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Spin Hamiltonian of Two Equivalent Nuclei: Application to the I_2^- Centers*

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The second-order hyperfine splittings observed in the ESR spectrum of an unpaired electron spin interacting with two equivalent nuclei depend upon the relative magnitude of the quadrupole interaction $\mathcal{H}_Q$ and the second-order effect $\mathcal{H}_{\rm hf}^2$ of the hyperfine interaction $\mathcal{H}_{\rm hf}$. If the first-order effect of $\mathcal{H}_Q$ is much smaller than $\mathcal{H}_{\rm hf}^2$ (case A), then a perturbation analysis of the spin Hamiltonian can be conveniently carried out in the coupled $|I_1I_2IM_I\rangle$ representation, and for the allowed ESR transitions the I_1+I_2+1 values of I are good quantum numbers. If, however, $\mathcal{H}_Q$ is much larger than $\mathcal{H}_{\rm hf}^2$ (case B), then the perturbation analysis must be carried out in the $|I_1I_2, M_1^2+M_2^2, M_I\rangle$ representation, and $M_1^2+M_2^2$ replaces I as a good quantum number. The second-order hyperfine patterns are qualitatively and quantitatively quite different for the two cases. As a specific example, the ESR spectra of the V_K-type I_2^- center in KI, and the V_K- and V_F-type I_2^- centers in Pb^{++}-doped KCl:KI and KBr:KI are discussed. The ESR analysis is limited to the situation where the magnetic field is parallel to the internuclear axis ($\theta=0°$), and it is shown that the I_2^- spectra are very well described by the case B perturbation solution. The $\theta=0°$ spectrum shows weakly allowed transitions from which the quadrupole term can be accurately determined. In these transitions M_1 and M_2 change by one unit but in opposite senses, so that M_I remains unchanged. A short discussion of the formation and decay of the I_2^- centers is also given.

INTRODUCTION

In the ESR spectra of paramagnetic molecules or molecular complexes one often observes hyperfine interaction of the unpaired electron spin with two (or more) equivalent nuclei. Two nuclei are equivalent with respect to a given orientation of the external magnetic field **H** (which is an axial or pseudovector) if (a) they are identical and (b) they show an equal hyperfine interaction with the unpaired electron spin **S** for that particular orientation of **H**. This does not necessarily require that the two nuclei are related to each other by inversion symmetry, but if they are, the two nuclei are equivalent with respect to *all* orientations of **H**.

To first order, the hyperfine interaction of two equivalent nuclei each with nuclear spin **I** gives an ESR spectrum of $4I+1$ equally spaced lines whose intensities are $1:2:3:\cdots:(2I+1):\cdots:3:2:1$, i.e., most lines are degenerate. This degeneracy originates in the fact that there are several combinations of the individual nuclear quantum numbers M_1 and M_2 that give rise to the same total nuclear quantum number $M_I=M_1+M_2$. Quadrupole and second-order hyperfine effects lift part or all of this degeneracy and if the hyperfine interaction is large enough and/or if the linewidths are narrow enough, these second-order hyperfine splittings are experimentally observable.

Many of the systems in which second-order splittings have been observed contain equivalent ^1H or ^{19}F nuclei which have nuclear spin $I=\frac{1}{2}$, and therefore show no quadrupole effects.[1] Typical examples of hyperfine interaction with two equivalent nuclei, where both quadrupole and second-order hyperfine effects are present, are offered by the homonuclear X_2^- molecule ions ($X=$ Cl, Br, I) which are produced at low temperatures by ionizing radiation in pure or doped alkali-halide crystals.[2–4] These molecule ions are embedded in a crystalline environment, so that in general the **g** tensor and hyperfine tensor **A** deviate somewhat from axial symmetry. Therefore, the spin Hamiltonian proposed to analyze the X_2^- ESR spectra is[2]

$$\mathcal{H}/g_0\beta=(1/g_0)[g_zH_zS_z+g_xH_xS_x+g_yH_yS_y]+\sum_{k=1}^{2}[A_zS_zI_{z,k}+A_xS_xI_{x,k}+A_yS_yI_{y,k}]+\sum_{k=1}^{2}PI_{z,k}^2-\frac{g_N\beta_N}{g_0\beta}\sum_{k=1}^{2}\mathbf{H}\cdot\mathbf{I}_k\,, \quad (1)$$

in which β is the Bohr magneton and β_N is the nuclear magneton, $g_0=2.0023$ and g_N are, respectively, the free electron and nuclear g factor. The direction of the molecular axis is z, and axial symmetry was assumed for the quadrupole term P.

The importance of both the second-order hyperfine and quadrupole effects in connection with the second-order hyperfine splittings was already stressed by Castner and Kanzig.[2] Their discussion was not very detailed but they presented numerical results for the splitting of the $|M_I|=2$ lines of the $\theta=45°$ spectrum of Br_2^- in KBr. However, as will be shown in this paper, the second-order hyperfine patterns depend very markedly both qualitatively and quantitatively on the relative magnitude of the quadrupole and second-order hyperfine effects.

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In the first half of this paper a perturbation-theory analysis of (1) will be given. This treatment follows in many respects the one given by Feuchtwang in Ref. 5, where the analysis of the ENDOR spectrum of the *F* center in KCl was reduced, for a nonspecial orientation of the magnetic field, to a problem of two equivalent nuclei. However, the discussion here is specifically applied to the ESR spectrum of two equivalent nuclei, and the two important cases that can be distinguished, viz., whether the first-order quadrupole effect is smaller or larger than the second-order hyperfine effects, are discussed in detail. In the second half the formulas are applied to various types of I_2^- centers in the alkali halides. The I_2^- centers were chosen because they exhibit well resolved second-order hyperfine patterns (the nuclear spin of ^{127}I is $\frac{5}{2}$ and it has a large nuclear moment and quadrupole moment), and since ^{127}I is a 100% abundant isotope, the experimental spectrum is not complicated by the superposition of various spectra involving different isotopic combinations, as is the case for Br_2^- and Cl_2^-.[2]

Since, except for a short paper,[4] not much has been published on the ESR spectra of the I_2^- centers, it seemed interesting to go beyond a mere application of the formulas, and to present also a short description of the more important formation and decay properties of these centers. The experimental details are the same as in a previous paper.[6]

