

Electron paramagnetic resonance of $\text{Cr}(\text{CN})_6^{3-}$ in NaCl: Evidence for motion of the associated cation vacancies

D. M. Wang

*Physics Department, Monash University, Clayton, Victoria 3168, Australia
and Department of Molecular Spectroscopy, University of Nijmegen, 6525 ED, Toernooiveld, The Netherlands*

E. de Boer

*Department of Molecular Spectroscopy, University of Nijmegen, 6525 ED, Toernooiveld, The Netherlands
(Received 30 November 1988)*

The electron-paramagnetic resonance spectra of the $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl show evidence for the association of cation vacancies with the complex. The $\text{Cr}(\text{CN})_6^{3-}$ complex goes into the lattice substitutionally, replacing NaCl_6^{5-} , and simultaneously, two cation vacancies are created. Two different centers (one with D_{2h} symmetry and one with C_s symmetry) were formed in as-grown crystals at room temperature. They were also observed in KCl as previously reported. However, the present study has provided strong evidence for the motion of the associated cation vacancies in the neighborhood of a substitutional trivalent ion in an alkali-metal halide. It was observed that half of the $\text{Cr}(\text{CN})_6^{3-}$ ions constituting the center with C_s symmetry were converted into a new center, also with C_s symmetry, at low temperature. This new center begins to emerge as the temperature decreases to ~ 265 K. It is found that below 215 K the two centers with C_s symmetry have an equal population, each amounting to $(\sim 20 \pm 5)\%$ of the total concentration. The formation of this new center occurs when a vacancy jumps from the next-nearest cation site to the nearest cation site. All possible configurations for a trivalent impurity ion in an alkali-metal halide associated with two cation vacancies are discussed for cases where the vacancies occupy the nearest and the next-nearest cation sites. It is shown that for a trivalent substitutional impurity ion, a vacancy jump, in most cases, corresponds to an interconversion between different configurations. Finally, we point out that the configuration, which has been reported for all previously investigated trivalent impurity ions or complexes in alkali-metal halides, is not present in either $\text{KCl}:\text{Cr}(\text{CN})_6^{3-}$ or $\text{NaCl}:\text{Cr}(\text{CN})_6^{3-}$. This absence raises questions about the correctness of those interpretations.

I. INTRODUCTION

In the last few decades, a considerable amount of work has been done on the nature of divalent impurity ions in alkali-metal halides, especially in those with the NaCl structure.¹⁻⁹ The divalent ions normally go in substitutionally for alkali-metal ions and one extra charge is, in most cases, compensated for by a cation vacancy. Experimental evidence has been accumulated showing the association of the cation vacancy with the impurity ion and a reasonably good agreement has been found between experimental observation and theoretical calculation. Studies of motion of the associated vacancies in the neighborhood of the divalent impurity ion has also been of considerable interest.¹⁰⁻¹²

In contrast, trivalent impurity ions have received little attention in these respects, probably due to the complication of charge compensation. When a trivalent ion is incorporated into an alkali-metal halide lattice substitutionally, each impurity ion has two extra charges to be compensated. If the charge compensation is achieved by introduction of cation vacancies, and if the vacancies are associated with the trivalent impurity ion, then there will be a large number of different configurations of the two vacancies. Previous studies of trivalent ions or complexes

in alkali-metal halides have given evidence for the association of the cation vacancies with the impurity ions.¹³⁻¹⁸ Among these studies, three different configurations have been proposed. The first of these has both cation vacancies occupying the nearest cation sites along $\langle 110 \rangle$ and has D_{2h} symmetry. The second configuration has one vacancy at the nearest and the other one at the next-nearest cation site, reducing the local symmetry to C_s with $\{100\}$ as the mirror plane. The third configuration assumes both vacancies at the next-nearest cation sites along $\langle 100 \rangle$ and it has D_{4h} symmetry. The second configuration with C_s symmetry was reported for all trivalent ions or complexes studied. Some trivalent ions or complexes were also reported to form, simultaneously, more than one configuration. For instance, all three configurations were reported to be present in $\text{KCl}:\text{Cr}(\text{CN})_6^{3-}$.¹⁸ However, all these interpretations are based on relatively indirect measurements such as ionic conductivity,¹⁶ dielectric loss,¹⁶ optical and vibration spectrum,¹³⁻¹⁸ and excitation spectrum.^{17,18} In most cases, the proposed configurations are deduced from energy considerations based on the point-charge model. Therefore, these interpretations are not convincing, and in some cases,^{17,18} some of the interpretations have been proved to be incorrect.¹⁹

It is well known that the electron-paramagnetic-resonance spectrum of a paramagnetic ion is very sensitive to the local environment. An EPR study of the $\text{Cr}(\text{CN})_6^{3-}$ complex in KCl has provided direct information about the type of configurations of the charge-compensating vacancies located around a trivalent impurity ion.¹⁹ While the assignment of the configuration with D_{2h} symmetry to one of the two identified centers (center I) agrees with all experimental observations, the other center (center II) cannot be attributed to the second configuration, although it also has C_s symmetry. A different configuration, also with one cation vacancy at the nearest and the other one at the next-nearest cation site, but with $\{110\}$ as the mirror plane, was found to describe the symmetry of center II. The absence of the second configuration, and the observation of this new configuration raises doubt about the correctness of previous interpretations.

