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Cr^+ and Cr^{3+} defects in CaF_2 and SrF_2

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We study x-irradiated chromium-doped CaF_2 and SrF_2 using EPR. A cubic EPR signal which shows a superhyperfine (SHF) interaction with eight fluorine nuclei is associated with Cr^+ ions in a substitutional cation site. The spin Hamiltonian parameters are $g=2.001\pm0.001$ for CaF_2 and SrF_2, $A_{\parallel}^F=39\pm2$ MHz, $A_{\perp}^F=24\pm2$ MHz for CaF_2, and $A_{\parallel}^F=30\pm2$ MHz, $A_{\perp}^F=18\pm2$ MHz for SrF_2. The hyperfine interaction with the ^{53}Cr isotope is resolved giving an hyperfine constant of 66 ± 2 MHz in both matrices. Another signal with a trigonal symmetry is associated with Cr^{3+} ions in a cation substitutional position whose environment has been distorted by a static Jahn-Teller effect. The g value is isotropic and equal to 1.965 ± 0.005 for both CaF_2 and SrF_2 lattices. A SHF interaction with six fluorine nuclei is resolved. The SHF constants are $A_{\parallel}^F=31\pm2$ MHz in CaF_2, 30 ± 2 MHz in SrF_2, and $A_{\perp}^F<3$ MHz in both cases. The hyperfine splitting with ^{53}Cr corresponds to $A_{\parallel}=45\pm2$ MHz and $A_{\perp}=53\pm2$ MHz for CaF_2 and $A_{\parallel}=47\pm2$ MHz and $A_{\perp}=54\pm2$ MHz for SrF_2.

I. INTRODUCTION

Many interesting features concerning the spectroscopic properties of transition-metal ions can be obtained from the study of $3d$-ion-doped fluorite-type crystals (see Gehlhoff and Ulrici[1] for a review). The $3d$ ions usually enter these matrices in a divalent charge state occupying a cation substitutional position with an unusual eightfold coordination. X irradiation of the doped crystals can induce changes in the charge state of the impurity ions as well as in their environments. In this way a wider field for spectroscopic studies can be achieved.

Optical and magnetic resonance measurements performed in "as-grown" and x-irradiated crystals during the last fifteen years have provided detailed information concerning charge states, local environments, hyperfine interactions, etc. for many of the $3d$ impurities in fluorite-type crystals. However, this information is still lacking for some of the ions and for some others it is far from being complete. This is the situation for Cr^+ and Cr^{3+} ions.

To our knowledge the first of these ions has not yet been observed in fluorite-type crystals. In the case of Cr^{3+}, several optical and EPR studies have been reported which indicate that these ions are in a trigonally distorted octahedral coordination (see Gehlhoff and Ulrici[1] for references). However, detailed information concerning Cr^{3+} environment in this kind of matrix has only been reported by Zaripov *et al.*[2] in CaF_2. Using EPR techniques they have found a resolved superhyperfine (SHF) structure due to interaction with two fluorine ions on the trigonal axis of the center. This result suggests that the cube of fluorines that surrounds a cation position has been trigonally distorted around Cr^{3+} with a compression of the fluorines along the C_3 axis. On the other hand, optical measurements on CdF_2:Cr^{3+} seem to be in favor of an elongation of the cube.[3] Moreover, no information concerning hyperfine interaction with the ^{53}Cr isotope (nuclear spin $I=\frac{3}{2}$, natural abundance 9.55%) has been reported for Cr^{3+} ions in fluorite-type crystals. All these reasons make it desirable to have a detailed spectroscopic study of Cr^+ and Cr^{3+} ions in this type of matrix.

Both monovalent and trivalent charge states of chromium have been obtained in several crystals by x irradiation of Cr^{2+}-doped samples.[4–6] Because of this we have undertaken the EPR study of CaF_2:Cr and SrF_2:Cr x irradiated at different temperatures.