I. PERTURBATION-THEORY ANALYSIS OF THE SPIN HAMILTONIAN

In order to perform a perturbation-theory analysis for an arbitrary orientation of **H**, spin Hamiltonian (1) will be recast into a suitable form.[2,7,8] First, (S_x,S_y,S_z) are transformed to $(S_{x'},S_{y'},S_{z'})$ by an orthogonal transformation which is chosen such that no terms in $S_{x'}$ and $S_{y'}$ occur. This transformation thus produces the result that the electron spin is always quantized along the direction of the external static magnetic field **H**. Second, $(I_{x,k},I_{y,k},I_{z,k})$ are transformed to $(I_{x'',k},I_{y'',k},I_{z'',k})$ and this transformation is chosen so that no terms in $S_{z'}I_{x'',k}$ and $S_{z'}I_{y'',k}$ occur. As a result the nuclear spins are quantized along the local field generated by the electron spin at each nucleus, although some important off-diagonal operators remain. The transformed spin Hamiltonian has the following form:

$$\mathcal{H}/g_0\beta=\mathcal{H}_Z+\mathcal{H}_N\,,$$

with

$$\mathcal{H}_Z=(g/g_0)HS_{z'} \tag{2}$$

and

$$\mathcal{H}_N=\mathcal{H}_{\mathrm{hf}}{}^1+\mathcal{H}_{\mathrm{hf}}{}^2+\mathcal{H}_Q+\mathcal{H}_{NZ}\,,$$

with

$$\mathcal{H}_{\mathrm{hf}}{}^1=KS_{z'}\sum_{k=1}^{2}I_{z'',k}\,,$$

$$\mathcal{H}_{\mathrm{hf}}{}^2=\sum_{k=1}^{2}\left[BS_{y'}I_{y'',k}+CS_{x'}I_{x'',k}+DS_{y'}I_{z'',k}\right],$$

$$\mathcal{H}_Q=\sum_{k=1}^{2}\left[R^2I_{y'',k}{}^2+RS(I_{y'',k}I_{z'',k}+I_{z'',k}I_{y'',k})+S^2I_{z'',k}{}^2\right],$$

$$\mathcal{H}_{NZ}=TH\sum_{k=1}^{2}I_{z'',k}\,,$$

and

$$g^2=g_z{}^2\cos^2\theta+g_\perp{}^2\sin^2\theta\,,$$

$$g_\perp{}^2=g_x{}^2\cos^2\varphi+g_y{}^2\sin^2\varphi\,,$$

$$K^2g^2=A_z{}^2g_z{}^2\cos^2\theta+A_\perp{}^2g_\perp{}^2\sin^2\theta\,,$$

$$A_\perp{}^2g_\perp{}^2=A_x{}^2g_x{}^2\cos^2\varphi+A_y{}^2g_y{}^2\sin^2\varphi\,,$$

$$B=A_zA_\perp/K,\quad C=A_\perp\,,$$

$$D=(g_zg_\perp/g^2)[(A_z{}^2-A_\perp{}^2)/K]\sin\theta\cos\theta\,,$$

$$R^2=P(A_\perp{}^2g_\perp{}^2/K^2g^2)\sin^2\theta\,,$$

$$S^2=P(A_z{}^2g_z{}^2/K^2g^2)\cos^2\theta\,,$$

$$T=\frac{A_zg_z\cos^2\theta+A_\perp g_\perp\sin^2\theta}{Kg}\left(-\frac{g_N\beta_N}{g_0\beta}\right),$$

in which (θ,φ) are the polar coordinates of the external magnetic field **H** with respect to (x,y,z). In the transformed spin Hamiltonian, all terms except the electron Zeeman term $\mathcal{H}_Z$ and the first-order hyperfine term $\mathcal{H}_{\mathrm{hf}}{}^1$ were simplified to axial symmetry. For the halogen X_2^- molecule ions in the alkali halides, this is a good approximation. Also, only the first-order part of the nuclear Zeeman term $\mathcal{H}_{NZ}$ was retained. The electron Zeeman term $\mathcal{H}_Z$ is assumed to be larger than $\mathcal{H}_N$. It lifts the degeneracy of the two electron spin states but leaves the nuclear spin degeneracy. The latter is lifted by $\mathcal{H}_N$ and the dominant term here is $\mathcal{H}_{\mathrm{hf}}{}^1$, which is diagonal in any representation that diagonalizes $I_{z''}=I_{z'',1}+I_{z'',2}$. $\mathcal{H}_{\mathrm{hf}}{}^2$ has only off-diagonal elements and contributes only in second order, and $\mathcal{H}_Q$ and $\mathcal{H}_N$ are assumed to be much smaller than $\mathcal{H}_{\mathrm{hf}}{}^1$. However, $\mathcal{H}_{\mathrm{hf}}{}^1$ does not lift *all* of the nuclear degeneracy, but only that part that is dependent upon the total nuclear quantum number $M_I=M_1+M_2$. $\mathcal{H}_{\mathrm{hf}}{}^2$ and $\mathcal{H}_Q$ lift the remaining degeneracy and it is these terms that give rise to the second-order splittings of the lines that have the same M_I. The first-order effects of $\mathcal{H}_Q$ may be smaller, comparable to, or larger than the second-order hyperfine effects caused by $\mathcal{H}_{\mathrm{hf}}{}^2$ and in the perturbation analysis it is important to make these distinctions. We should start out, therefore, by treating $\mathcal{H}_Q$ and $\mathcal{H}_{\mathrm{hf}}{}^2$ on an equal basis, and this can be done by using the Pryce

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[6] D. Schoemaker, Phys. Rev. **149**, 693 (1966).

[7] B. Bleaney, Phil. Mag. **42**, 441 (1951).

[8] W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), p. 54.

perturbation procedure[9]: The eigenvalues of $\mathcal{H}/g_0\beta$ in (2) corresponding to a given degenerate eigenvalue $E(m)$ of $\mathcal{H}_Z$ can be obtained from the effective Hamiltonian

$$\mathcal{H}'(m)=E(m)+\mathbf{P}_m\mathcal{H}_N\mathbf{P}_m+\sum_{n\neq m}\frac{\mathbf{P}_m\mathcal{H}_N\mathbf{P}_n\mathcal{H}_N\mathbf{P}_m}{E(m)-E(n)}, \quad (3)$$

where $\mathbf{P}_m$ and $\mathbf{P}_n$ are projection operators, operating within the manifold of states belonging to $\mathcal{H}_Z$. Since in the case we are considering $S=\frac{1}{2}$, $\mathcal{H}_Z$ has only two eigenstates, namely, $E(M_S)=(g/g_0)HM_S=H_0M_S$, with $M_S=\pm\frac{1}{2}$. Consequently, there are only two projection operators and there is no summation in (3). Calculation of (3) leads to the following two effective *nuclear* spin Hamiltonians:

$$\begin{aligned}\mathcal{H}'(M_S)=M_S\frac{g}{g_0}H+M_SK\sum_{k=1}^{2}I_{z'',k}&\\ +M_S\frac{D^2}{2H_0}\left(\sum_{k=1}^{2}I_{z'',k}\right)^2&\\ +M_S\frac{B^2+C^2}{4H_0}\left[\left(\sum_{k=1}^{2}I_{x'',k}\right)^2+\left(\sum_{k=1}^{2}I_{y'',k}\right)^2\right]&\\ +M_S\frac{B^2-C^2}{4H_0}\left[\left(\sum_{k=1}^{2}I_{y'',k}\right)^2-\left(\sum_{k=1}^{2}I_{x'',k}\right)^2\right]&\\ +\frac{BC}{4H_0}\sum_{k=1}^{2}I_{z'',k}+\mathcal{H}_Q+\mathcal{H}_{NZ}.&\quad (4)\end{aligned}$$

Two clear-cut cases can be distinguished: It may be that the first-order effect of $\mathcal{H}_Q$ is much larger than the second-order hyperfine effects $\mathcal{H}_{\mathrm{hf}}^2$, i.e., $\mathcal{H}_Q\gg\mathcal{H}_{\mathrm{hf}}^2$, or it may be that $\mathcal{H}_Q\ll\mathcal{H}_{\mathrm{hf}}^2$. The distinction between these two cases is not very important for a single nucleus spin Hamiltonian, but for a system of two equivalent nuclei it leads to quite different second-order hyperfine patterns. These two cases will now be discussed, and we will limit ourselves to a first-order analysis of (4). This means, e.g., that we can ignore the term involving B^2-C^2 since it only contributes in a higher-order calculation. Furthermore, $B\approx C$ when the hyperfine interaction is not strongly anisotropic. Only when $B\gg C$, which can happen for $\theta\neq0°$ when there is large anisotropy, may it be necessary to include the effect of this term.