In order to improve our understanding of the interaction of an impurity ion with local defects in simple lattices such as alkali-metal halides, the exact nature of these configurations is of essential importance. Furthermore, motion of the associated vacancies in the neighborhood of a trivalent impurity ion is also of interest. Therefore, we have undertaken a systematic EPR study of the $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl and KBr. In addition to having gained further support for the interpretation given for $\text{Cr}(\text{CN})_6^{3-}$ in KCl, this study has provided for the first time evidence for the motion of the associated cation vacancies in the neighborhood of a trivalent impurity ion in alkali-metal halides. Because the $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl and KBr lattices shows quite different temperature-dependent behavior, in this paper, only the experimental results in NaCl will be presented and those in KBr will be reported in a subsequent publication. The spectrum of $\text{Cr}(\text{CN})_6^{3-}$ in KCl, between room temperature and liquid-helium temperature, showed no significant changes.

II. EXPERIMENTAL

The crystals used in this study were grown at room temperature by slowly evaporating a saturated aqueous solution of NaCl containing 0.5 mol % $\text{K}_3\text{Cr}(\text{CN})_6$. The EPR measurements at room temperature were performed at Monash University on a Varian E12 spectrometer. The angular dependence measurements of the spectrum was carried out using a two-circle goniometer based on the design of Morton *et al.*²⁰ The EPR measurements at low temperatures were performed at Nijmegen on a Bruker ESP 300 spectrometer using a home-built cryostat. This cryostat covers a temperature range between room temperature and 1.5 K. In combination with the rotation of the magnet, the cryostat also offers a full range of rotation of the sample. However, due to a disadvantage of losing the effective modulation field as a result of rotation of the magnet, the sample was mounted in such a way that minimum rotation of the magnet was required. Magnetic field strength was measured to an accuracy of $\pm 20 \mu\text{T}$ and microwave frequencies were measured to an accuracy of $\pm 0.1 \text{ MHz}$.

III. THEORY

The EPR spectra of $\text{NaCl}:\text{Cr}(\text{CN})_6^{3-}$ were interpreted by the following spin Hamiltonian with $S = \frac{3}{2}$

$$\mathcal{H} = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2). \quad (1)$$

\mathbf{B} is the applied magnetic field and the other terms have their usual meaning. Since anisotropy of the g matrix is expected to be small for the trivalent Cr^{3+} ion, it was assumed that the principal axes of the g matrix coincide with those of the fine-structure tensor. The standard axis system^{21,22} is used in the presentation of the results.

The general features of the EPR spectrum described by the spin Hamiltonian (1) with $S = \frac{3}{2}$ have been discussed in detail by Wang and Pilbrow.²³ When the Zeeman and the fine-structure interactions have comparable strength, the four actual states are linear combinations of the four spin states $|M_s\rangle$ of the operator S_z . In this case, transitions between any pair of actual states are possible. As will be shown in Sec. IV A 1, all these possible transitions were observed in the X-band EPR spectrum of $\text{Cr}(\text{CN})_6^{3-}$ in NaCl.

In order to facilitate the discussion, some notations are introduced here.²⁴ The four actual states are denoted by $|n\rangle$ with n ranging from 1 to 4 in order of increasing energy. Transitions between any adjacent levels are called A transitions (A_{12} , A_{23} , and A_{34}) and those occurring between any nonadjacent levels are called F transitions (F_{13} , F_{24} , and F_{14}).

IV. RESULTS AND ANALYSIS

A. Identification and description of the $\text{Cr}(\text{CN})_6^{3-}$ centers

1. Spectrum at room temperature

The EPR spectrum of $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl at room temperature is very similar to the spectrum in KCl.¹⁹ It consists of two $\text{Cr}(\text{CN})_6^{3-}$ centers which, according to their fine structure, are similar to the two centers identified in $\text{KCl}:\text{Cr}(\text{CN})_6^{3-}$. Correspondingly, these two centers are denoted I and II, respectively. The principal axes of the fine-structure tensor of both centers are, within the errors of the measurements, the same as those of the corresponding centers in KCl. For center I, one of the six sets of the principal axes is $x \parallel [001]$, $y \parallel [110]$, and $z \parallel [\bar{1}\bar{1}0]$. For center II, only the principal x axis lies along a twofold crystallographic axis, for instance $[110]$. The principal y and z axes lie 45° from $\langle 100 \rangle$ in $\{110\}$ as shown in Fig. 1. It is easily shown that the overall symmetry of the crystal gives rise to 6 and 12 EPR distinguishable sites for centers I and II, respectively.