In the present paper the results of this study are reported. Two new radiation-induced paramagnetic centers related with chromium impurities have been observed in both matrices. One of these centers shows cubic symmetry and has been associated with Cr^+ ions in a cubic eightfold-coordinated cation substitutional position. The other one, which has trigonal symmetry, has been assigned to Cr^{3+} in an almost octahedral environment produced by a strong Jahn-Teller (JT) distortion of the cube of fluorines that surrounds a cation site. Hyperfine and superhyperfine parameters for the two types of centers have also been obtained.

II. EXPERIMENTAL

Single crystals used in our experiments were either grown in our laboratory by a standard Bridgman technique or purchased from Optovac, Inc. The chromium content in the starting materials ranged from 0.1 to 1%.

EPR measurements were performed in a Varian E-112 spectrometer working in the *X* band. Liquid-nitrogen-temperature (LNT) measurements were taken using a quartz immersion Dewar. Magnetic field values were determined with a Bruker model ER035M NMR gaussmeter. The diphenylpicrylhydrazyl (DPPH) ($g = 2.0037$) signal was used to check the resonance frequency. Samples were irradiated with a Cu-target x-ray tube operated at 40 kV and 20 mA.

III. EXPERIMENTAL RESULTS

Single crystals of CaF_2:Cr and SrF_2:Cr were x irradiated at room temperature (RT) and liquid-nitrogen temperature. After RT irradiation two new EPR signals were observed in both CaF_2 and SrF_2 samples. The spectrum measured at LNT with the external magnetic field along a $\langle 100 \rangle$ direction is given in Fig. 1. This spectrum is the same for both compounds, although the splitting of the lines in the high-field signal is slightly different. When CaF_2:Cr samples are irradiated at LNT and measured at the same temperature, the EPR spectrum coincides with the one observed in RT x-irradiated samples. In LNT x-irradiated SrF_2:Cr a new signal that has been previously identified as due to V_k centers[7,8] appears together with those given in Fig. 1.

The high-field signal in Fig. 1 is centered at $g \simeq 2.0$. It presents a structure consisting of nine equally spaced lines (10 and 8 G in CaF_2 and SrF_2, respectively) with a peak-to-peak width of about 2 G. The relative intensities of these lines follow the approximate sequence 1:8:28:56:70:56:28:8:1. As we will see later, this signal is due to Cr^+ ions with nuclear spin $I = 0$ in a cation substitutional position. The structure is due to the superhyperfine interaction with the eight fluorine nuclei that are placed in the corners of a cube surrounding the Cr^+ ion. In the following this signal will be denoted as the Cr^+-I signal.

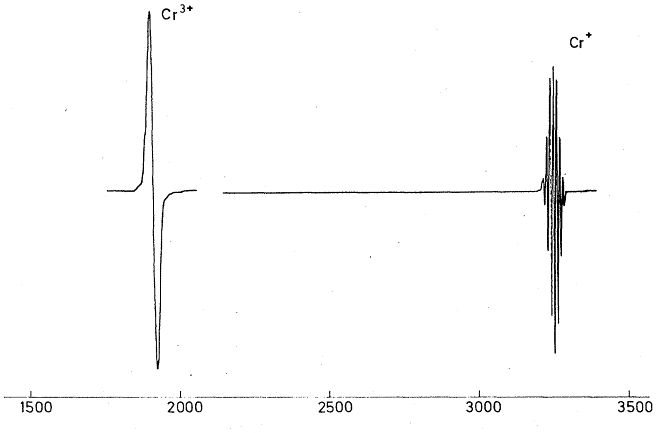

FIG. 1. EPR spectrum of a RT x-irradiated CaF_2:Cr sample measured at 77 K with the magnetic field parallel to a $\langle 100 \rangle$ direction. The Cr^{3+} signal has been magnified 10^2 times more than the Cr^+ one.

When the magnetic field is applied in a direction different from the $\langle 100 \rangle$ ones, the nine-line pattern changes, but the position of the central line remains the same. A SHF structure is also observed when the magnetic field is either along a $\langle 110 \rangle$ or a $\langle 111 \rangle$ direction. This structure is well resolved for CaF_2 crystals, but in the case of SrF_2 there are some overlapping problems and the measured relative intensities cannot be compared with the calculated ones. Regardless, the overall structure can be explained as due to the SHF interaction of Cr^+ with the surrounding cube of fluorines.

