PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

# Molecular Orbital Analysis of Optical and Magnetic Properties of KNiF<sub>3</sub>

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A molecular orbital analysis of  $KNiF_3$  is used to calculate the cubic field splitting 10 Dq and the admixture coefficients of the fluorine orbitals. The agreement between calculated and experimental values is excellent and indicates the need for revising our traditional thinking about these quantities. In particular it is shown that the  $\pi$ -bonding is very important and that the only contribution to 10 Dq with the correct sign comes from the off-diagonal matrix element between the nickel and fluorine orbitals.

#### Introduction

With a molecular orbital analysis of  $KNiF_{a}$ we have calculated the optical properties, the nuclear magnetic resonance shifts and the antiferromagnetic exchange interactions. In all three cases we have obtained excellent agreement with the experimental values. The calculations require a revision of the traditional physical picture of these crystalline properties. In this paper we shall try to emphasize the physical nature of our understanding while we shall present theoretical and experimental details elsewhere.

### The Molecular Orbital Model

Of the several models postulated<sup>1-8)</sup> to describe the hyperfine interactions with the F<sup>19</sup> nucleus observed in the nuclear magnetic resonance experiments only the molecular orbital model<sup>1-5)</sup> is satisfactory. The experimental results are<sup>3,9)</sup> that in single crystals of KNiF<sub>3</sub> large isotropic and anisotropic shifts of the F19 resonance from the normal  $F^{19}$  position are observed. These shifts have been interpreted in terms of the isotropic hyperfine interactions  $A_s$  and of the anisotropic hyperfine interactions  $A_{\sigma}$ . The observed hyperfine interactions can then be converted to  $\lambda_s^2/3$  and  $\lambda_{\sigma^2}/3$ , the spin density in F<sup>-2s</sup> and  $2p_{\sigma}$  orbitals, respectively, through the ratios:

$$\lambda_s^2/3 = 2A_sS/A_{2s}$$
 and  $\lambda_\sigma^2/3 = 2A_\sigma S/A_{2p}$ 

\* Present address: The Institute for Solid State Physics, University of Tokyo, Azubu Minato-ku, Tokyo, Japan.

\*\* Present address: Department of Theoretical Chemistry, Cambridge University, Cambridge, England. in which  $A_{2s}$  and  $A_{2p}$  are the hyperfine interactions of a single unpaired 2s or 2p electron in a free F<sup>-</sup> ion and S is the electronic spin. It has been shown<sup>5)</sup> how these parameters determine the *antibonding* molecular orbitals of the form:

$$\Psi_{\nu}^{a} = N_{\nu a}^{-1/2}(\phi_{\nu} - \lambda_{\nu}\phi_{\nu}) ,$$

where

and

$$\begin{split} \psi_e &= \mu_\sigma \chi_\sigma + \mu_s \chi_s , \qquad \psi_t = \psi_\pi , \\ \lambda_e &= \lambda_\sigma / \mu_\sigma = \lambda_s / \mu_s , \qquad \lambda_t = \lambda_\pi , \end{split}$$

 $\nu = e \text{ or } t$ ,

where the subscripts e and t refer to the transformation properties of the function being isomorphic with the  $e_g$  and  $t_{2g}$  irreducible representations,  $\phi$  refers to the Ni<sup>2+</sup> ion and  $\chi_{\sigma}$ ,  $\chi_s$  and  $\chi_{\pi}$  are linear combinations of F<sup>-</sup> atomic orbitals,  $\sigma$ , s and  $\pi$ , respectively. These antibonding orbitals are orthogonal to bonding orbitals of the form :

$$\Psi^b = N_b^{-1/2} \left( \gamma \phi + \phi \right) \,.$$

On the assumption that the  $\lambda$ 's,  $\gamma$ 's and the overlap integrals between the  $\phi$ 's and  $\chi$ 's are all small compared to unity, the following relations are obtained<sup>5)</sup> from the orthogonalization of  $\Psi^a$  and  $\Psi^b$ :