While a spectrum for an arbitrary orientation of the magnetic field is very complicated, the spectrum with \mathbf{B} along a crystal axis is significantly simplified due to coincidence of sites. In Fig. 2, the $\langle 100 \rangle$ spectrum of $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl is shown. With \mathbf{B} along $\langle 100 \rangle$, there are only two EPR distinguishable sites for both centers I and II. The four distinguishable sites are denoted a , b , c , and d in the figure. The lines in the group

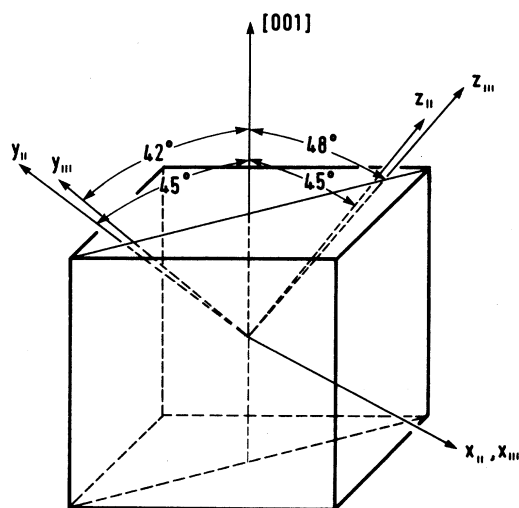


FIG. 1. Orientations of the principal axes of the fine-structure tensor of centers II and III of $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl with respect to the crystal axes.

centered at $g=2$ are all due to A transitions. F transitions are also present at low field, but, with rather weak intensities. The lines at ~ 170 mT were found to be F_{13} and F_{24} transitions and those at ~ 95 mT are four F_{14} transitions. Although nearly all the spectral lines in Fig. 2 could be attributed to the two identified centers, there are still a few small peaks, indicated by arrows in the

neighborhood of the line at 335 mT, of unknown origin. Because of the large number of spectral lines in the $g=2$ region, a detailed angular dependence study of these lines, which is required for their identification, was not possible, so that they remain unidentified.

The unusual spectral coincidence, which was observed for center I of the $\text{Cr}(\text{CN})_6^{3-}$ complex in KCl,¹⁹ and which was found to be due to the special symmetry in the case that $E/D = \frac{1}{3}$, together with the crystallographic equivalence of the principal y and z axes of the fine-structure tensor, has not been observed for center I in NaCl. If this unusual coincidence occurs, the two pairs of lines at ~ 210 mT and ~ 440 mT in the $\langle 110 \rangle$ spectrum which is shown in Fig. 3 would be two "single" lines as is the case for the spectrum of $\text{KCl}:\text{Cr}(\text{CN})_6^{3-}$ at room temperature. It is proved that the value of exactly $\frac{1}{3}$ for the ratio E/D for center I in KCl at room temperature is purely accidental.²⁵

The angular dependence of the spectra, measured in both $\{100\}$ and $\{110\}$ planes, agrees with what is predicted by the overall symmetry of the crystal. The values for the ratio E/D were estimated to be 0.30 and 0.27 for centers I and II, respectively, using the method discussed previously.²³

2. Spectrum at low temperature—emergence of a new center

The temperature dependence of the spectrum was measured between room and liquid-helium temperature. A new center was observed at low temperature. This new center, starting to emerge as the temperature is lowered