At both sides (low and high fields) of the Cr^+-I signal some other lines with the same splittings as those of the central group and following the same sequence of relative intensities can be observed for any orientation of the magnetic field with respect to the crystal axes. These lines—that we will call the Cr^+-II signal—are shown in Fig. 2 for CaF_2 measured at LNT with the magnetic field along a $\langle 110 \rangle$ direction.

The Cr^+-II lines are about 40 times weaker than those of the central group and this 1:40 ratio remains the same for different values of the total intensities which can be achieved by changing x-irradiation time. Although only two groups of lines of the Cr^+-II signal can be partly observed (see Fig. 2), there are four of them associated with the hyperfine interaction due to the $I = \frac{3}{2}$ ^{53}Cr isotope, which has a natural abundance of 9.55%.

The other main signal which appears at about $g \simeq 3.5$ when the magnetic field is along a $\langle 100 \rangle$ direction (see Fig. 1) is strongly dependent on the orientation of the external magnetic field with respect to the crystal axes. This signal is almost identical for CaF_2 and SrF_2 crystals.

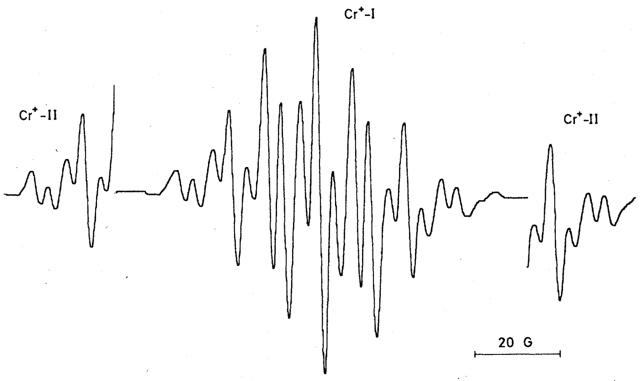

FIG. 2. Cr^+ EPR signal measured at 77 K with the magnetic field along a $\langle 110 \rangle$ direction in a RT x-irradiated CaF_2:Cr sample. The Cr^+-II signal has been magnified 40 times more than the Cr^+-I one.

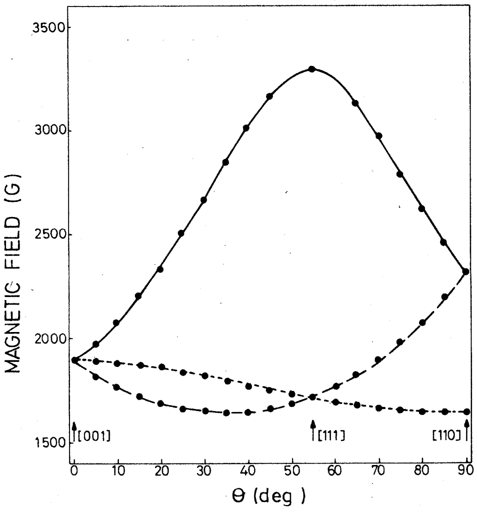

FIG. 3. Circles represent the positions of the observed Cr^{3+} EPR lines (in CaF_2) as a function of the orientation of the magnetic field in the $(1\bar{1}0)$ plane. Calculated evolution of the lines using the spin Hamiltonian given by Eq. (1) with the values of the parameter shown in Table I is represented by lines.

