Theoretical Calculation Explaining Negative Transferred Hyperfine Constants of the V_K Center*

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A quantitative calculation has been performed showing that the explanation of negative transferred hyperfine constants (THC) at nuclei of ions surrounding the V_K center is exchange polarization of the ligand cores by the unpaired σ_u electron of the molecule-ion. The moment-perturbed method was utilized and is shown to be capable of general calculations of exchange polarization in the solid state. The calculated values of THC in LiF for the nearest-neighbor Li^+ and F^- ions which lie on the nodal plane of the unpaired F_2^- molecular orbital are -5.03 and -6.60 MHz, respectively. These theoretical values compare favorably with the experimental results of Gazzinelli and Mieher.

I. INTRODUCTION

TRANSFERRED hyperfine interactions have provided a useful tool to analyze the electronic structure of ionic crystals containing paramagnetic ions or color centers. In the one-electron approximation there are two main mechanisms that have been proposed[1] for the origin of the transferred hyperfine constant (THC), namely, the Pauli-overlap and charge-transfer effects. The Pauli-overlap effect is the overlap term resulting from Schmidt orthogonalization of the valence electron with the ligand ions, or if one chooses to work with nonorthogonal basis functions, it arises from the consideration of nonorthogonality in the evaluation of the many-electron determinant. This effect is a direct consequence of the Pauli principle and acts in such a way as to convey to the ligand ion sites a spin density parallel to the unpaired spin of the paramagnetic defect. The other main effect is the charge transfer of the ligand orbitals. This can be thought of as a covalent effect where the electrons of the surrounding ligand ions are allowed to spend time in the unoccupied orbital of the paramagnetic defect. The direct process necessarily increases the spin density at the ligand sites and decreases it at the paramagnetic defect since only spin opposed to the unpaired electron is transferred. It has been realized for some time[2,3] that a third mechanism, the polarization of the ligand electrons through exchange with the unpaired electrons of the paramagnetic center, can make a significant contribution to THC. The need for a quantitative treatment of this third effect has been dramatized by the observation of negative THC[3–6] which cannot be explained by the first two effects. It is the purpose of this paper to show that a quantitative explanation of negative THC can be explained by exchange polarization.

In order to demonstrate that exchange polarization (EP) indeed provides a quantitative explanation of the negative THC, it is desirable to study a system where the overlap and charge-transfer effects are zero or small and can be neglected. Gazzinelli and Meiher[3] have carried out ENDOR measurements for Li^+ and F^- ion nuclei surrounding the paramagnetic F_2^- molecule ion of the V_K center in LiF and obtained sizable negative THC's. The ions marked $Li^+(A)$ and $F^-(B)$ in Fig. 1 both line on the nodal plane of the $\phi_{3\sigma_u}$ molecular orbital of the unpaired electron of F_2^-, and thus the contribution to the THC from overlap effects is zero. If charge transfer were present in this highly ionic system, it would be of such a nature as to lead to a positive negligible contribution to THC. It is opportune that theoretical calculations[7] have been carried out for the electronic wave functions for this system which allowed for displacements and electrostatic polarization of ions surrounding the V_K center. In this paper we report on a determination of the interaction energy between the unpaired electron of F_2^- and the nuclei in

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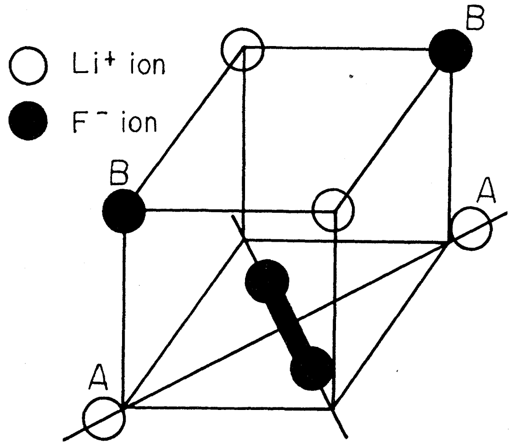

FIG. 1. Configuration of ions surrounding the V_K center. The Li^+ and F^- ions labeled A and B, respectively, lie on the nodal plane of F_2^-.

question through EP. The moment-perturbed (MP)[8] method was applied to determine this interaction energy. The MP method has been successfully applied to atoms[9] and to Knight shifts in metals.[10] This method has recently been extended by Ikenberry *et al.*[11] for the treatment of THC and has been applied to the calculation of EP contributions to the hyperfine fields in ZnF_2:Mn.[12]

In Sec. II we discuss the MP method and apply it to the V_K center in LiF in Sec. III to determine the THC for the nearest-neighbor Li^+ and F^- ions on the nodal plane of the unpaired $\phi_{3\sigma_u}$ moleculer orbital of F_2^-. In Sec. IV the results are discussed and compared with the experiment of Gazzinelli and Mieher.