 $\lambda_{\sigma} = \gamma_{\sigma} + S_{\sigma}, \quad \lambda_s = \gamma_s + S_s, \quad \lambda_{\pi} = \gamma_{\pi} + S_{\pi},$ in which

 $S_{\sigma} = (\phi_e | \chi_{\sigma}), \quad S_s = (\phi_e | \chi_s), \quad S_{\pi} = (\phi_t | \chi_{\pi}).$ 

The functions reduce to orthogonalized atomic orbitals by setting  $\gamma_s = \gamma_\sigma = \gamma_\pi = 0$ .

Obviously the observed hyperfine interactions can be described by molecular orbitals by choosing suitable values of  $\lambda$ . To fit two observables we adjust two parameters. It has been proposed that the F<sup>19</sup> hyperfine interactions in MnF<sub>2</sub> and KMnF<sub>3</sub> could be explained by the ionic model<sup>6)</sup> of orthogonalized atomic orbitals, i.e.,  $\lambda_s = S_s$  and  $\lambda_{\sigma} = S_{\sigma}$  by expanding<sup>7)</sup> the Mn<sup>2+</sup> radial function. This has the austerity of allowing only one parametric adjustment of the wavefunction through a scale factor to fit both  $\lambda_s$  and  $\lambda_{\sigma}$ . It is now clear that the rough agreement with the Mn<sup>2+</sup> results was fortuitous because of  $\sigma$ - $\pi$  cancellation and that this approach is not able to accommodate the separate bonding tendencies of the s and p electrons. For example, in KNiF<sub>3</sub> if we set  $\gamma_s = \gamma_{\sigma} = 0$  then the ionic model predicts that

 $\lambda_{\sigma^2}/\lambda_s^2 = S_{\sigma^2}/S_s^2 = (0.0639/0.0470)^2 = 1.85$ ,

while the observed ratio is (0.0378/0.00538) =7.0. The value of  $\lambda_s$  includes a ten per cent correction from the 1*s*-2*s* overlap proposed by Marshall<sup>7)</sup> and actually calculated by Freeman and Watson<sup>10)</sup>, while the value of  $\lambda_{\sigma^2}$  includes a ten per cent reduction<sup>7)</sup> arising from the non-spherical nature of Ni<sup>2+</sup>.

It has also been proposed that the  $F^{19}$ hyperfine interactions arise from exchange polarization on the ionic model<sup>8</sup>). However, besides the wrong sign, this also conflicts with the experimental observation<sup>9</sup>) that the isotropic interaction in K<sub>2</sub>NaCrF<sub>6</sub>, where the ground state molecular orbital does not involve the fluorine *s* electrons, is 25 times smaller than the isotropic interaction observed when *s* electron covalency mixing is allowed; this observation is easily understood<sup>5</sup>) with the use of a molecular orbital picture.

## Theoretical

We have made non-empirical calculations of three different properties of KNiF<sub>3</sub> by starting from the free ion Hartree-Fock functions. The parameters calculated are;

Table I. Comparison of theoretical and experimental values of optical and magnetic properties of KNiF<sub>3</sub>.

Property	Experiment	Theory 0.394	
λe	0.36		
λt	(?~0.3)	0.386	
10Dq	7200 cm <sup>-1</sup>	5900 cm <sup>-1</sup>	
$T_N$	275°K	300°K*	

\* Reference 15.

1—the F<sup>-</sup> admixture parameters  $\lambda_e$  and  $\lambda_t$ , 2—the cubic crystal field splitting 10*Dq*,

while T. Moriya and P.W. Anderson<sup>15</sup> have calculated

3-the Néel temperature  $T_N$ .

The agreement between the calculated and measured values of these quantities is shown in Table I. We would like to emphasize that all these calculations are ab initio, without any adjustable parameters.