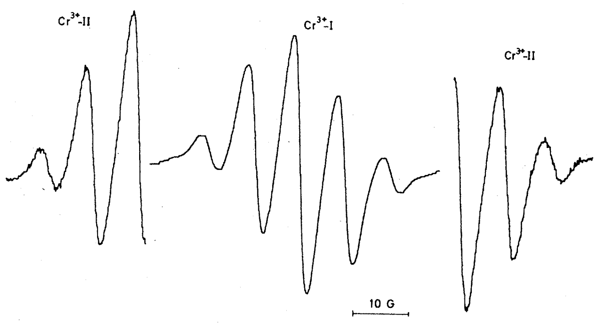

FIG. 4. Cr^{3+} EPR signal taken at LNT with the magnetic field along a ⟨110⟩ direction perpendicular to the threefold C_3 axis of the defect.

The evolution of the signal when the magnetic field is rotated in the $(1\bar{1}0)$ plane is given in Fig. 3. This pattern indicates that the center responsible for this signal has trigonal symmetry.

A resolved structure can be observed in some of the lines when the magnetic field is either parallel or perpendicular to the trigonal axis. When the magnetic field is along a ⟨111⟩ direction the high-field signal is split into seven equally spaced (~6.0 G in CaF_2 and 4.7 G in SrF_2) lines whose relative intensities follow the approximate sequence of 1:6:15:20:15:6:1. Some deviations of this sequence appear, mainly in SrF_2 crystals, due to overlapping problems. When the magnetic field is along a ⟨110⟩ direction the low-field signal shows a structure consisting of five equally spaced (~8 G) lines with relative intensities 1:4:6:4:1. In both cases ($\mathbf{H}\|\langle 111\rangle$ and $\mathbf{H}\|\langle 110\rangle$) the peak-to-peak distance of any individual line is about 2.5 G.

As will be discussed later, the centers responsible for these signals are Cr^{3+} ions in a trigonally distorted octahedral environment. The structure is due to the SHF interaction with six surrounding fluorine nuclei. The signal will be referred to hereafter as Cr^{3+}-I.

As in the case of the Cr^{+} centers, some groups of lines having the same structure and intensity sequence as the central ones, but about 40 times weaker, can be observed symmetrically placed at both sides of the Cr^{3+}-I signal. This can be seen in Fig. 4 for CaF_2:Cr measured at LNT with the magnetic field parallel to a ⟨110⟩ direction. This signal will be denoted as Cr^{3+}-II.

The Cr^{3+}-II lines are always present independent of the magnetic field orientation, and their intensities are always 1:40 with respect to those of the Cr^{3+}-I signal. Consequently, as for Cr^{+} centers, they will be assigned to the ^{53}Cr isotope.

IV. DISCUSSION

Since the cubic and trigonal EPR signals given in Fig. 1 do not appear in CaF_2 and SrF_2 doped with $3d$ ions other than Cr,[9] it is likely that they are in some way associated with this impurity. Usually, $3d$ ions enter fluorite-type crystals in a divalent state and it is known that changes in their charge states are easily produced by x irradiation. In the present case we will show that the trigonal EPR signal is due to Cr^{3+} ions in a distorted cube of fluorines, while the cubic signal will be tentatively associated with Cr^{+} ions in an eightfold-coordinated cubic position. A similar production of Cr^{+} and Cr^{3+} centers by x irradiation has been reported by several authors in other matrices.[4–6]

The angular evolution given in Fig. 3 is typical of the $M_S=+\frac{1}{2}\rightarrow-\frac{1}{2}$ transition of an ion with $S=\frac{3}{2}$ in a trigonal environment with a high zero-field splitting. The experimental line positions have been explained using the spin Hamiltonian

$$\mathscr{H}=g\mu_B\mathbf{H}\cdot\mathbf{S}+D[S_z^2-\tfrac{1}{3}S(S+1)]\ . \qquad (1)$$

The values for the resonant magnetic fields have been obtained by perturbations up to second order assuming $D \gg g\mu_B H$. The best fit, corresponding, for CaF_2, to the positions given by the lines in Fig. 3, has been attained with the g values shown in Table I. Since only the $M_S=-\frac{1}{2}\leftrightarrow\frac{1}{2}$ transition can be measured with our exper-

TABLE I. Spin Hamiltonian parameters for Cr^{3+} centers at 77 K. (The hyperfine constants are given in MHz.)