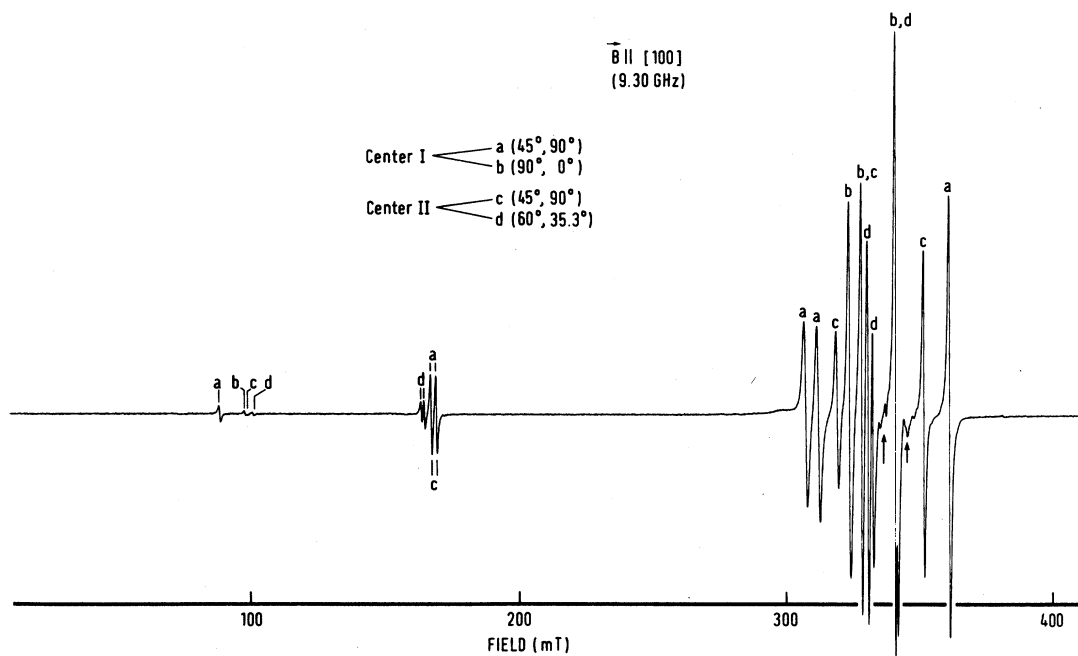


FIG. 2. EPR spectrum of $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl observed at room temperature with \mathbf{B} along $\langle 100 \rangle$. In this spectrum, both centers I and II have only two distinguishable sites as denoted as a, b and c, d , respectively. The polar angles given in brackets indicate the orientation of \mathbf{B} with respect to the principal-axis system of the corresponding site. All possible transitions are observed except F_{13} and F_{24} for site b which should have occurred at ~ 150 mT.

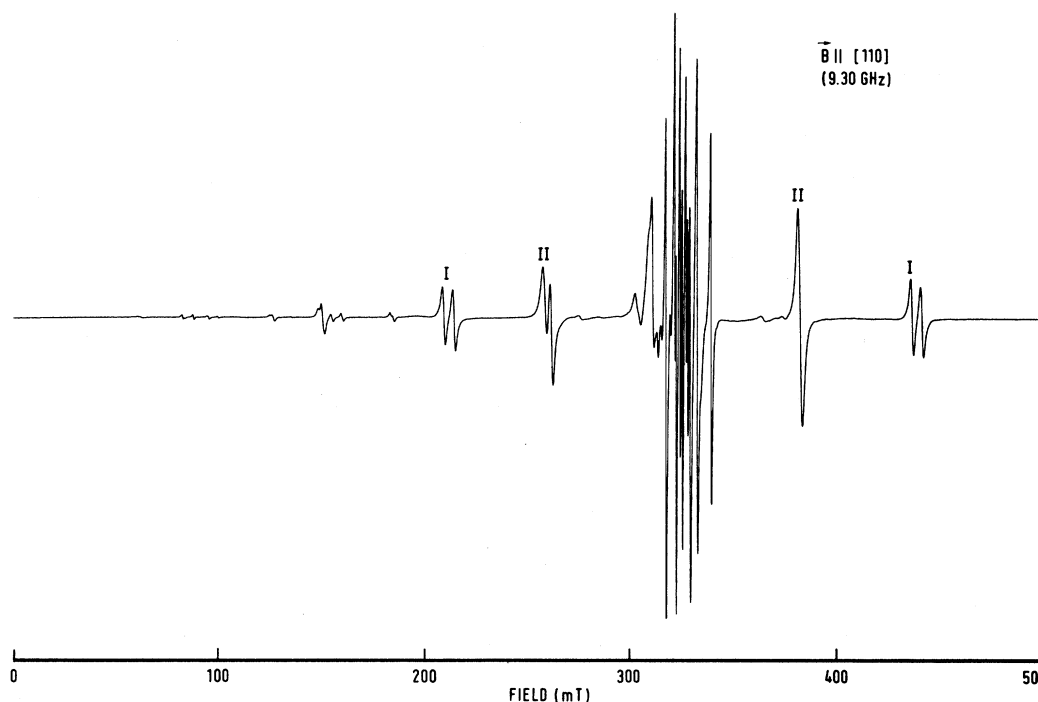


FIG. 3. EPR spectrum of $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl observed at room temperature with \mathbf{B} along $\langle 110 \rangle$. Because lines overlap in the region between 320 to 350 mT, no indication is given there. Weak lines at low field are due to F transitions.

down to ~ 265 K, is also attributed to the $\text{Cr}(\text{CN})_6^{3-}$ complex perturbed by local charge-compensating vacancies. It has a fine structure similar to that of center II. This new center is denoted center III. Accompanied with the emergence of center III, the relative population of center II to center I was observed to change (see Fig. 4).

A more detailed description of the process of emergence of center III can be stated as follows. As temperature decreases from room temperature, broad lines of center III begin to emerge at ~ 265 K. These lines become sharper and sharper as the temperature decreases further. At ~ 215 K, the linewidths of these lines reached their characteristic linewidths, which are about twice as large as the linewidths of the lines belonging to center II. Meanwhile, the relative intensity of center II to center I decreases. At 215 K, it seems that the new center has acquired a population equal to that of center II. In other words, half of the ions constituting center II at room temperature were converted into center III at 215 K. Below 215 K, no further conversion was detected within the experimental error. When warming up, a reverse process was observed.

