{n}]$ crystal axes are equivalent, and the 12 remaining sites associated with the [$\bar{1}$00], [0$\bar{1}$0], and [00$\bar{1}$] axes are indistinguishable from the 12 above-mentioned sites through an inversion of coordinates in the magnetic field. When the magnetic field $\hat{H}$ is in the Z direction, the symmetry of the Sm^{2+}-K^+ vacancy remains C_s. When the magnetic field is in any other direction, the site symmetry is lowered to C_1 as the magnetic field destroys the reflection plane of the C_s complex. There are two nondegenerate representations A' and A'' in the C_s point group. While J_Z transforms as A', J_+ and J_- transform as A''. It follows, therefore, that at $\theta_H=0°$, the Zeeman shifts will occur only through diagonal matrix elements and/or nondiagonal matrix elements between states of the same representation. On the other hand, at $\theta_H=90°$, the Zeeman shifts will occur through nondiagonal matrix elements between the two unlike representations only. For intermediate values of θ_H, all three types of matrix elements will contribute to the energy shifts. A group of sites will be magnetically equivalent if and only if their orientations with respect to the magnetic-field direction are identical in terms of the angles θ_H and ϕ_H, and of α, the angle between $\hat{H}$ and the Sm^{2+}-vacancy axis. When $\hat{H}$ is in the [100] direction, there are two identical groups of sites: (i) a, a', b, b' ($\alpha=35°16'$, $\theta_H=90°$, $\phi_H=35°16'$) and (ii) c, c', d, d', e, e', f, f' ($\alpha=65°54'$, $\theta_H=45°$, $\phi_H=54°44'$). As $\hat{H}$ is rotated away from the [100] direction in the (001) plane, there are six groups of equivalent sites: a, a'; b, b'; c, c'; d, d'; e, f'; and $e'f$, which should give rise to a maximum of six lines. With $\hat{H}$ in the [110] direction, the fluorescence lines of the sites (i) a, a', c, c' ($\alpha=30°$, $\theta_H=60°$, $\phi_H=0°$); (ii) b, b', d, d' ($\alpha=73°13'$, $\theta_H=60°$, $\phi_H=70°32'$); (iii) e, f' ($\alpha=54°44'$, $\theta_H=90°$, $\phi_H=54°44'$); and (iv) $e'f$ ($\alpha=90°$, $\theta_H=0°$, $\phi_H=0°$) should merge to give only four lines. Further rotation of $\hat{H}$ to the [010] direction should give rise to a mirror image return to the initial two lines. As $\hat{H}$ is rotated away from the [010] direction in the (101) plane (see Fig. 1), there should be seven lines arising from the sites d; c, d'; b', e'; b, e; c'; a', f'; and a, f. When $\hat{H}$ is in the [$\bar{1}$11] direction, the seven lines should

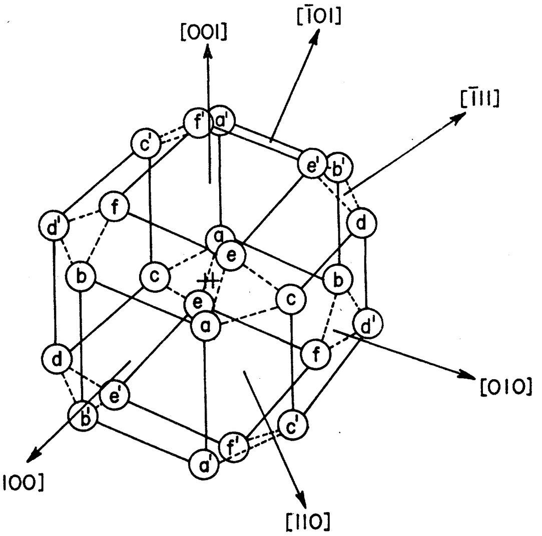

FIG. 1. The 24 equivalent sites of the $C_s(2,1,1)$ Sm^{2+}-K^+ vacancy pairs. At the center of the coordinate system is the divalent cation denoted by the symbol ++. The system of notation is explained in the text.