Assuming the wave functions  $\Psi^a$  to be exact solutions of the Hartree-Fock equation,

$$H\Psi^a = E^a \Psi^a$$

the orbital energy  $E^a$  may be expressed as

$$E^{a} = (\phi |H|\phi) - \lambda(\phi |H|\psi) ,$$

where the higher order small quantity,  $\lambda(\phi|\phi)$ , is neglected. A similar expression for the corresponding bonding energy  $E^b$  may be obtained by using the bonding orbital wavefunction,  $\Psi^b$ .



Fig. 1. Schematic energy level diagram of the antibonding,  $e_g^*$  and  $t_{2g}^*$ , and bonding molecular orbitals,  $e_g$  and  $t_{2g}$ .

The energy levels of the antibonding and bonding orbitals are schematically shown in Fig. 1. As was pointed out by Tanabe and Sugano<sup>11,12)</sup> and as is seen in Fig. 1, the crystal field splitting 10Dq is the energy difference between the  $t_{2g}$  and  $e_g$  antibonding orbitals,

$$10Dq = E_{e}^{a} - E_{t}^{a} = [(\phi_{e}|H|\phi_{e}) - (\phi_{t}|H|\phi_{t})] \\ - [\lambda_{e}(\phi_{e}|H|\psi_{e}) - \lambda_{t}(\phi_{t}|H|\psi_{t})] .$$

The F<sup>-</sup> admixture parameters  $\lambda_e$  and  $\lambda_t$ were calculated by minimizing the bonding orbital energies with the simultaneous use of the orthogonality relation between the bonding and antibonding wavefunctions.

The first order Hartree-Fock Hamiltonian used was

$$H = -\Delta/2 + V_{\rm M} + V_{\rm L},$$

in which the first term is the kinetic energy operator and  $V_{M}$  is the Coulomb aud exchange interaction operator coming from all the Ni<sup>2+</sup> electrons and nucleus. The contribution of the ligands is

$$V_L = V_L^0 + V_L^K + V_L^E$$

in which  $V_{L^0} = \sum_{i}^{\infty} 1/|r - R_i|$  is the point charge potential of six ligands centered at  $R_i$ ;

$$V_{L}^{K} = \sum_{i}^{6} \left[ -\frac{8}{|\boldsymbol{r} - \boldsymbol{R}_{i}|} + \int d\tau_{2} r_{12}^{-1} \sum_{\substack{k=2s \\ 2p}} |\phi_{ik}(2)|^{2} \right]$$

is Kleiner's correction<sup>13</sup>) of the point charge potential which arises from the imperfect screening of the fluorine nuclear charge by their electrons whose atomic orbitals are  $\phi_{ik}$ ; finally

$$V_L{}^{B} = -\sum_{i}^{6} \int d au_2 r_{12}^{-1} \sum_{\substack{k=28\\2p}} \phi_{ik}^{*}(2) \phi_{ik}(1) P_{12}$$

is the exchange interaction introduced in the previous paper<sup>12)</sup> where  $P_{12}$  is the permuta-

Table II. Values of the matrix elements listed in the first column are shown in the second in atomic units. In the third column the contributions to 10Dq from the respective matrix elements are listed in cm<sup>-1</sup>, in which the effects of normalization factors are taken into account.

Matrix Element	Values of Matrix Elements (a.u.)	Contribution to $10Dq (cm^{-1})$
$(\phi_e \mid H \mid \phi_e) \ (\phi_t \mid H \mid \phi_t)$	$^{+0.1201}_{+0.1364}$	- 2700
$egin{array}{c c c c c c c c c c c c c c c c c c c $	$-0.1924 \\ -0.0871$	+15800
$egin{array}{c c c c c c } (\psi_e \mid H \mid \psi_e) \ (\psi_t \mid H \mid \psi_t) \end{array}$	$-0.3511 \\ -0.0847$	- 7200
Calculated 10Dq		+ 5900
Obser	+ 7250*	

\* K. Knox, R. G. Shulman and S. Sugano: Bull. Am, Phys. Soc. 5 (1960) 415. tion operator of electrons 1 and 2. All the two center integrals were calculated on an IBM 7090 with Switendick and Córbato's program. The results are presented in Table II.