A. Case A: $\mathcal{H}_Q\ll\mathcal{H}_{\mathrm{hf}}^2$

If we neglect $\mathcal{H}_Q$ for a moment, the structure of (4) is such that it is natural to introduce the total nuclear spin operator

$$\mathbf{I}=\mathbf{I}_1+\mathbf{I}_2\,.$$

Since

$$\left(\sum_{k=1}^{2}I_{x'',k}\right)^2+\left(\sum_{k=1}^{2}I_{y'',k}\right)^2=\mathbf{I}^2-I_{z''}{}^2,$$

the first-order energies $E'(M_S)$ of the effective nuclear spin Hamiltonians (4) are easily determined in the coupled $|I_1I_2IM_I\rangle$ representation with

$$\begin{gathered}I=I_1+I_2,\quad I_1+I_2-1,\quad\cdots,\quad I_1-I_2=0,\\ M_I=I,\quad I-1,\quad\cdots,\quad -I,\end{gathered}\quad (5)$$

and inspection of $E'(M_S)$ shows that the degeneracy of all the I manifolds is lifted.

For the allowed ESR transitions $M_S=+\frac{1}{2}$ to $M_S=-\frac{1}{2}$ the selection rules are

$$\Delta I=0,\quad \Delta M_I=0,$$

and the second-order term linear in $I_{z''}$ and the nuclear Zeeman term do not contribute anything. Putting $E'(+\frac{1}{2})-E'(-\frac{1}{2})=H_0=h\nu/g_0\beta$ (ν is the microwave frequency) and solving for the magnetic field H, one obtains the following formula giving the ESR line positions in gauss:

$$\begin{aligned}H(I,M_I)=(g_0/g)H_0-(g_0/g)\{KM_I+(D^2/2H_0)M_I{}^2&\\ +[(B^2+C^2)/4H_0][I(I+1)-M_I{}^2]\},&\quad (6)\end{aligned}$$

in which I and M_I take on the values given in (5).

Solution (6) is definitely applicable when $I_1=I_2=\frac{1}{2}$, since such nuclei do not possess a nuclear quadrupole moment. A typical example is the F_2^- molecule ion produced by ionizing radiation in the alkali fluorides.[2,10] The 100% abundant ^{19}F isotope has nuclear spin $\frac{1}{2}$ and from (6) the second-order separation between the $H(1,0)$ line and the $H(0,0)$ line is $(g_0/g)(B^2+C^2)/2H_0$.

The effect of $\mathcal{H}_Q$ on $E'(M_S)$ can be calculated with conventional perturbation theory. $\mathcal{H}_Q$ involves squares and products of the components of the individual nuclear spin operators and the formulas giving the necessary matrix elements in the coupled $|I_1I_2IM_I\rangle$ representation are well known.[11] We will not perform this calculation since the condition $H_Q\ll\mathcal{H}_{\mathrm{hf}}^2$ is not realized at X-band frequencies for the Cl_2^-, Br_2^-, and I_2^- molecule ions which we are considering, and they are probably representative for most systems in this respect. Furthermore, the effect of $\mathcal{H}_{\mathrm{hf}}^2$ can be made much smaller by working at higher microwave frequencies, i.e., at higher magnetic fields H_0.

However, in order to discuss what the qualitative effect of $\mathcal{H}_Q$ is, we have to bring out something that was implicit in the foregoing. Spin Hamiltonian (1) is invariant under exchange of the two nuclei. Therefore the nuclear eigenstates should belong to the even (symmetric) or uneven (antisymmetric) representations of the permutation or the inversion group, i.e., the nuclear eigenfunctions should have a definite parity. This is a rigorous requirement and independent of the relative magnitude of the various terms in (1). For the magnetic dipole ESR transitions parity $\mathcal{P}=\pm1$ must be

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[9] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

[10] C. E. Bailey, Phys. Rev. **136**, A1311 (1964).

[11] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), p. 64.

conserved, but this condition is intrinsically satisfied by the $\Delta I=0$ selection rule. This is so because the parity of $|I_1I_2IM_I\rangle$ for all M_I is given by $(-1)^{I+1}$ when $I_1=I_2=i$ is a half-integer or by $(-1)^I$ when i is an integer. Thus there are $(i+1)(2i+1)$ symmetric and $i(2i+1)$ antisymmetric nuclear states.[12] So, in second order, $\mathcal{H}_Q$ will mix states into $|I_1I_2IM_I\rangle$ differing in I (and M_I), but since parity must be maintained, it follows from the previous discussion that only states for which ΔI is even can be mixed. This means that when $\mathcal{H}_Q$ becomes larger, transitions of the type

$$\Delta I=\pm 2,\ \pm 4,\ \cdots, \tag{7}$$

but *not* of the type $\Delta I=\pm 1$, ± 3, $\cdots$, will become weakly allowed and more and more so as $\mathcal{H}_Q$ becomes stronger. Consequently, I ceases to be a good quantum number when $\mathcal{H}_Q$ becomes comparable to, or larger than, $\mathcal{H}_{\mathrm{hf}}^2$. The latter case will now be discussed.

B. Case B: $\mathcal{H}_Q \gg \mathcal{H}_{\mathrm{hf}}^2$

Inspection of $\mathcal{H}_Q$ and $\mathcal{H}_{\mathrm{hf}}^1$ in (4) now indicates that the following functions, which obey the parity requirement and which diagonalize simultaneously $I_{z''}=I_{z'',1}+I_{z'',2}$ and $I_{z'',1}^2+I_{z'',2}^2$ (and of course also $\mathbf{I}_1^2$ and $\mathbf{I}_2^2$), are suitable zero-order functions for a first-order perturbation analysis:

$$|I_1I_2,\,M_1^2+M_2^2,\,M_I\rangle = \tfrac{1}{2}\sqrt{2}\left(|I_1I_2{}^1M_1{}^2M_2\rangle \pm |I_1I_2{}^1M_2{}^2M_1\rangle\right). \tag{8}$$

The left upper indices 1 and 2 on the M's temporarily identify the nuclei and the lower indices 1, 2, 3, $\cdots$, on the M's distinguish between the quantum numbers.