II. MP METHOD

The MP method is briefly outlined below, and for details the reader is referred to Refs. 8 and 11. The MP method differs from the regular EP method for exchange polarization only in the order of application of the perturbations. The nucleus is permitted to perturb the core function, and the resulting MP function is used to calculate EP effects correct to second order in the perturbations. The utility of the MP over other methods is in its flexibility since it has been demonstrated that the perturbed core functions[8] are not greatly altered by the configuration of the outer valence electrons, and hence, the same core perturbed functions may be used in a variety of different environments. Essentially what is done for THC is to construct a determinantal wave function for the system in which ligand orbitals include the perturbation due to the nuclear moment. With this determinant, one calculates the total energy of the system and retains only terms linear in the nuclear moment μ_N. By this method we are able to separate out a number of physical mechanisms which contribute to THC.

The MP functions are determined by solving the integrodifferential equation

$$(\mathcal{H}_{ns}-\epsilon_{ns})\delta\psi_{ns,N}=\sum_{n's}(\epsilon_{n's}-\epsilon_{ns})\langle\psi_{n's}|\delta\psi_{ns,N}\rangle\psi_{n's}-\mathcal{H}_N\psi_{ns}+\sum_{n's}\langle\psi_{n's}|\mathcal{H}_N|\psi_{ns}\rangle\psi_{n's}, \quad (1)$$

where Eq. (1) must be solved for all occupied core ns states. Here $\mathcal{H}_N$ is the Fermi contact perturbation Hamiltonian given by

$$\mathcal{H}_N=(16\pi/3)\gamma_e\gamma_N\hbar^2\mathbf{I}\cdot\mathbf{S}\delta(\mathbf{r}), \quad (2)$$

where γ_e and γ_N are the gyromagnetic ratios of the electron and proton, respectively, and $\mathcal{H}_{ns}$ is the one-electron Hamiltonian. To solve Eq. (1) the following approximation is made:

$$(V_{ns}-\epsilon_{ns})=\nabla^2\psi_{ns}/\psi_{ns}, \quad (3)$$

which is an identity if the operators are allowed to act on the zero-order wave functions ψ_{ns}. Substitution of Eq. (3) into Eq. (1) results in

$$\left(-\nabla^2+\frac{\nabla^2\psi_{ns}}{\psi_{ns}}\right)\delta\psi_{ns,N}=\sum_{n's}(\epsilon_{n's}-\epsilon_{ns})\langle\psi_{n's}|\delta\psi_{ns,N}\rangle\psi_{n's}-\mathcal{H}_N\psi_{ns}+\sum_{n's}\langle\psi_{n's}|\mathcal{H}_N|\psi_{ns}\rangle\psi_{n's}. \quad (4)$$

The approximation of using Eq. (3) in Eq. (1) has been termed the local approximation by some authors,[13,14] and the consequence of using it for the core states has been considered by Duff and Das.[14] These authors show that this approximation is quite acceptable for 1s and 2s electrons. The exchange term is calculated with the resulting MP function.

The particular case considered here is the type-I situation of Ref. 11 and is illustrated in Fig. 2. We want to consider the case where there are a number of core states on B, the site of the nuclear moment, interacting with the valence electron and core states of site A. The exchange energy is given by Eq. (16) of Ref. 11,

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[12] D. Ikenberry and T. P. Das, Phys. Rev. (to be published).

[13] P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. **44**, 505 (1966).