	CaF_2	SrF_2
g	1.965±0.005	1.965±0.005
$A_{\|}(^{53}Cr)$	45±2	47±2
$A_{\perp}(^{53}Cr)$	53±2	54±2
$A_{\|}^{F}$	31±2	30±2
$A_{\perp}^{F}$	<3	<3
F^-—Cr^{3+}—F^- angle (deg)	85±4	78±4

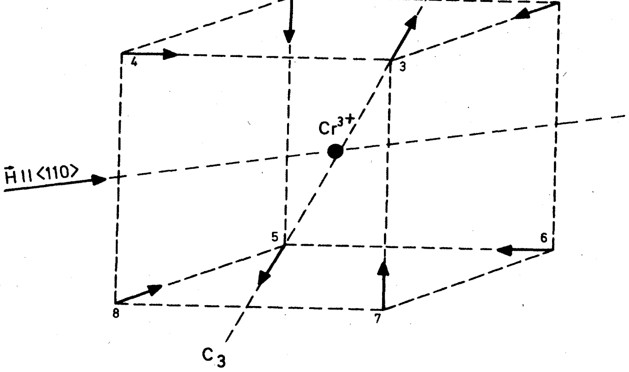

FIG. 5. Model for the Cr^{3+} centers in CaF_2 and SrF_2 showing the trigonal distortion.

imental setup, values of the zero-field-splitting parameter D have not been obtained. The g values given in Table I are similar to those reported in the literature for Cr^{3+} in other fluorite-type crystals.[1]

The structure of the Cr^{3+}-I signal can be associated with the superhyperfine interaction with the neighboring fluorine nuclei (^{19}F, $I=\frac{1}{2}$, natural abundance 100%). When the magnetic field is along the trigonal axis of the center, the SHF structure corresponds to the interaction with six equivalent fluorines. When the magnetic field is perpendicular to the axis of the center and along a $\langle 110\rangle$ direction, an interaction with four equivalent fluorines is observed.

The trigonal symmetry of Cr^{3+} ions as well as the SHF structure can be explained with the model given in Fig. 5, in which a trigonal distortion of the environment is produced by a displacement of fluorines 3 and 5 along a $\langle 111\rangle$ direction away from the Cr^{3+} ion and an inwards movement of the other six fluorine ions.

If the interactions of Cr^{3+} with fluorines 3 and 5 is not resolved, it is clear that a SHF interaction with six equivalent fluorine nuclei will be observed when the magnetic field is along the trigonal axis of the center [F(3)-F(5) direction in Fig. 5]. On the other hand, in order to understand the SHF structure observed with $\mathbf{H}||\langle 110\rangle$ and perpendicular to the center axis, it should be concluded that only the interaction with fluorines 2, 4, 6, and 8 is resolved for this magnetic field orientation. The interaction with fluorines 1 and 7 is so small that the associate splitting is smaller than the linewidth and, consequently, it is not resolved. Because of this we have assumed in the analysis of the SHF structure (see below) that $A_\perp^{\rm F}({\rm Cr}^{3+})$ is almost zero.

The SHF interaction constants as well as an estimation of the (F^-—Cr^{3+}—F^- angles) can be obtained from the comparison of the SHF line positions with those calculated by adding to (1) the Hamiltonian corresponding to the interaction with the six nearest fluorines,

$$\mathscr{H}_{\rm SHF}=\sum_{j=1}^{6}[\,A_\perp^{\rm F}({\rm Cr}^{3+})(S_{x_j}I_{x_j}^j+S_{y_j}I_{y_j}^j)+A_\parallel^{\rm F}({\rm Cr}^{3+})S_{z_j}I_{z_j}^j\,]\,, \qquad (2)$$

where $A_\perp^{\rm F}({\rm Cr}^{3+})$ and $A_\parallel^{\rm F}({\rm Cr}^{3+})$ are the SHF parameters of the Cr^{3+}—F^- interaction, which is assumed to be axial along the Cr^{3+}—F^- bonding direction (z_j).