In representation (8), $\mathcal{H}_Q$ lifts part of the degeneracy of the lines for which ${}^1M_1+{}^2M_2={}^1M_3+{}^2M_4$ since ${}^1M_1{}^2+{}^2M_2{}^2\neq{}^1M_3{}^2+{}^2M_4{}^2$. This still leaves a twofold degeneracy of the lines because ${}^1M_1+{}^2M_2={}^1M_2+{}^2M_1$. We will drop the left upper indices from now on since it will cause no confusion. $M_1^2+M_2^2$ is, to this order of approximation, a good quantum number except when $|M_1-M_2|=1$. To see this, the fourth term in (4) is rewritten as follows:

$$M_S\frac{B^2+C^2}{4H_0}\sum_{k=1}^{2}\left[\mathbf{I}_k^2-I_{z'',k}^2\right] + M_S\frac{B^2+C^2}{4H_0}\left(I_{+,1}I_{-,2}+I_{-,1}I_{+,2}\right), \tag{9}$$

where $I_\pm=I_x\pm iI_y$.

The last term represents a pseudo (i.e., transmitted through the unpaired electron spin) dipolar coupling between the two nuclei and it splits each twofold-degenerate energy level for which $|M_1-M_2|=1$ into its symmetric and antisymmetric components. From (4) and (8) the energy levels are found to be

$$\begin{aligned}E'(M_S)=\ &M_S(g/g_0)H+M_SKM_I+M_S(D^2/2H_0)M_I^2\\&+M_S[(B^2+C^2)/4H_0][2i(i+1)-(M_1^2+M_2^2)]\\&+M_S\mathcal{P}[(B^2+C^2)2H_0][i(i+1)-M_1M_2]\\&\times[\delta(M_1,M_2-1)+\delta(M_1,M_2+1)]\\&+(BC/4H_0)M_I+(S^2-\tfrac{1}{2}R^2)(M_1^2+M_2^2)\\&+THM_I,\end{aligned} \tag{10}$$

with $M_I=M_1+M_2$, $\mathbf{i}=\mathbf{I}_1=\mathbf{I}_2$, and M_1, $M_2=i$, $i-1$, $\cdots$, $-i$. $\mathcal{P}$ has the values ± 1 depending upon the parity of the nuclear spin wave function (8) and δ is the Kronecker symbol.

For the allowed ESR transitions $M_S=+\frac{1}{2}$ to $M_S=-\frac{1}{2}$ the selection rules are now

$$\Delta(M_1^2+M_2^2)=0,\quad \Delta M_I=0,\quad \Delta\mathcal{P}=0,$$

and the last three terms of (9) do not contribute anything. Putting $E'(+\frac{1}{2})-E'(-\frac{1}{2})=H_0$ and solving for the magnetic field H, one obtains the following formula giving the ESR line positions in gauss:

$$\begin{aligned}H(M_1,M_2,\mathcal{P})=\ &(g_0/g)H_0-(g_0/g)\{KM_I+(D^2/2H_0)M_I^2\\&+[(B^2+C^2)/4H_0][2i(i+1)-(M_1^2+M_2^2)]\\&+\mathcal{P}[(B^2+C^2)/2H_0][i(i+1)-M_1M_2]\\&\times[\delta(M_1,M_2-1)+\delta(M_1,M_2+1)]\}.\end{aligned} \tag{11}$$

Note that though (11), to this approximation, does not show any explicit[13] quantitive effect of the quadrupole interaction upon the line positions, the presence of an $\mathcal{H}_Q \gg \mathcal{H}_{\mathrm{hf}}^2$ profoundly affects the second-order hyperfine pattern. Formula (6) lifts the degeneracy of *all* the lines with the same $M_I=M_1+M_2$ value, but (11) yields nondegenerate lines only when $|M_1-M_2|=0$ or 1, while the lines for which $|M_1-M_2|\geqslant 2$ remain doubly degenerate. Therefore, the qualitative appearance of the experimental ESR spectrum immediately tells whether or not an appreciable quadrupole interaction is present.

Actually, for the X_2^- molecule ions $\mathcal{H}_Q$ is large enough so that in second order it does influence the line posi-

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[12] The two nuclei of the halogen X_2^- centers are *identical*, but since the molecule is not rotating in the crystal, the two nuclei are *distinguishable*. Therefore both the symmetric and antisymmetric nuclear states do exist. If the molecule were rotating, the two nuclei would have to be treated as indistinguishable particles. Since all halogen nuclei are fermions, this means that the total wave function comprising the electronic, rotational, and nuclear parts should be antisymmetric under exchange of the two nuclei. Thus, if X_2^- were in its lowest, totally symmetric, rotational state, only the symmetric nuclear states could exist since the ${}^2\Sigma_u^+$ electronic ground state is antisymmetric. (See Refs. 2 and 3.) Such effects have been observed experimentally for other systems; see H. M. McConnell, J. Chem. Phys. **29**, 1422 (1958); R. L. Morehouse, J. J. Christiansen, and W. Gordy, *ibid.* **45**, 1751 (1966). The continuous change in orientation that the X_2^- centers undergo above their disorientation temperature does not constitute a rotation, since the disorientation involves a breaking of the X_2^- molecular bond and subsequent reformation of a new X_2^- molecule ion in another orientation, and so on. (See Refs. 3 and 18.)

[13] That is, one cannot extract a value of P from the second-order shifts or splittings of the allowed ESR lines.

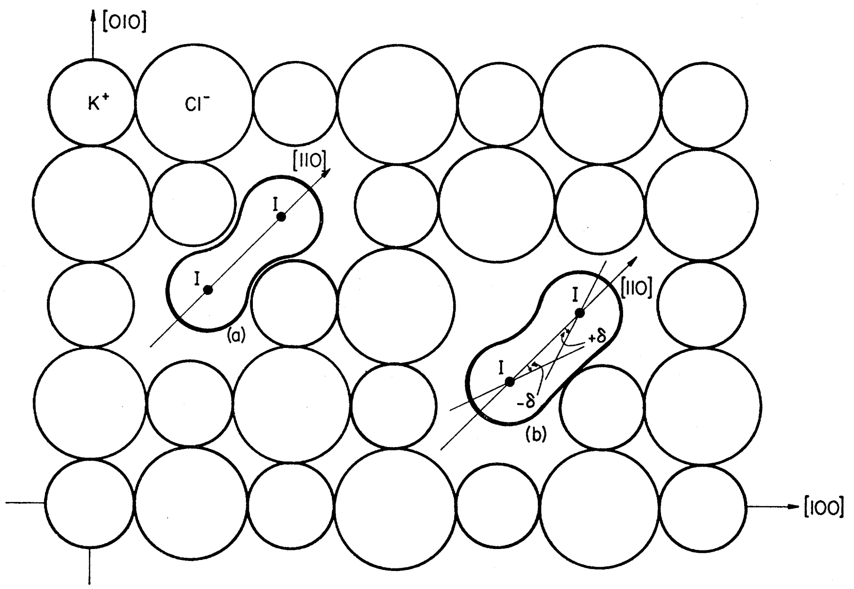

FIG. 1. (a) Model of a V_K-type I_2^- center in a I^--doped KCl lattice; (b) model of the V_F-type I_2^- center in a Pb^{++}- and I^--doped KCl lattice. The molecule ions are represented by an approximate contour of the total electronic density. These centers are the same in I^--doped KBr and in KI.

tions. The calculation is straightforward and the supplementary terms that must be added to (11) are[7]

$$\frac{g_0}{g}\sum_{k=1}^{2}\{(2R^2S^2/K)[4I_k(I_k+1)-8M_k^2-1]M_k \\ -(R^4/2K)[2I_k(I_k+1)-2M_k^2-1]M_k\}.$$

This correction is zero for $\theta=0°$.