[14] K. J. Duff and T. P. Das, Phys. Rev. **168**, 43 (1968).

namely,

$$E_{eN}{}^{(2)}=-2\sum_l\Big[\langle\psi_{AV}'(1)\delta\phi_{Bl}(1)|g_{12}|\psi_{AV}'(2)\phi_{Bl}'(2)\rangle$$
$$-\sum_{l'}\langle\psi_{AV}'(1)\phi_{Bl}'(1)|g_{12}|\psi_{AV}'(2)\phi_{Al'}(2)\rangle$$
$$\times\langle\phi_{Al'}|\delta\phi_{Bl}\rangle\Big],\quad(5)$$

where $g_{12}=e^2/|\mathbf{r}_1-\mathbf{r}_2|$, ψ_{AV} is the one-electron orbital for the valence electron on site A, $\phi_{Al'}$ are the wave functions for the core electrons of A, ϕ_{Bl} are the core states on site B, and $\delta\phi_{Bl}$ are the MP functions on B determined from Eq. (4). Here the sum over l is over the core states of B, and the sum over l' is over the core states of A. The functions ϕ_{Bl}' and ψ_{AV}' are given by

$$\phi_{Bl}'=(\phi_{Bl}-\sum_k S_{lk}\phi_{Ak})/(1-\sum_k S_{lk}{}^2)^{1/2}\quad(6)$$

and

$$\psi_{AV}'=(\psi_{AV}-\sum_l S_{lV}\phi_{Bl}+\sum_{lk} S_{lV}S_{lk}\phi_{Ak})/$$
$$(1-\sum_l S_{lV}{}^2)^{1/2},\quad(7)$$

where

$$S_{lk}=\langle\phi_{Bl}|\phi_{Ak}\rangle$$

and

$$S_{lV}=\langle\phi_{Bl}|\phi_{AV}\rangle.$$

Since $\delta\phi_{Bl}$ is proportional to μ_N it is seen that Eq. (5) is linear in the nuclear moment.

III. APPLICATION TO V_K CENTER

To calculate the THC for F_2^- in LiF, we shall make use of the work of Jette, Gilbert, and Das.[7] These authors combined the SCF molecular-orbital calculations of Gilbert and Wahl[15] for F_2^- with a detailed consideration of the crystalline environment using a first-order Mott-Littleton approximation[16] to obtain the lattice distortion and energies. The molecular orbitals are symmetrized combinations of Slater-type functions centered on the nuclei of the molecule-ion. The electronic configuration of F_2^- in the ground $^2\Sigma_u{}^+$ state is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(\pi_u)^4(\pi_g)^4(3\sigma_u)^1$. Thus, the valence electron is in a $\phi_{3\sigma_u}$ molecular orbital, and in this work, only the paired states $3\sigma_g$, π_u, and π_g were explicitly considered since the contribution from the inner-core orbitals is quite small.

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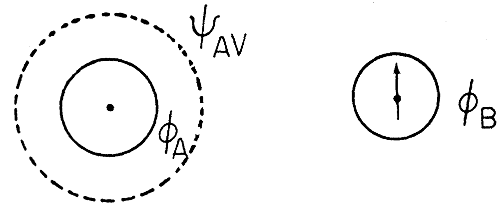

FIG. 2. Model system for nuclear moment centered on site B.

For the $Li^+(A)$ nuclei of Fig. 1, we have the following expression for THC:

$$a_{\mathrm{THC}}=\frac{E_{eN}{}^{(2)}}{ISh}=-\frac{2A}{ISh}\int\phi_{3\sigma_u}{}^*(1)\delta\phi_{N,\mathrm{Li}^+}{}'^*(1)$$
$$\times\frac{e^2}{r_{12}}\phi_{\mathrm{Li}^+}{}'(2)\phi_{3\sigma_u}(2)d\tau_1d\tau_2,\quad(8)$$

where

$$A=(16\pi/3)\gamma_e\gamma_N\hbar^2(2m/\hbar^2a_0)\mathbf{I}\cdot\mathbf{S}.\quad(9)$$

m is the electronic mass and a_0 is the Bohr radius. $\delta\phi_{N,\mathrm{Li}^+}{}'$ and $\phi_{\mathrm{Li}^+}{}'$ are the MP and s orbital of Li^+, respectively, orthogonalized to the core states of F_2^-, viz.,