In all energy determinations we have assumed a potential well model in which the NiF<sub>6</sub><sup>4-</sup> complex is located in a constant potential arising from the rest of the crystal. This model can be proven to be a good approximation. It also explains the observation that the cubic field parameter is insensitive to distant ions beyond the ligands. The transfer integrals  $(\phi \mid H \mid \phi)$  include sizeable contributions ( $\sim 30\%$  of their values) from three center integrals of the form  $(\phi | V_{Li} | \phi_{ik})$ in which  $\phi_{ik}$  is an atomic function of the F<sup>-</sup> ion at  $R_i$  while  $V_{Lj}$  is the potential from the ligand at  $R_j(i \neq j)$ . These integrals were evaluated numerically on the IBM 7090 on the point charge assumption that  $V_{Li} =$  $1/|r-R_i|$ .

The contributions of the separate terms to 10Dq contradict the traditional physical picture. In the naive crystal field theory the  $(\phi|H|\phi)$  terms without exchange interaction were supposed to give 10Dq, but such a contribution is almost zero as shown in Table III. The exchange terms in  $(\phi|H|\phi)$  stabilize the  $e_g$  orbitals pointing towards the ligands more than the  $t_{2g}$  orbitals pointing between the ligands and thus give a wrong sign for 10Dq.

Table III. Separate contributions to the nickel diagonal terms,  $(\phi \mid H \mid \phi)$ , of the components of  $W_L$  in atomic units.

	$V_L^0$	$V_L^K$	$V^E_L$
$(\phi_e \mid V_L \mid \phi_e)$	1.58687	-0.03017	-0.02396
$(\phi_t \mid V_L \mid \phi_t)$	1.58055	-0.02069	-0.01082
Difference	0.00632 (1387 cm <sup>-1</sup> )	-0.00948 (-2081 cm <sup>-1</sup> )	-0.01314 $(-2884 \mathrm{cm}^{-1})$

The main contribution to 10Dq and the only one with the correct sign comes from the  $\lambda(\phi | H | \phi)$  terms. This indicates that the itinerancy of the electrons between the metal ion and ligands plays the essential role in determing 10Dq. This contradicts the popular understanding of the crystal field strength in which the itinerancy is ignored.

The validity of our molecular orbital treat-

ment is shown by the superb agreement with experiment both of 10Dq and of the values of  $\lambda$  shown in Table I. The calculated value of  $\lambda_t$ , which is in excellent agreement with the  $\sigma$ - $\pi$  cancellation observed<sup>9)</sup> in KMnF<sub>3</sub> and the large value of  $\lambda_t$  measured<sup>9)</sup> in K<sub>2</sub>NaCrF<sub>6</sub>, confirms the importance of  $\pi$ bonding. Now that our method of calculating these parameters has been confirmed in KNiF<sub>3</sub> we plan to extend the calculations to other halides to investigate the difference of "covalency" between fluorides, chlorides, bromides and iodides.

In Anderson's<sup>14)</sup> elegant reformulation of the superexchange mechanism in ionic crystals the starting wavefunctions are the antibonding molecular orbitals  $\Psi^a$  defined above. The exchange integral is

$$J=(\Psi_A^a |H| \Psi_B^a)^2/U,$$

where A and B refer to near neighbor metal ions. Upon substituting it is obvious that for KNiF<sub>3</sub> all of the important contributions to the numerator have been evaluated and are listed in Table II. With these matrix elements Moriya and Anderson<sup>15)</sup> have calculated a preliminary value of  $T_N$  which is shown in Table I to be in excellent agreement with the observed value of 275°K.

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