Using perturbation calculations up to first order for $\mathscr{H}_{\rm SHF}$, the values for the parameters given in Table I have been obtained. As we have already said, the upper limit for $A_\perp^{\rm F}({\rm Cr}^{3+})$ values has been derived from the width of the lines. The angles F^-—Cr^{3+}—F^- are also given in that table.

The Cr^{3+}-II signal can be understood as being due to Cr^{3+} centers involving the ^{53}Cr isotope ($I=\frac{3}{2}$, natural abundance 9.55%). Because of the hyperfine interaction an EPR signal consisting of four equally spaced groups of lines, centered at the same magnetic field as the Cr^{3+}-I, signal should be observed, each of the groups being a replica of the central signal with an intensity about 40 times smaller. In our measurements only a part of the most external groups can be observed because of the overlapping with the Cr^{3+}-I signal. However, the observed lines give a clear replica of the central group and the intensity ratio is about 1:40. Thus we have concluded that they are due to the hyperfine splitting of $^{53}Cr^{3+}$ centers. This hyperfine interaction has been taken into account by including in the spin Hamiltonian (1) a new term of the usual form

$$\mathscr{H}_{\rm HF}=A_\parallel(^{53}{\rm Cr})S_zI_z+A_\perp(^{53}{\rm Cr})(S_xI_x+s_yI_y)\;. \qquad (3)$$

Values of the HF parameters have been obtained by perturbation methods up to first order. These values are given in Table I. To our knowledge this is the first time that the HF structure for Cr^{3+} ions has been observed in fluorite-type crystals. The HF constants are similar to those reported in the literature for Cr^{3+} in other matrices.[10]

As we have already said, trigonal Cr^{3+} centers in fluorite-type crystals have been reported by several authors. Although in some cases the trigonal field has been associated with the presence of impurities, it is usually proposed that the trigonal distortion is due to a Jahn-Teller (JT) coupling between the $^4T_{1g}(^4F)$ ground term of Cr^{3+} in an eightfold cubic coordination with a τ_{2g} normal mode of the cube of fluorines. In principle, both signs of the shifts of fluorines 3 and 5 (see Fig. 5) are possible, and in this way either a compressed or an elongated cube can appear.

To our knowledge, only in the case of Cr^{3+} in CaF_2 has a SHF interaction with the surrounding fluorines been resolved.[2] From this structure more detailed information concerning the type of distortion around Cr^{3+} can be obtained. The Cr^{3+} centers reported by Zaripov *et al.*[2] show a SHF interaction with two F^- ions on the trigonal axis of the center. This suggests that the distorted cube is a compressed one, although this interpretation is not unique.[11] However, in our case, Cr^{3+} centers in both CaF_2 and SrF_2 show a SHF interaction with six equivalent F^- ions when $\mathbf{H}||C_3$. This seems to be in favor of an elongated cube of fluorines.

Since two different types of JT distortion around the same ion are not expected, it should be concluded that at least one of the Cr^{3+} centers in CaF_2 is perturbed by some

TABLE II. Spin Hamiltonian parameters for Cr^+ centers at 77 K. (The hyperfine constants are given in MHz.)

	CaF_2	SrF_2
g	2.001 ± 0.001	2.001 ± 0.002
$A(^{53}\mathrm{Cr})$	66 ± 2	66 ± 2
$A_\parallel^F$	39 ± 2	30 ± 2
$A_\perp^F$	24 ± 2	18 ± 2

other defects. Since the center reported by Zaripov *et al.*[2] appears in crystals grown in a fluorine atmosphere, the trigonal distortion could be due to interstitial fluorines in a next-nearest-neighbor position. The observation of two different types of trigonal Cr^{3+} centers in CdF_2 (Ref. 12) suggests that perturbations by other defects are also present in these crystals. It seems that more detailed experiments are still required in order to solve this problem.