Center III was measured in detail at both 77 and 4.2 K. At both temperatures, the principal axes of the fine-structure tensor were found to have the same orientations with respect to the crystal axes and it is shown in Fig. 1. Both the y and z axes lie in $\{110\}$ and the x axis shares $\langle 110 \rangle$ with the x axis of center II. Even though in the figure the two y axes (or two z axes) are shown to have only a 3° difference in direction, one must realize that because of the cubic symmetry of the crystal, there exists an

ambiguity in determining the y and z axes. Figure 1 only shows one of the possibilities. The other one, involving an exchange of the principal y and z axes of center II, has an angle of 87° between the two y axes and an angle of 93° between the two z axes.

It is obvious that the symmetry as revealed by the fine structure of the spectrum of center III is also C_s with $\{110\}$ as the mirror plane. Therefore, center III also has 12 EPR distinguishable sites for an arbitrary orientation

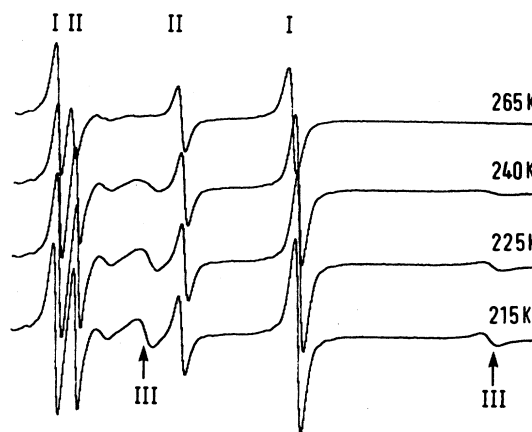


FIG. 4. Temperature dependence of the high-field part of the spectrum in Fig. 2. Emergence of center III lines as the temperature is lowered is indicated by arrows.

TABLE I. Spin-Hamiltonian parameters of $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl measured at 290, 77, and 4.2 K.

Center	g value	D^a	E	D_{ZFS}^b	E/D
290 K					
I	1.992 ± 0.001	1.625 ± 0.007	0.497 ± 0.007	3.68	0.31
II	1.992 ± 0.001	1.268 ± 0.010	0.347 ± 0.010	2.81	0.27
77 K					
I	1.9940 ± 0.0004	1.750 ± 0.005	0.523 ± 0.002	3.94	0.30
II	1.9935 ± 0.0006	1.344 ± 0.006	0.360 ± 0.004	2.96	0.27
III	1.9940 ± 0.0005	2.469 ± 0.005	0.547 ± 0.004	5.29	0.22
4.2 K					
I	1.9908 ± 0.0006	1.770 ± 0.003	0.527 ± 0.004	3.98	0.30
II	1.9914 ± 0.0007	1.344 ± 0.004	0.373 ± 0.006	2.98	0.28
III	1.9910 ± 0.0006	2.486 ± 0.004	0.550 ± 0.004	5.32	0.22

^aThe sign of D is not determined. D and E are given in units of GHz.

^b D_{ZFS} is the zero-field splitting, also in GHz.

of the magnetic field. Site splitting and coincidence of the spectrum of center III as the orientation of the magnetic field is varied is exactly the same as that for center II. For example, when \mathbf{B} is along $\langle 100 \rangle$, there are also only two EPR distinguishable sites.

As the orientations of the y and z axes of the fine-structure tensor of center II in the mirror plane are not restricted by symmetry, they may vary as temperature changes. An attempt to detect such changes was made at both 77 and 4.2 K. Within the experimental error of $\pm 0.3^\circ$, the orientations of both y and z axes were exactly the same as found at room temperature.

At low temperature, a few A_{23} transitions in the $\langle 100 \rangle$ and $\langle 110 \rangle$ spectra show partially resolved hyperfine and superhyperfine structures. These structures are thought to be due to ^{53}Cr (9.5% natural abundance), K^+ and/or Cl^- nuclei. Due to the complexity of the spectrum, their orientation dependence was not measured.

B. Quantitative analysis of the spectra

1. Evaluation of the spin-Hamiltonian parameters

All the spectra have been interpreted by the spin Hamiltonian (1) with $S = \frac{3}{2}$. A least-squares fitting program was used, in which exact computer diagonalization of the Hamiltonian was employed in obtaining the energy levels. The spin-Hamiltonian parameters were evaluated at three different temperatures 290, 77, and 4.2 K.

For each fitting, nine A transitions were used. When all A transitions in three principal axis spectra could be precisely measured, only these transitions were selected. Otherwise, transitions with \mathbf{B} along other directions had to be included. All parameters were adjusted during the fitting process. The results are listed in Table I. The anisotropy in the g matrix was negligible, therefore, in Table I, only the isotropic g values are given.

2. Relative concentrations between the centers

As already mentioned above, the emergence of center III at low temperature is accompanied by a decrease in

the intensity of center II relative to that of center I as shown in Fig. 4. A more precise calculation of the relative occupancy between the centers was carried out at different temperatures based upon the comparison of the area of spectral lines.²⁶ The results are given in Table II.