$$\delta\phi_{N,\mathrm{Li}^+}{}'=\delta\phi_{N,\mathrm{Li}^+}-\langle\delta\phi_{N,\mathrm{Li}^+}|\phi_{3\sigma_g}\rangle\phi_{3\sigma_g}$$
$$-\langle\delta\phi_{N,\mathrm{Li}^+}|\phi\pi_u\rangle\phi\pi_u\quad(10)$$

and

$$\phi_{\mathrm{Li}^+}{}'=(\phi_{\mathrm{Li}^+}-\langle\phi_{\mathrm{Li}^+}|\phi_{3\sigma_g}\rangle\phi_{3\sigma_g}-\langle\phi_{\mathrm{Li}^+}|\phi_{\pi_u}\rangle_{\pi_u})$$
$$\times(1-|\langle\phi_{\mathrm{Li}^+}|\phi_{3\sigma_g}\rangle|^2-|\langle\phi_{\mathrm{Li}^+}|_{\pi_u};\rangle|^2)^{-1/2}.\quad(11)$$

Overlaps involving the MP function $\delta\phi_{N,\mathrm{Li}^+}$ and the Li^+ s orbital ϕ_{Li^+}, with the paired orbital ϕ_{π_g} are zero because of symmetry. Similar to (8) we have for the $F^-(B)$ THC the expression

$$a_{\mathrm{THC}}=-\frac{2A}{ISh}\bigg(\int\phi_{3\sigma_u}{}^*(1)\delta\phi_{N,1s}{}'^*(1)\frac{e^2}{r_{12}}\phi_{1s}{}'(2)\phi_{3\sigma_u}(2)$$
$$\times d\tau_1d\tau_2+\int\phi_{3\sigma_u}{}^*(1)\delta\phi_{N,2s}{}'^*(1)$$
$$\times\frac{e^2}{r_{12}}\phi_{2s}{}'(2)\phi_{3\sigma_u}(2)d\tau_1d\tau_2\bigg).\quad(12)$$

The functions $\delta\phi_{N,1s}$ and $\delta\phi_{N,2s}$ are the MP functions for the core states ϕ_{1s} and ϕ_{2s}, respectively, of F^-. These functions are also orthogonalized to the core states of F_2^-,

$$\delta\phi_{N,ns}{}'=\delta\phi_{N,ns}-\langle\phi_{ns}|\phi_{3\sigma_g}\rangle\phi_{3\sigma_g}-\langle\phi_{ns}|\phi_{\pi_u}\rangle\phi_{\pi_u}\quad(13)$$

and

$$\phi_{ns}{}'=(\phi_{ns}-\langle\phi_{ns}|\phi_{3\sigma_g}\rangle\phi_{3\sigma_g}-\langle\phi_{ns}|\phi_{\pi_u}\rangle\phi_{\pi_u})$$
$$\times(1-|\langle\phi_{ns}|\phi_{3\sigma_g}\rangle|^2-\langle\phi_{ns}|\phi_{\pi_u}\rangle|^2)^{-1/2}.\quad(14)$$

TABLE I. Individual contributions to THC for $Li^+(A)$ in units of e^2/a_0.

Term	Form	Value
	$\langle 1\ 1 \vert e^2/r_{12} \vert 2\ 2 \rangle$	
(a)	$-2\langle \phi_{3\sigma_u} \delta\phi_{N,\,\mathrm{Li}^+} \vert e^2/r_{12} \vert \phi_{\mathrm{Li}^+} \phi_{3\sigma_u} \rangle$	-0.000732
(b)	$-2\langle \delta\phi_{N,\,\mathrm{Li}^+} \vert \phi_{3\sigma_g} \rangle \langle \phi_{\mathrm{Li}^+} \vert \phi_{3\sigma_g} \rangle \langle \phi_{3\sigma_u} \phi_{3\sigma_g} \vert e^2/r_{12} \vert \phi_{3\sigma_g} \phi_{3\sigma_u} \rangle$	-0.000632
(c)	$+2\langle \phi_{\mathrm{Li}^+} \vert \phi_{3\sigma_g} \rangle \langle \phi_{3\sigma_u} \delta\phi_{N,\,\mathrm{Li}^+} \vert e^2/r_{12} \vert \phi_{3\sigma_g} \phi_{3\sigma_u} \rangle$	$+0.000378$
(d)	$+2\langle \delta\phi_{N,\,\mathrm{Li}^+} \vert \phi_{3\sigma_g} \rangle \langle \phi_{3\sigma_u} \phi_{3\sigma_g} \vert e^2/r_{12} \vert \phi_{\mathrm{Li}^+} \phi_{3\sigma_u} \rangle$	$+0.000292$
Sum of all other terms		-0.000030
Total		-0.000724

It should be noted that considerable simplification in (8) and (12) results from the fact that the valence orbital of F_2^- is orthogonal to the core s orbitals of the ligands A and B.