When the magnitude of $\mathcal{H}_Q$ is reduced, the relative importance of the second-order hyperfine terms (9) increases. The pseudo dipolar coupling term in (9) mixes $|(M_1\pm1)^2+(M_2\mp1)^2,\ M_I\rangle$ states into $|M_1^2+M_2^2,\ M_I\rangle$. This means that in the limit of $\mathcal{H}_Q=0$ the functions that diagonalize (4) to first order will consist of linear combinations of (8), of the same parity, and for which either $|M_1-M_2|$ is even (including zero) or uneven. These functions are, of course, nothing but the $|I_1I_2M_I\rangle$ functions of the coupled representation that we used in Sec. IA, and the condition $\Delta\mathcal{P}=0$ is intrinsically satisfied by $\Delta I=0$.

The foregoing discussion indicates that even when $\mathcal{H}_Q\gg\mathcal{H}_{\mathrm{hf}}^2$, transitions of the type

$$M_1^2+M_2^2\rightarrow(M_1\pm1)^2+(M^2\mp1)^2, \qquad (12)$$

with $\Delta\mathcal{P}=0$, and which leave $\Delta M_I=0$, do have a nonzero transition probability. These transitions, which give rise to satellite lines whose intensity is proportional to $[(B^2+C^2)/H_0P]^2$ are easily calculated from (10) and the separation between them is determined by the quadrupole interaction. When, e.g., states with $M_1=M_2$ are involved, there are two satellite lines whose separation is, to first order, given by

$$4(g_0/g)(S^2-\tfrac{1}{2}R^2). \qquad (13)$$

These weakly allowed transitions, which are observed experimentally for the I_2^- centers, are unique for a system of two equivalent nuclei: Nothing analogous to it exists for a single nucleus spin Hamiltonian.[7]

There is of course another class of more or less weakly allowed transitions. These are of the type

$$\Delta M_1=\pm1,\quad \Delta M_2=0 \qquad (14)$$

or vice versa. They are analogous to the $\Delta M_I=\pm1$ transitions of a single-nucleus system.[7] Their strength with respect to the allowed lines is proportional to $(P/K)^2$ but the angular variation of the intensity is such that these lines vanish for $\theta=0°$.[7] These transitions, which can be calculated from (11), have been observed experimentally in $\theta\neq0°$ spectra of the Cl_2^-, Br_2^-, and I_2^- centers[14] but they will not be discussed in this paper.

II. APPLICATION TO I_2^- CENTERS

A. V_K-Type I_2^- Center in KCl:KI:Pb^{++}

The V_K-type I_2^- center, depicted in Fig. 1(a), can be produced as follows. A KCl crystal strongly doped with I^- ions (~1 mole % KI added to the melt) and containing electron traps[15] such as Pb^{++} ions[3] (~1 wt% of $PbCl_2$ added to the melt) is warmed to a few hundred degrees centigrade for several minutes and quenched[16] and then irradiated at 77°K with x or γ rays. This irradiation creates electrons, many of which are trapped

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[14] D. Schoemaker and J. L. Kolopus (unpublished).

[15] The V_K-type I_2^- center can also be produced in KCl:KI crystals that have no intentionally added electron traps (see Ref. 4). The Cl_2^- concentration produced by x or γ irradiation at 77°K and the resulting I_2^- concentration after warm up to, e.g., room temperature, is then considerably lower, however.

[16] This quenching is a routine procedure for Pb^{++}-doped crystals. It apparently disperses precipitates of Pb^{++} ions and vacancies and enhances the number of Pb^{++} ions that can trap electrons, resulting in a higher concentration of hole centers. In the heavily I-doped crystals the precipitates also involve I^- ions giving the crystal a yellowish color, which disappears after the quenching treatment.

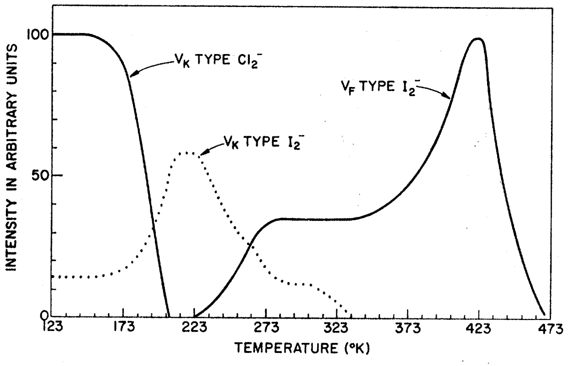

FIG. 2. Pulse-annealing results in a I^-- and Pb^{++}-doped KCl crystal after x irradiation at 77°K. The successive temperature intervals were 10°K and at each temperature and the crystal was held for 2 min and then cooled rapidly to ~85°K, where the changes were measured. The experimental points are not shown. The relative intensity between the two types of I_2^- centers is roughly correct, but not between the Cl_2^- and the I_2^- centers. The ICl^- center is not observable at 85°K and its behavior could not be followed.

by the Pb^{++} ions forming Pb^+, and positive holes which become self-trapped and form V_K-type Cl_2^- centers.[2,3] Some of the holes are also trapped by the substitutional I^- ions and form ⟨110⟩ oriented ICl^- centers.[17] With the high doping concentrations of KI that are being used, the probability of having two I^- ions in substitutional positions next to each other is appreciable and some of these pairs also trap holes and form ⟨110⟩ oriented V_K-type I_2^- centers.[4] Above −100°C the Cl_2^-, or the holes for that matter, become thermally unstable and move through the lattice.[3,18] These holes are trapped and stabilized by the I^- ions (single or pairs) and enhance the ICl^- and I_2^- concentrations. The foregoing is illustrated by Fig. 2, which gives the results of a pulse-annealing experiment on an irradiated $KCl:KI:Pb^{++}$ crystal. Figure 3(a) gives the V_K-type I_2^- ESR spectrum for **H**‖[110] at ~85°K.[19] The ICl^- center is not observable at this temperature.[17] The 11-line $\theta=0°$ spectrum caused by the hyperfine interaction with the two equivalent ^{127}I nuclei (nuclear spin $\frac{5}{2}$) is clearly visible. The well resolved splittings of the lines are caused by the second-order effects described in the first half of this paper. Figures 3(b) and 3(c) give the calculated spectra, respectively, based on solution (11) of case B ($\mathcal{H}_Q \gg \mathcal{H}_{hf}^2$) and on solution (6) of case A ($\mathcal{H}_Q \ll \mathcal{H}_{hf}^2$). It is abundantly clear from this figure that the case B solution gives a very good qualitative and quantitative description of the experimental I_2^- spectrum, while this is definitely not true for the case A solution. The quantitative accuracy of the case B solution can be judged from Table I, where the measured and calculated line positions are compared and it is seen to be very good. Thus the qualitative appearance of the experimental I_2^- spectrum immediately shows that an