One can see from Table II that center I has a constant population of ($\sim 60 \pm 8$)% over the whole temperature range, and center III originates from center II. Within the experimental uncertainty, centers II and III have an equal population at 215 K, which is constant to low temperatures (see values at 77 and 4.2 K). Therefore, below 215 K, there is no further conversion of center II to center III.

V. DISCUSSION

Although the Zeeman interaction of the identified centers is essentially isotropic, the fine-structure interaction is a very sensitive probe to the local environment. The orthorhombic or lower symmetry revealed by the fine-structure tensor provides strong evidence for perturbation of the $\text{Cr}(\text{CN})_6^{3-}$ complex by local defects. Because the crystals studied are as-grown crystals, these defects are assumed to be cation vacancies which compensate for the extra charges on the substitutional Cr^{3+} ions. Before we discuss models for the identified centers, we will consider all possible configurations of the two charge-compensating vacancies, assuming that the cation vacancies can occupy both the nearest and the next-nearest cation sites to the impurity ion.

TABLE II. Relative concentrations of $\text{Cr}(\text{CN})_6^{3-}$ ions among different centers.

Temperature (K)	Center I	Center II	Center III
290	60 ± 8 %	40 ± 8 %	
215	60 ± 8 %	20 ± 5 %	20 ± 5 %
77	60 ± 8 %	20 ± 5 %	20 ± 5 %
4.2	60 ± 8 %	20 ± 5 %	20 ± 5 %

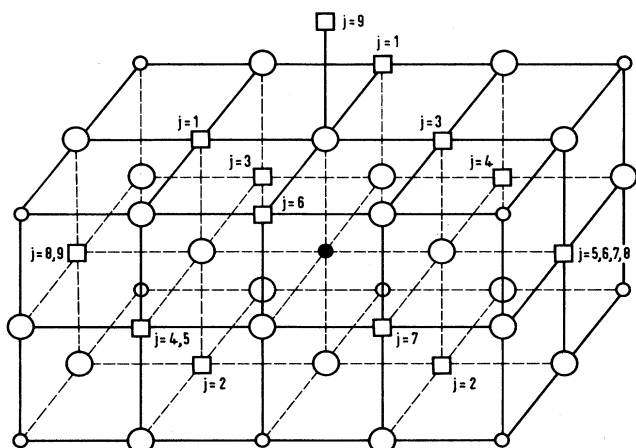


FIG. 5. Nine possible configurations of two cation vacancies arranged in the neighborhood of a trivalent impurity ion in an alkali-metal halide with the NaCl structure, assuming that the vacancies independently occupy the nearest and the next-nearest cation sites. ●, the trivalent ion; □, cation vacancy; ○, cation and ○, anion.

A. Possible configurations

1. Both vacancies at the nearest cation sites

In an alkali-metal halide with the NaCl structure, there are 12 nearest cation sites. If both vacancies occupy the nearest sites, a simple statistical calculation shows that there will be 66 different combinations. Obviously, these combinations are not all structurally inequivalent. In fact, there are only four distinctive combinations (configurations) which are shown in Fig. 5 denoted as $j=1, 2, 3,$ and 4 .²⁷ It is clear that the local symmetry is greatly reduced due to the presence of two vacancies. These local symmetries, together with some characteristic EPR features deduced from them, are summarized in Table III.

2. One vacancy at the nearest and the other one at the next-nearest cation site

In this case, there are 72 (12×6) combinations because there are 6 next-nearest cation sites in the crystal. They form three different configurations ($j=5, 6,$ and 7) as shown in Fig. 5. All three configurations have C_s symmetry, but the mirror plane for configuration $j=6$, the $\{110\}$ plane, is different from that for the other two, the $\{100\}$ plane.

3. Both vacancies at the next-nearest cation sites

If both vacancies occupy the next-nearest cation sites, there are 15 combinations which belong to two configurations (see Fig. 5, $j=8$ and 9). Configuration $j=8$ has D_{4h} symmetry, which is the only one which would give a center with axial symmetry. Any centers which can be attributed to all other configurations in Fig. 5 must be described by the orthorhombic spin Hamiltonian (1).

The number of configurations is much greater if the third-nearest cation sites are involved. For instance, if one vacancy is at the nearest and the other one at the third-nearest cation site, then there will be 288 combinations which form 7 configurations. Since there is no experimental evidence for their occupation, they will not be considered.

B. Models for the observed centers

It is shown in Table I that the g matrix of all three centers is isotropic ($g \approx 1.992$). This property was also reported for the $\text{Cr}(\text{CN})_6^{3-}$ complex in other host lattices with symmetries varying from octahedral to monoclinic.²⁸⁻³² Therefore, an isotropic Zeeman interaction with g around 1.992 is one of the EPR features of the $\text{Cr}(\text{CN})_6^{3-}$ complex. Such a feature, observed for all three centers of $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl, indicates that the whole complex enters the lattice replacing NaCl_6^{5-} , as reported for other metal cyanide complexes in alkali-metal halides.¹³⁻¹⁵

TABLE III. Symmetry and its implied features of the corresponding EPR spectrum for the configurations considered in Fig. 5.