Physically, there are three types of terms that occur in Eqs. (8) and (12). First, there is the direct-exchange polarization of the ligand s cores by the unpaired $\phi_{3\sigma_u}$ molecular orbital. Second, there is an indirect process where $\phi_{3\sigma_u}$ exchange polarizes the paired F_2^- orbitals $\phi_{3\sigma_g}$ and ϕ_{π_u}, and these polarized cores then overlap the ligand cores and produce a net spin density at the ligand nucleus. The third type of contribution is a mixture of the above two and would be zero if the paired electrons of the V_K center did not overlap the ligands.

The MP function for the $1s$ state of Li^+ was determined by Gaspari *et al.*,[8] and we can use their results. The MP functions for the $1s$ and $2s$ cores of F^- were determined by solving Eq. (4) using a noniterative procedure as discussed by Duff and Das.[14] The wave functions of F^- and Li^+ are due to Clementi,[17] and Löwdin's alpha-function technique[18] was used to handle the multicentered integrals. All three center integrals were neglected since they are one order higher in the overlap effect and contribute little to THC. The internuclear distance of F_2^- and the $F_2^- - Li^+(A)$ and $F_2^- - F^-(B)$ distances measured in the nodal plane of $\phi_{3\sigma_u}$ are given in Ref. 7, namely, 4.00, 3.32, and 4.65 a.u., respectively.

IV. RESULTS AND DISCUSSION

Our results for $Li^+(A)$ are presented in Table I with a breakdown showing the leading terms. Term (a) is the direct EP of the ligand and is quite large and negative as is term (b), resulting from the second effect described in Sec. III. In contrast, the third type of contribution, described by terms (c) and (d), is positive and also large. It would seem reasonable to group together the indirect terms which all depend on the overlap of the paired orbitals of F_2^- and the ligand, namely, (b), (c), and (d). When this is done, their sum is negligible indicating that indirect polarization involving the F_2^- cores is not the explanation of negative THC. What remains is the direct-exchange polarization of the ligand with the unpaired F_2^- orbital. Similar conclusions hold for $F^-(B)$, where we have two core s states, the outer $2s$ core contributing over 90% of the final result. It should be pointed out that Gazzinelli and Mieher[3] carried out a somewhat qualitative calculation of THC for these ions but included only terms of type (b). Their approach had to give a negative result for the THC since the competition from terms (c) and (d) was not included. Thus, they concluded that the indirect EP of the ligand cores was the explanation of negative THC, in contrast to the conclusion reached here from a detailed quantitative analysis.

TABLE II. Theoretical and experimental values of THC in units of MHz.

Ion	Theory	Experiment[a]
$Li^+(A)$	-5.03	-4.12
$F^-(B)$	-6.60	-6.69

[a] Gazzinelli and Mieher, Ref. 3.

Our results for the THC for $Li^+(A)$ and $F^-(B)$ are seen from Table II to be in good agreement with the experimental values and allow us to conclude that the negative sign of the THC can be explained by EP. General comments about the role of EP in ionic crystals with paramagnetic ions or color centers can be made by considering the results of the THC at the ligand nuclei adjacent to an F center in LiF[11] and the THC at the ligand F^- nuclei adjacent to Mn^{++} in ZnF_2[12] in combination with the results found here. There exists a variance in overlap integral between the unpaired valence orbital and the ligand core s orbitals in these systems; zero for the Li^+ and F^- ions on the nodal plane of the F_2^- molecule-ion in LiF, 0.07 for ZnF_2:Mn and 0.10 for Li^+ ions adjacent to the F center in LiF. The THC due to EP are negative, very small, and positive, respectively, allowing one to conclude that the contribution to the THC from EP becomes more positive with increasing overlap. This phenomenon may have the following physical interpretation for a paramagnetic center with an overlapping charge distribution with ligands. When the overlap is small or zero, the exchange potential attracts charge density into the area of unpaired spin and away from the nucleus where the

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[18] P. O. Löwdin, Advan. Phys. 5, 1 (1956); see also R. R. Sharma, J. Math. Phys. 9, 505 (1968).