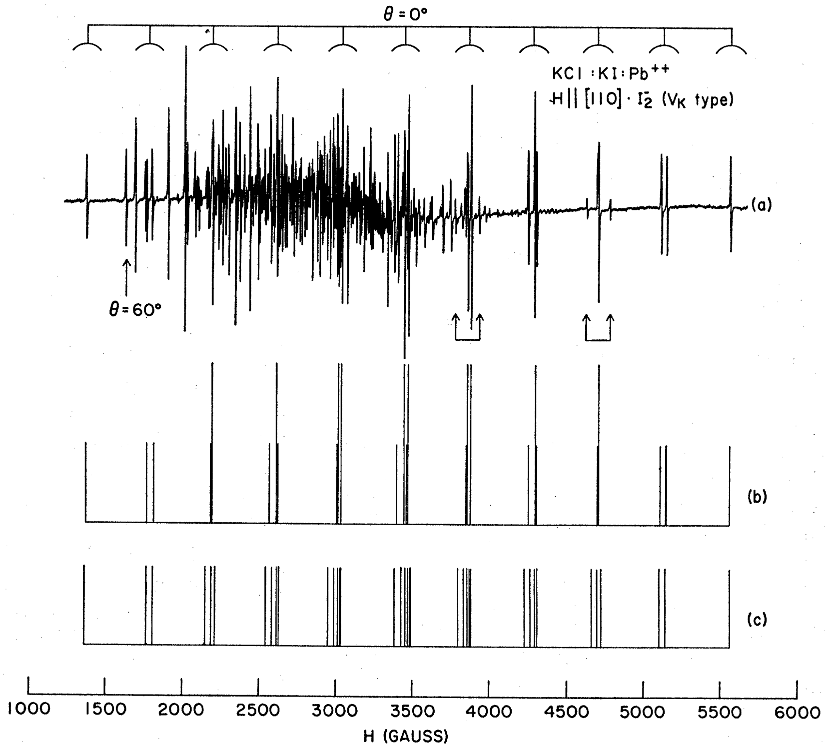

FIG. 3. (a) Experimental V_K-type I_2^- spectrum in $KCl:KI:Pb^{++}$ observed at ~85°K for **H**‖[110]. The 11 groups of lines in the $\theta=0°$ spectrum are readily seen. The bracketed arrows indicate pairs of transitions of the type (12); (b) computed I_2^- spectrum with formula (11) of case B; (c) computed spectrum with formula (6) of case A. The microwave frequency is $\nu=9.260$ kMc.

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[17] M. L. Meistrich and L. S. Goldberg, Solid State Commun. 4, 469 (1966).

[18] F. J. Keller and R. B. Murray, Phys. Rev. **150**, 670 (1966); F. J. Keller, R. B. Murray, M. H. Abraham, and R. A. Weeks, *ibid.* **154**, 812 (1967).

[19] With the variable temperature setup (see Ref. 6) it is not possible to cool the sample all the way to 77°K.

TABLE II. Spin Hamiltonian parameters at ~85°K of the V_K- and V_F-type I_2^- centers in various alkali halides obtained from the analysis of the $\theta=0°$ spectra. ΔH is the linewidth between points of maximum slope and δ is the bending angle.

Crystal	Type of center	g_z[a] (±0.0003)	A_z (±0.3 G)	$A_\perp$ (±2 G)	$\lvert P\rvert$ (±0.5 G)	δ	ΔH (±0.5 G)
KCl:KI(Pb^{++})	$I_2^-(V_K)$	1.9118	+397.9	+147	34.9	0°	5.0
KBr:KI(Pb^{++})	$I_2^-(V_K)$	1.9069	+388.2	+144	33.9	0°	10.0
KI(TI^+)[b]	$I_2^-(V_K)$	1.9037	+384.8	+140	33.2	0°	11.0
KCl:KI:Pb^{++}	$I_2^-(V_F)$	1.9285	+461.8	+192	40.3	(6.0°±0.5°)[c]	5.0
KBr:KI:Pb^{++}	$I_2^-(V_F)$	1.9226	+440.5	+182	38.8	(5.1°±0.5°)[c]	10.0

[a] $g_\perp$ is estimated to be around 2.27.
[b] Measured at 77°K.
[c] Estimated from g_z.

appreciable quadrupole interaction is present even though the spectrum does not show an explicit[13] effect of $\mathcal{H}_Q$ for this orientation. However, the quadrupole term P can be accurately determined from the weakly allowed transitions of the type (12) that are observed in the $\theta=0°$ spectrum. Two pairs are visible in Fig. 3(a) and they are indicated by arrows. From (13) the separation of a pair equals $4(g_0/g_z)P$, whence $|P|=34.9$ G. This may be compared with the $|P|\approx 50$-G estimate.[6] The spin Hamiltonian parameters, which are more accurate than the earlier ones,[4] are given in Table II. The reasons for giving both A_z and $A_\perp$ a positive sign have been presented in Ref. 6. No attempt was made to analyze the $\theta\neq 0°$ spectra. The large second-order shifts, especially those caused by the term in D, and the prominence of transitions of the types (12) and (14) make a ready identification of the lines difficult, especially for large θ. Therefore, if the $\theta\neq 0°$ spectra are studied (to determine g_x, g_y, A_x, A_y), it may well be necessary to perform the measurements at higher microwave frequencies so as to minimize the second-order effects that depend on H_0^{-1}.

TABLE I. Comparison between the experimental and calculated [formula (11) of case B] line positions of the V_K-type I_2^- center in KCl:KI (Pb^{++}). Microwave frequency $\nu=9260.34$ Mc ($H_0=3304.24$ G).