The cubic EPR signal shown in Fig. 1 is created by x irradiation simultaneously with the trigonal one due to Cr^{3+}. Our tentative explanation for that cubic signal is that it is due to Cr^+ ions which provide a nonlocal charge compensation for Cr^{3+}. The structure observed when the magnetic field is along a $\langle 100\rangle$ direction corresponds to the interaction with eight equivalent fluorine nuclei and indicates that Cr^+ is in the center of a cube of fluorines. This is consistent with the fact that the ground state of Cr^+ in a cubic environment is a $^6A_{1g}(^6S)$ and, consequently, no JT distortion is expected. No Cr^+ centers have been previously reported in fluorite-type crystals.

Using this model and taking only into account the chromium isotopes with $I=0$, the Cr^+-I EPR spectra in CaF_2 and SrF_2 can be explained using the following spin Hamiltonian:

$$\mathcal{H}=g\mu_B\mathbf{H}\cdot\mathbf{S}+\sum_{j=1}^{8}[A_\perp^F(\mathrm{Cr}^+)(S_{x_j}I^j_{x_j}+S_{y_j}I^j_{y_j}) + A_\parallel^F(\mathrm{Cr}^+)S_{z_j}I^j_{z_j}]\ , \qquad (4)$$

with $S=\frac{5}{2}$, $I^j=\frac{1}{2}$. Higher-order interactions do not seem to give a signficant contribution for Cr^+ in CaF_2 and SrF_2. As in the case of Cr^{3+} ions, $A_\perp^F(\mathrm{Cr}^+)$ and $A_\parallel^F(\mathrm{Cr}^+)$ in Eq. (4) describe the superhyperfine interaction of Cr^+ with each of the eight fluorine nuclei, which is assumed to have axial symmetry around the bonding axes (z_j) that coincide with the $\langle 111\rangle$ directions. A best fit of the calculated positions to the experimental ones has been obtained for the parameters given in Table II. As expected for an ion with an S ground state, the g value is close to the free-electron one.

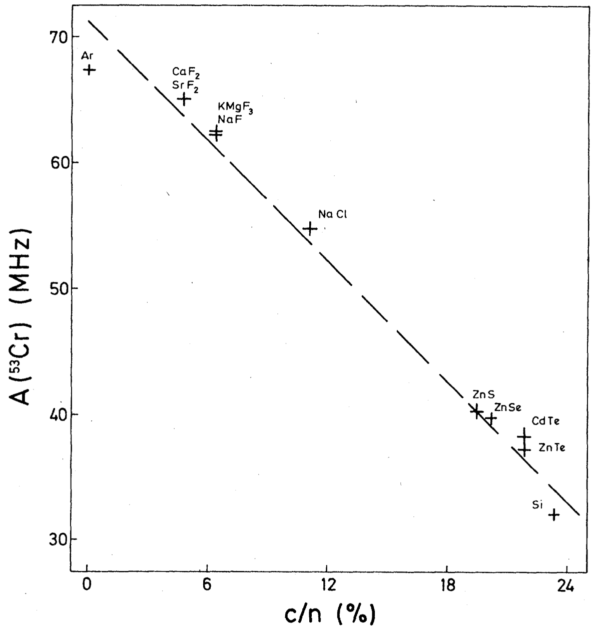

FIG. 6. Hyperfine constant of $^{53}\mathrm{Cr}^+$ as a function of c/n (see text).

As in the case of Cr^{3+} ions, the Cr^+-II signal can be associated with the HF interaction due to $^{53}\mathrm{Cr}$ isotope. An analysis of this HF structure using perturbation methods up to first order gives the parameters shown in Table II. It has been previously reported[13,14] that there is a linear relationship between the HF-interaction parameter of Cr^+ in different compounds and c/n, where c is Pauling's covalency and n is the coordination number of Cr^+. We show in Fig. 6 the plot of $A(^{53}\mathrm{Cr})$ versus c/n for Cr^+ in different compounds given by Davies,[14] in which our results have been included. The parameter c has been calculated using the empirical expression of Hannay and Smith[15] and the electronegativities given by Gordy and Thomas.[16] It can be seen that our results fit reasonably well the observed linear dependence.

ACKNOWLEDGMENT

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