Configuration j	Number of equivalent combinations ^a	Symmetry	Principal axis ^b	Distance between vacancies ^c
1	24	C_s	$\langle 110 \rangle$	$\sqrt{2}/2$
2	12	C_{2v}	[100] [010] [001]	1
3	24	C_2	$\langle 110 \rangle$	$\sqrt{6}/2$
4	6	D_{2h}	[100] [011] [01 $\bar{1}$]	$\sqrt{2}$
5	24	C_s	$\langle 100 \rangle$	$\sqrt{10}/2$
6	24	C_s	$\langle 110 \rangle$	$\sqrt{6}/2$
7	24	C_s	$\langle 100 \rangle$	$\sqrt{2}/2$
8	3	D_{4h}	$\langle 100 \rangle$	2
9	12	C_{2v}	[100] [011] [01 $\bar{1}$]	$\sqrt{2}$

^aFor all configurations except configurations $j=4$ and 8 , the equivalent combinations are related to each other by the inversion symmetry, so that the number of EPR distinguishable sites is equal to half of the number of equivalent combinations.

^bFor configurations $j=2, 4,$ and 9 , only one of the possible sets of the principal axes is given.

^cIn units of the lattice constant a (for NaCl, $a = 5.64 \text{ \AA}$).

Centers I and II are structurally the same as their corresponding centers in KCl. This conclusion is drawn on the basis of the symmetry revealed in the fine structure, and is also supported by the relative magnitude of the zero-field splittings. As shown in Table I, the zero-field splitting of center II is 31% (at 290 K) or 33% at both 77 and 4.2 K larger than that of center I in NaCl, which can be compared with the corresponding value of 29% in KCl at 290 K.¹⁹ Configurations responsible for centers I and II have been discussed in a previous paper¹⁹ and they are configurations $j=4$ and 6 in Fig. 5, respectively.

Another possibility we have not mentioned is that there may be only one cation vacancy associated with the trivalent impurity ion with the other one being remote. If this is the case, the trivalent impurity ion will resemble a divalent ion and the associated vacancy can either occupy the nearest or the next-nearest cation site. This possibility was suggested by the EPR data of V^{2+} in NaCl.⁴ V^{2+} is isoelectronic to Cr^{3+} . In NaCl, two V^{2+} centers, one with the cation vacancy occupying the nearest (center I) and one with the cation vacancy occupying the next-nearest site (center II), were reported.⁴ An increase of the zero-field splitting of center II to that of center I by 29% at 290 K was found, which is similar to what is observed between the two $Cr(CN)_6^{3-}$ centers in NaCl and KCl. However, while the observed symmetry D_{2h} , for center I may imply only one local cation vacancy at the nearest site, the C_s symmetry inferred from the fine structure for center II must be due to more than one local vacancy. Therefore, the situation in which only one vacancy is associated with the trivalent impurity ion is unlikely.

Center III is also perturbed by local defects as indicated by the fine structure of the spectrum. Based on the symmetry argument, there are only two configurations in Fig. 5, which can be considered as candidates for center III. They are configurations $j=1$ and 3. Both configurations have two vacancies at the nearest cation sites. From Table III, it can be seen that only one of the principal axes of the fine-structure tensor is determined by the symmetry and this axis for both configurations has the same orientation with respect to the crystal axes. Therefore, these two configurations cannot, in principle, be distinguished by EPR. We know through the analysis of the relative concentrations that center III originates from center II. If the three configurations ($j=1, 3,$ and 6) are compared (see Fig. 6), the conversion of configuration $j=6$ to either configuration $j=1$ or $j=3$ also appears to have an equal probability because either conversion only involves a single vacancy jump from the next-nearest site to the nearest site. However, if the Coulomb interaction between the vacancies is taken into consideration, obviously, configuration $j=3$ will be more favorable because the two cation vacancies in this configuration are further apart. Furthermore, a theoretical calculation for Pr^{3+} in KCl (Ref. 33) has shown that the association energy for configuration $j=1$ was less than the energy for the isolated defects. Therefore, we conclude that configuration $j=3$ is responsible for center III.

Although quantitative contributions to the zero-field

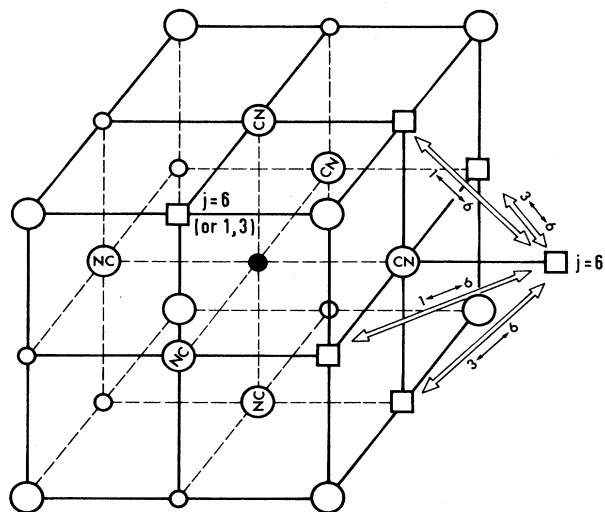


FIG. 6. Schematic representation of the two possible pathways of interconversion between centers II and III. The interconversion between configurations $j=6$ and $j=3$ is more likely.