Line ($M_1,M_2,\mathcal{P}$)	Expt. (±0.1 G)	Calc. (G)	Line ($M_1,M_2,\mathcal{P}$)	Expt. (±0.1 G)	Calc. (G)
$(\frac{5}{2},\frac{5}{2},+)$	5527.9	5527.4	$(-\frac{5}{2},-\frac{5}{2},+)$	1359.4	1359.9
$(\frac{5}{2},\frac{3}{2},-)$	5114.5	5114.0	$(-\frac{5}{2},-\frac{3}{2},+)$	1746.9	1746.0
$(\frac{5}{2},\frac{3}{2},+)$	5079.5	5080.0	$(-\frac{5}{2},-\frac{3}{2},-)$	1779.3	1780.0
$(\frac{5}{2},\frac{1}{2},\pm)$	4673.1	4673.5	$(-\frac{3}{2},-\frac{3}{2},+)$	⋯	2166.2
$(\frac{3}{2},\frac{3}{2},+)$	4666.7[a]	4666.7	$(-\frac{5}{2},-\frac{1}{2},\pm)$	2173.0	2173.0
$(\frac{3}{2},\frac{1}{2},-)$	4270.6	4270.3	$(-\frac{3}{2},-\frac{1}{2},+)$	⋯	2548.9
$(\frac{5}{2},-\frac{1}{2},\pm)$	4257.0	4256.7	$(-\frac{5}{2},\frac{1}{2},\pm)$	⋯	2589.7
$(\frac{3}{2},\frac{1}{2},+)$	4215.8	4215.9	$(-\frac{3}{2},-\frac{1}{2},-)$	⋯	2603.3
$(\frac{5}{2},-\frac{3}{2},\pm)$	3847.2	3846.8	$(-\frac{1}{2},-\frac{1}{2},+)$	⋯	2986.1
$(\frac{3}{2},-\frac{1}{2},\pm)$	3825.8	3826.4	$(-\frac{3}{2},\frac{1}{2},\pm)$	2992.2[a]	2992.9
$(\frac{1}{2},\frac{1}{2},+)$	3820.7[a]	3819.6	$(-\frac{5}{2},\frac{3}{2},\pm)$	3012.4[a]	3013.3
$(\frac{5}{2},-\frac{5}{2},\pm)$	3443.2	3443.6			
$(\frac{1}{2},-\frac{1}{2},-)$	3433.1	3433.4			
$(\frac{3}{2},-\frac{3}{2},\pm)$	3416.1	3416.4			
$(\frac{1}{2},-\frac{1}{2},+)$	3372.2[a]	3372.2			

[a] Error: ±0.5 G.

B. V_F-Type I_2^- Center in KCl:KI:Pb^{++}

A pulse anneal in a KCl:KI crystal in which NO_2^- ions instead of Pb^{++} were present as electrons traps shows that the V_K-type I_2^- center decays around +120°C. No other center is detected after such treatment. However, in a KCl:KI crystal containing Pb^{++} ions the V_K-type I_2^- center decays in the region between −50 and 0°C and another I_2^- center, the V_F-type[20] I_2^- center, is formed. The model for this center is depicted in Fig. 1(b): It consists of an I_2^- molecule ion associated with a positive ion vacancy. The internuclear axis z is still oriented exactly along the [110] direction, but because of the presence of the positive ion vacancy the molecular bond is bent in the (001) plane. The two hyperfine tensors are still equal in magnitude, but the two symmetry axes do not coincide with the internuclear axis z but make angles δ and $-\delta$ with it. These conclusions regarding the model and the symmetry of this type of I_2^- center cannot be drawn from the analysis of the $\theta=0°$ spectrum to which this study was limited. They are based upon the very close parallels that exist between the formation and the properties of this V_F-type I_2^- center with the V_F-type Br_2^-, Cl_2^-, and $ClBr^-$ centers[21,22] that have been found and extensively analyzed in Pb^{++}- and Br^--doped KCl.

The doping with Pb^{++} ions is essential for the occurrence of the V_F-type centers, because its incorporation also introduces positive ion vacancies in the lattice in order to maintain charge neutrality of the crystal. It is these positive ion vacancies that are used in the formation of the V_F-type centers.

Since V_K-type I_2^- centers in KCl are thermally stable to at least +100°C, as shown by the experiments with NO_2^--doped crystals, it is believed that between −50 and 0°C positive ion vacancies diffuse toward the V_K-type I_2^- to form the V_F-type I_2^- centers. This migration is undoubtedly helped by the fact that there is an electrostatic attraction between the positive ion vacancy, which has an effective negative charge, and the V_K-type center which has an effective positive charge.

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[20] W. Kanzig, J. Phys. Chem. Solids 17, 80 (1960).

[21] D. Schoemaker, in International Symposium on Color Centers, Urbana, 1965, Abstract Nos. 167 and 168 (unpublished).

[22] D. Schoemaker, C. J. Delbecq, and P. H. Yuster, Bull. Am. Phys. Soc. 9, 629 (1964).

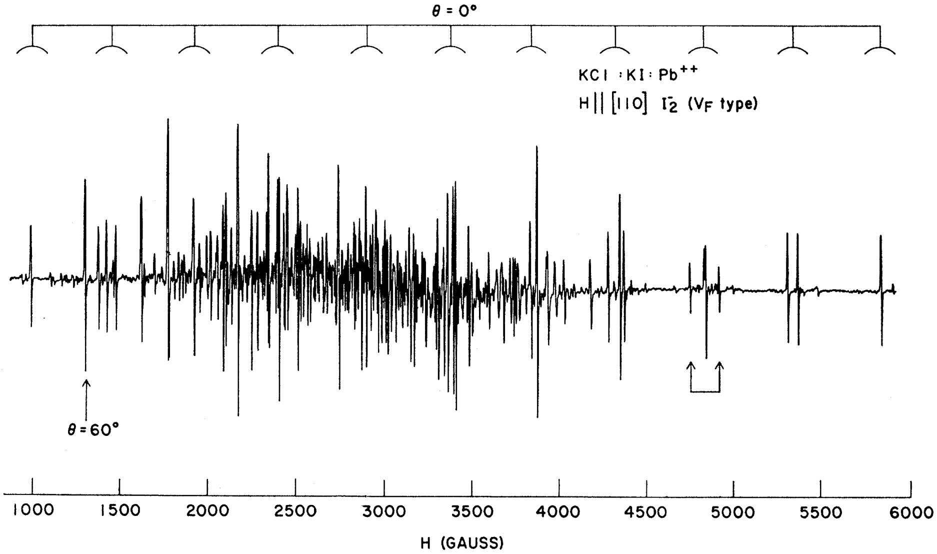

FIG. 4. The experimental V_F-type I_2^- spectrum observed at ~85°K in KCl: KI:Pb^{++} for $\mathbf{H}\|[110]$. The $\theta=0°$ spectrum is seen to be qualitatively identical to that of the V_K-type I_2^- spectrum in Fig. 3.

The foregoing points will be dealt with extensively in forthcoming papers on the V_K- and V_F-type Cl_2^- and $ClBr^-$ centers.[23] We will simply state here that very likely the model for the V_F-type I_2^- center as depicted in Fig. 1(b) is the correct one. The V_F-type I_2^- does not have inversion symmetry and the two nuclei are *not* equivalent for *all* orientations of the magnetic field **H**. But for the case to which we limit ourselves, namely, **H** parallel with the internuclear axis z, i.e., $\theta=0°$, they are equivalent. The $\theta=0°$ spectrum observed when $\mathbf{H}\|[110]$, is shown in Fig. 4, and as can be seen it is qualitatively identical to that of the V_K-type I_2^- center. Clearly, it again belongs to case B. The bending angle δ is quite small, only a few degrees, and its effect on the $\theta=0°$ spectrum is practically negligible. Therefore formula (11) was used to analyze the experimental V_F-type I_2^- spectrum and it was indeed found that an almost as accurate description of the V_F-type I_2^- spectrum was obtained as for the V_K type. Transitions of the type (12) are also strongly visible in Fig. 4, and from them the quadrupole term P is easily determined. These satellites are stronger than for the V_K-type center, reflecting the fact that $A_\perp(V_F)>A_\perp(V_K)$. Actually, with respect to the sum of the twofold-degenerate $H(\frac{5}{2},\frac{1}{2},\pm)$ line and the two satellite lines, these satellite lines are about 2.0 times stronger for V_F than for V_K. This agrees with $[A_\perp^2(V_F)P(V_K)]^2/[A_\perp^2(V_K)P(V_F)]^2 = 192^4\times 34.9^2/147^4\times 40.3^2=2.2$. The spin Hamiltonian parameters are given in Table II together with an estimate of the bending angle δ. This estimate was obtained from an analysis of the g_z factor and will be discussed in another paper.[24]