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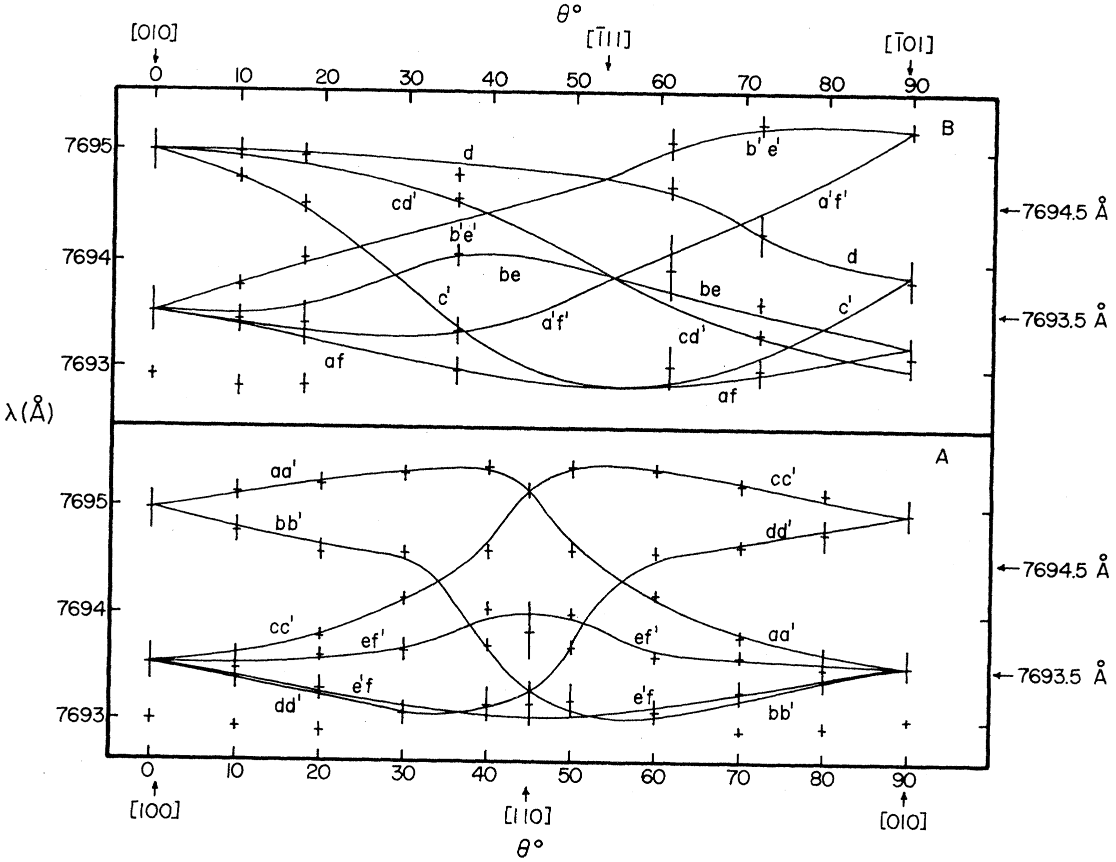

FIG. 2. High-resolution $C_s(2,1,1)$ ZAF patterns associated with the no-field lines at 7694.5 and 7693.5 Å ($^5D_0 \rightarrow {}^7F_3$) with $\hat{H}$ rotating in (A) the (001) plane and (B) the (101) plane. The lines were observed at 20-μ slit and 40-min exposures, with the grating operated at second order. The no-field lines are indicated on the right of the drawing.

merge into three lines arising from the three groups of sites: (i) b', d, e' ($\alpha=19°28'$, $\theta_H=90°$, $\phi_H=19°28'$); (ii) a', b, c, d', e, f' ($\alpha=61°52'$, $\theta_H=35°16'$, $\phi_H=35°16'$); and (iii) a, c', f ($\alpha=90°$, $\theta_H=90°$, $\phi_H=90°$). When $\hat{H}$ is in the [101] direction, there should be four lines due to the groups: (i) a', b', e', f' ($\alpha=30°$, $\theta_H=60°$, $\phi_H=0°$); (ii) c', d ($\alpha=54°44'$, $\theta_H=90°$, $\phi_H=54°44'$); (iii) a, b, e, f ($\alpha=73°13'$, $\theta_H=60°$, $\phi_H=70°32'$); and (iv) c, d' ($\alpha=90°$, $\theta_H=0°$, $\phi_H=0°$).

These theoretical expectations are tested on the high-resolution ZAF lines measured in the wavelength region corresponding to the two most intense $0\rightarrow 3$ no-field lines at 7694.5 and 7693.5 Å, with $\hat{H}$ rotating in the (001) and (101) planes (Fig. 2). The excellent fit leaves little doubt as to the C_s origin of the ZAF patterns. If we attribute the C_s patterns to the no-field line at 7694.5 Å, the line at ~7693.0 Å observed in addition to the ZAF patterns is most likely associated with the no-field line at 7693.5 Å. In Fig. 3, the fits of the expected C_s ZAF patterns to experimental observations made for the relatively weak no-field lines at 8122.5 and 8128.6 Å ($^5D_0 \rightarrow {}^7F_4$) and those for the strong line at 8778.4 Å ($^5D_0 \rightarrow {}^7F_5$) are shown.