splitting from individual cation vacancies cannot easily be obtained, one can, in general, expect that vacancies at the nearest site will produce a larger perturbation than vacancies at the next-nearest site, and consequently, result in a larger zero-field splitting. Therefore, the above proposed models are in a qualitative agreement with the relative magnitudes of the zero-field splitting between the centers. However, this qualitative analysis does not account for the larger zero-field splitting of center III, 34% larger than that of center I at both 77 and 4.2 K.

C. Motion of cation vacancies

It has been reported that the cation vacancy, associated with a substitutional divalent impurity ion in alkali-metal halides, can jump among the nearest and the next-nearest sites.¹⁰⁻¹² For example, an EPR study of x-irradiated NaCl:Fe²⁺ crystals has shown that the cation vacancy, associated with Fe⁺ jumps from the nearest cation site to the next-nearest site at 170 K, and then moves away, leaving Fe⁺ unperturbed at 215 K.¹² The present study provides strong evidence for vacancy jumps in the neighborhood of a trivalent impurity ion in an alkali-metal halide. Because there are two cation vacancies in the neighborhood of a trivalent impurity ion, vacancy jumps are, in most cases, accompanied by interconversions between different configurations. If we call the jump of a vacancy to its nearest cation site the primary jump as observed during the conversion process between centers II and III, then a large number of interconversions between the configurations considered in Fig. 5 could happen through only one such primary jump. For example, interconversions between configuration $j=3$ and any of the configurations $j=1, 2, 4, 5,$ and 6 all involve only one primary jump. Apparently, for $Cr(CN)_6^{3-}$ in NaCl, the interconversion between configurations $j=3$ and 6 is most favorable in the temperature range

studied. Vacancy jumps have also been observed in $\text{KBr}:\text{Cr}(\text{CN})_6^{3-}$. Experiments at high temperature are in progress. All conversion processes will be studied in detail and the results will be reported in due course.

VI. SUMMARY

A detailed study has been made of the EPR spectrum of the $\text{Cr}(\text{CN})_6^{3-}$ complex in NaCl over the temperature range between 290 and 4.2 K. In addition to having obtained further support to the previous study of $\text{Cr}(\text{CN})_6^{3-}$ complex in KCl,¹⁹ experimental evidence was found for vacancy jumps. While center I remained basically the same over the temperature range studied, with a constant population of ($\sim 60 \pm 8$)% of the total occupancy, about half of the ions constituting center II formed, at low temperature, a new center. The formation of this new center corresponds to a vacancy jump from the next-nearest site to the nearest cation site. The proposed models for the observed centers are all in agreement with the symmetry revealed in the fine structure of the corresponding spectra. They also qualitatively explain the rel-

ative magnitudes of the zero-field splitting of the centers.

The absence of configuration $j=5$, the one which was reported for all previously studied trivalent ions or complexes in alkali-metal halides, in both $\text{KCl}:\text{Cr}(\text{CN})_6^{3-}$ and $\text{NaCl}:\text{Cr}(\text{CN})_6^{3-}$, renders the previous interpretations questionable. The EPR study of $\text{Cr}(\text{CN})_6^{3-}$ complex in KCl and NaCl has shown that the interaction of a trivalent ion with its local defects in alkali-metal halides cannot, even qualitatively, be accounted for by the point-charge model. It is hoped that the planned further studies will shed more light on our understanding of the behavior of a trivalent impurity ion in alkali-metal halides.

ACKNOWLEDGMENTS

We wish to acknowledge discussions with Dr. J. R. Pilbrow, Dr. E. J. Reijerse, Professor D. Schoemaker, and Dr. E. Goovaerts. We would like to thank A. A. K. Klaassen and G. E. Janssen for their skillful experimental assistance. One of the authors (D.M.W.) acknowledges financial support from the Physics Department, Monash University, and from the University of Nijmegen.

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²⁵We have also measured the EPR spectrum of $\text{KCl}:\text{Cr}(\text{CN})_6^{3-}$ at low temperature. The special spectral coincidence of the spectrum of center I observed at room temperature was absent at low temperature. It was found that the value for the ratio E/D at 4.2 K is 0.31.

²⁶Three lines in the $\langle 100 \rangle$ spectrum (the three lines at high field in Fig. 4) were used. The double integration of the spectral lines was performed by a subroutine in the Bruker ESP 300 software package. The differences in the transition probabilities were negligible compared with the errors in the integration, therefore, they were not taken into account. No data are given between 215 and 265 K because the calculation becomes difficult due to line broadening.

²⁷For a systematic reason, the configurations here are numbered differently from those discussed in Ref. 19.

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