The V_F-type I_2^- center in Pb^{++}-doped KCl decays at +170°C (see Fig. 2). This is probably caused by the fact that the trapped electrons, presumably in the form of Pb^+, are liberated (leaving behind Pb^{++}) and destroy the V_F-type I_2^- center. Before it decays, however, there is a strong increase in the V_F-type I_2^- concentration around +130°C. Obviously, some center decays in this temperature region which enhances the V_F-type I_2^- concentration. The exact nature of this center is not known, but it probably involves both a trapped hole and a positive ion vacancy. The hole and the vacancy would be thermally liberated from this center at this temperature and be retrapped by a pair of substitutional I^- ions producing the V_F type I_2^- center. One possibility for this unknown center is an ICl^- molecule ion associated with a positive ion vacancy. The analogous center, namely, a $ClBr^-$ molecule ion associated with a positive ion vacancy, has been observed and thoroughly studied[21–23] in Pb^{++}-doped KCl:KBr crystals. However, the ESR spectrum of such an ICl^- center has not been observed at either 77 or 20°K. So the exact nature of this center that decays at +130°C remains at this point unknown.

C. V_K- and V_F-Type I_2^- Centers in KBr:KI:Pb^{++}

The V_K- and V_F-type I_2^- centers can also be produced in Pb^{++}- and I^--doped KBr crystals. The pulse-annealing results are shown in Fig. 5. After x or γ irradiation at 77°K of a heavily I^--doped (~1 mole % KI) KBr crystal also containing Pb^{++}, positive holes either have been self-trapped, forming V_K-type Br_2^- centers, or have been trapped by single or pairs of substitutional I^- ions, forming $\langle 110\rangle$ oriented IBr^- and I_2^- centers. In contrast to ICl^- in KCl,[17] the ESR spectrum of IBr^- can be observed at 85°K.[24] The Br_2^- decay around −130°C and the liberated holes enhance the IBr^- and I_2^- concentrations. The IBr^- center decays around −80°C by losing its hole and leaving behind a substitutional I^- ion. This hole may be retrapped and stabilized again by a pair of substitutional I^- ions

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[23] C. J. Delbecq, D. Schoemaker, and P. H. Yuster (unpublished).
[24] D. Schoemaker (unpublished).

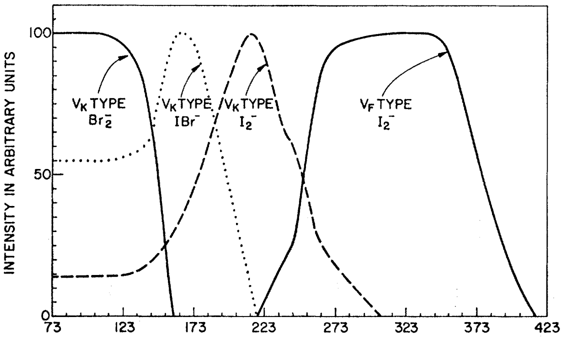

FIG. 5. Normalized pulse-annealing results in a I^-- and Pb^{++}-doped KBr crystal after x irradiation at 77°K.

enhancing the V_K-type I_2^- concentration. Above -60°C the V_K-type I_2^- center decays and the V_F-type I_2^- center is formed. Since experiments in an NO_2^--doped KBr:KI crystal show that the V_K-type I_2^- center is thermally stable to about 0°C, it is believed again that it is the positive ion vacancies moving toward the V_K-type I_2^- centers that are responsible for the formation of the V_F-type I_2^- centers. This center decays around $+100$°C and again probably through electrons that are thermally liberated from Pb^+ ions. In contrast to the KCl, case there is now no enhancement of the V_F-type I_2^- center in a temperature region below $+100$°C. This probably reflects the fact that no IBr^- center associated with a positive ion vacancy is produced in these crystals. Figure 5 shows indeed that IBr^- decays at temperatures below where the vacancy starts to move and, e.g., forms the V_F-type I_2^- center out of V_K-type I_2^-. The spin Hamiltonian parameters are given in Table II.

D. V_K-Type I_2^- Center in KI

The existence of the I_2^- ESR spectrum in KI:Tl^+ was mentioned briefly by Castner and Kanzig[2] but no results or analysis were presented. The optical-absorption spectrum of the I_2^- center was subsequently determined by Delbecq, Hayes, and Yuster,[3] who found that it is strongly produced by x or γ irradiation at 77°K in KI containing Tl^+, Ag^+, or NO_2^- ions as electron traps. A thermal-decay curve can be found in Ref. 18 and it shows that the I_2^- decay around 105°K. Therefore, in order to avoid thermal decay, the ESR measurements were performed at 77°K by immersing the sample in liquid nitrogen using a little Dewar with a narrow tail that could be inserted in the microwave cavity. The ESR spectrum for $\mathbf{H}\|[110]$ is qualitatively identical to that of Fig. 3(a) but the linewidth is 11 G. The spin Hamiltonian parameters are given in Table II, and are more accurate than the earlier ones.[6,25]

Since it appears to be somewhat difficult to introduce Pb^{++} in KI, no attempt was made to produce the V_F-type I_2^- center.

III. CONCLUSION

In a perturbation treatment of a spin Hamiltonian of two equivalent nuclei (and consequently also for systems with more than two equivalent nuclei) it is important to distinguish whether the first-order effect of the quadrupole interaction is larger or smaller than those parts of the second-order hyperfine effects which are nondiagonal in M_I^2. The nuclear energy levels and the nuclear wave functions are influenced considerably by a large quadrupole interaction, but because of its particular nature, its first-order effect on the energy levels is subtracted out when calculating the allowed ESR transitions. The presence of a large quadrupole term is therefore only seen through its effect on the nuclear wave functions and this manifests itself in different selection rules, i.e., in different second-order ESR hyperfine patterns, compared to the case where the quadrupole effect is neglected or small. These calculations have been applied to the ESR spectra of the I_2^- centers in the alkali halides and it was found that the quadrupole effects dominate the second-order hyperfine effects that are nondiagonal in M_I^2. This is also true for the Br_2^- and Cl_2^- molecule ions which were not discussed in this paper, and quite likely also for most other systems of two equivalent nuclei that show quadrupole interaction.

ACKNOWLEDGMENTS

The author wishes to thank P. H. Yuster and C. J. Delbecq for helpful comments.

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[25] E. Boesman, thesis, University of Ghent, 1962 (unpublished).