IV. DISCUSSION

From the relative intensities reported by Bron and Heller,[5] we estimate that approximately 26% of the total fluorescence intensity in the $J=3$, 4, 5, and 6 manifolds can be attributed to the $C_s(2,1,1)$ site as compared with the 37% attributable to fluorescence lines ($0\rightarrow 4$ and $0\rightarrow 6$ transitions) which have been identified in terms of ZAF patterns to be of C_{4v}-site origin.[3,6] These observations are to be contrasted with the fact that only one weak line at 8746.4 Å has been assigned, through a ZAF spectroscopic determination,[3] to the C_{2v}-site symmetry. The dominant lines in $J=0$, 1, and 2 show no detectable Zeeman effects at 26.5 kG even with the grating operated at second order. Although Bron and Heller, in their detailed study[5] of the polarized emission of the KCl:Sm^{2+} system, have assigned these as well as all the other lines to the unique existence of the $C_{2v}(1,1,0)$ site, their crystal-field calculation of the Stark splittings of $J=1$ and 2 have been shown[3] to be inconsistent with our own calculations including the

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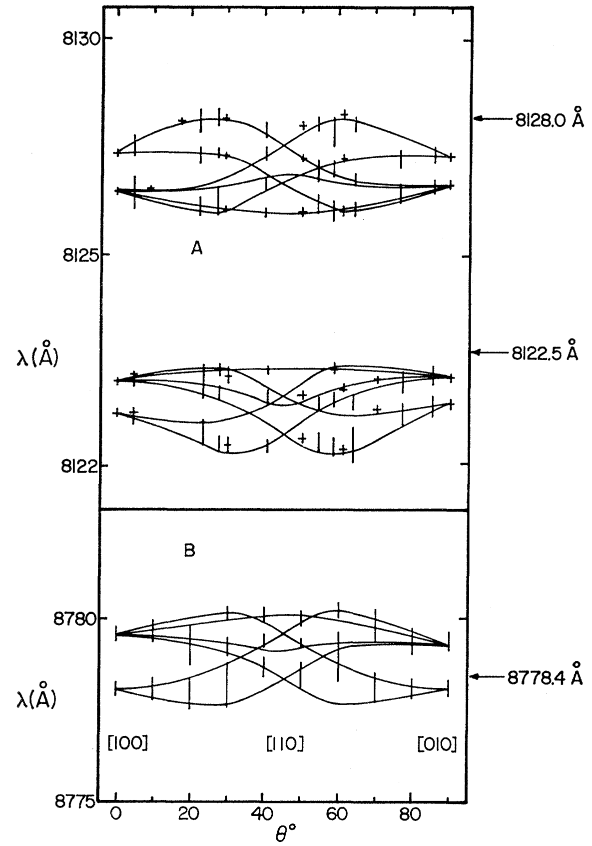

FIG. 3. ZAF patterns associated with (A) the no-field lines at 8128.0 and 8122.5 Å ($^5D_0 \rightarrow {}^7F_4$), and (B) the no-field line at 8778.4 Å ($^5D_0 \rightarrow {}^7F_5$) with $\hat{H}$ rotating in the (001) plane. In (A), spectral lines of two different exposures are shown: + represents 20-μ slit, 10-min exposures, and | represents 50-μ slit, 40-min exposures. In (B), all the measurements were made with 20-μ slit and 10-min exposures. The no-field lines are indicated on the right of the drawing.

magnetic field. In fact, every single one of their crystal-field assignments of the KCl:Sm^{2+} fluorescence lines associated with $J \geqq 3$ is seen to be in error.[7]

The results reported herein are of fundamental importance in the understanding of numerous phenomena in polar crystals. Much of the earlier work[2,8–10] on compensated lattices in KCl:M^{2+} and related systems such as CaF$_2$:M^{3+} in which a F$^-$ interstitial is the compensation was based on the assumption that the impurity cation is either in close association with the compensation or it is beyond any significant influence of the distant compensation. On the other hand, the unique existence of the nearest-neighbor C_{2v} sites was postulated[5,11] in the interpretation of the Sm^{2+} optical bands in alkali halides. In view of the present work, it appears certain that at least for the temperature and concentration ranges given above, most of the existing theories on ionic conductivity,[8] dielectric relaxation,[9] valence reduction of rare-earth (RE) ions,[4,10] and electronic-vibronic transitions of RE^{2+} ions[11] in compensated lattices must be reassessed. In this direction, initial efforts in explaining the additive reduction of RE^{2+} ions to the monovalent state in KCl[12] and the anomalous dispersion region due to dielectric relaxation observed[13] for KCl:M^{2+} in terms of the above-described distribution in sites have been made with considerable success.

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[7] All the lines associated with $^5D \rightarrow {}^7F_J$ ($J = 3$, 4, 5, and 6) which were attributed to irreducible representations of the C_{2v} point groups by Bron and Heller (Ref. 5) are actually either of C_{4v} origin or of C_s origin. The one line at 8746.4 Å ($J = 5$) which indeed is of C_{2v} origin (Ref. 3), however, was not even reported by these authors.

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