THC is being measured, and with increasing overlap the unpaired electron gets more inside the neighboring charge distribution and attracts charge density toward the nucleus where THC is being determined. This second mechanism can become competitive with the first since it is closer in to the ligand nucleus and less unpaired density is needed for a sizable contribution to the THC. Thus, a cancellation between the two mechanisms can occur, and the THC due to EP can be negative, small, or positive depending on the relative sizes of the two mechanisms. Of course, with increasing overlap, other mechanisms such as covalency effects contribute to the THC and have to be considered.

With the MP method we have demonstrated that the negative THC observed by Gazzinelli and Mieher can be explained by EP. Because of a cancellation among the indirect terms, the main contribution to the THC was shown to be the direct-exchange polarization of the ligands by the valence electron, in contrast to what was concluded earlier.[3] Finally, the good agreement with experiment lends support to the accepted model[7] of the V_K center in the alkali halides.

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Color Centers in $KMgF_3$†

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Polarized bleaching experiments on irradiated $KMgF_3$ crystals show that F_2 centers absorb light at 282 and 445 nm, F_3 centers absorb at 250 and 395 nm, and V_K centers at 340 nm. The temperature dependence of the width at half maximum of the F and F_2 bands has been studied. An analysis of the F_2-band data, assuming a linear-coupling model, indicates that the emission from this center should occur around 2.32 eV, which is close to the 2.19-eV emission observed by other workers and attributed to this center. The suppression of coloration caused by electron-trapping impurities is compared with that expected for two possible inhibition mechanisms, depending respectively on a reduced formation rate for F centers and an enhanced destruction rate of F centers. The experiments favor the latter possibility.

INTRODUCTION

APPARENTLY, only two color-center investigations of radiation damage in $KMgF_3$ have been made: one by Hall[1] on self-trapped holes (V_K centers) produced by x irradiation at low temperatures and the other by Hall and Leggeat[2] tentatively identifying F-center and F_2-center (M-center) absorption by means of ESR and polarized luminescence experiments. $KMgF_3$ has the cubic perovskite structure with a lattice constant $a=3.973$ Å. In crystals of this structure the F center has D_{4h} symmetry and F_2 centers have C_{2v} symmetry. Color-center studies of this material are not only valuable in themselves, but should also prove important for future investigations of the isomorphic materials, $KMnF_3$ and $BaTiO_3$, which are antiferromagnetic and ferroelectric, respectively.

Hall and Leggeat[2] suggest that a band at around 270 nm is due to F centers and one at 445 nm is due to F_2 centers. Earlier, Hall[1] proposed that a band at about 340 nm, which is present only at low temperatures, is the result of V_K-center formation. We felt that it would be highly desirable to confirm these observations by polarized bleaching experiments on the 340- and 445-nm bands and on a band occurring at about 395 nm, which could be due to F_3 centers. Moreover, a comparison of the radiation damage properties of $KMgF_3$ with those of the alkali halides should be very useful. Thus, the purpose of this paper is to report on the anisotropic absorption of these bands following polarized bleaching, on the temperature dependence of the half-width of the 445- and 270-nm bands, and on the production of F and F_2 centers by high-energy electrons as a function of temperature.

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[2] T. P. P. Hall and A. Leggeat, Solid State Commun. **7**, 1657 (1969).

EXPERIMENTAL PROCEDURE

The crystals were grown by the Stockbarger method in an argon atmosphere using purified starting material[3] consisting of equal parts of MgF_2 and KF. A graphite crucible was used, and the highest temperature in the furnace was 1070°C. The growth rate was controlled at 3 mm/h. Chemical analyses were made by means of wet chemistry and mass spectroscopy. The results of these analyses are shown in Table I.

[3] We would like to thank R. B. Quincy for preparing the starting material and for some very helpful discussions.