Table I. Experimental values[a] for the dimensions as defined in Fig. 1. For comparison, the radius of the sphere having one-half the volume of the Brillouin zone is $k_s = 1.44$.

	Morse	Burdick	
k_{100}	1.41	1.51 ± 0.03	
k_{110}	1.38	1.39 ± 0.03	
k_d	1.22	1.21 ± 0.03	
k_n	1.10	1.11 ± 0.02	
k_e	0.32	0.44 ± 0.06	
k_r	0.24	0.24 ± 0.03;	0.22 ± 0.06

[a] All values are to be multiplied by the factor 10^{-19}.

Table I. The possible computational errors are as indicated but the author has no information concerning the possible experimental errors. The dimensions are given in cgs momentum units. The two theoretical values listed for k_r correspond to the "neck" radius as computed along a line passing through the center of the hexagonal face and one corner and along a line passing through the center and the midpoint of one edge, respectively. As can be seen from an examination of Table I, the only difference in topology is that the author's "belly" region in the plane of the figure is slightly more egg-shaped than the experimental model indicates. However, even this difference is a slight one.

As those who heard the two talks of Segall before the American Physical Society (referred to above) will realize, these results agree closely with his, thereby giving important verification of the fact that energy bands as computed by different methods can agree with each other and with experiment to a greater extent than has been generally realized.

The details of the computations, the density-of-states curve, and a discussion of the energy band structure will be published at a later date.

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[1] B. Segall and E. L. Kreiger, Bull. Am. Phys. Soc. 6, 10 (1961); B. Segall, Bull. Am. Phys. Soc. 6, 231 (1961). We are greatly indebted to Dr. Segall for private communication of many of his results.

[2] M. I. Chodorow, Ph.D. thesis, Massachusetts Institute of Technology, 1939 (unpublished).

[3] Quarterly Progress Reports, Solid-State and Molecular Theory Group, April 15, 1954 to date (unpublished), contributions from D. J. Howarth, M. M. Saffren, J. H. Wood, and others.

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CALCULATION OF THE CRYSTAL FIELD SPLITTING

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By starting with wave functions determined by nuclear magnetic resonance measurements[1] in $KNiF_3$, we have been able to calculate a value for the cubic crystal field splitting which is in good agreement with the observed value. The cubic crystal field splitting, $10Dq$, is the energy separation between the orbital triplet t_{2g} and the e_g doublet which arise from the d levels split by a cubic field. Measured values of $10Dq$ have been used with considerable success to explain optical and magnetic properties. However, it has not yet been possible to calculate a value which agrees with experiment. We follow the method of Tanabe and Sugano,[2] the main difference being the use of molecular orbitals with Hartree-Fock atomic functions as our basis set. We define

$$10Dq \equiv E(t_2^{\,5}e^{3}\,{}^3T_2) - E(t_2^{\,6}e^{2}\,{}^3A_2) = (\Psi_e|h|\Psi_e) - (\Psi_t|h|\Psi_t), \tag{1}$$

in which the wave functions are assumed to be

$$\Psi_e = N_e^{-1/2}[\Phi_e - \lambda_e \psi_e], \tag{2}$$

$$\Psi_t = N_t^{-1/2}[\Phi_t - \lambda_t \psi_t]. \tag{3}$$

In these expressions Φ_e and Φ_t (subscript t is abbreviation for t_2) may be the Ni^{++} $3d_{x^2-y^2}$ and $3d_{xy}$ functions, respectively, with Watson's Hartree-Fock radial functions.[3] Furthermore, $\Psi_e = \mu_{\sigma e}\chi_\sigma + \mu_{se}\chi_s$ and $\mu_{\sigma e}^2 + \mu_{se}^2 = 1$ while χ_σ, χ_s,

Table I. 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 differences between the e_g and t_{2g} energies are listed in cm^{-1}. The calculated value of 5270 cm^{-1} agrees fairly well with the experimental[a] value of 7250 cm^{-1}.

Matrix element	Value (a.u.)	Contribution to $10Dq$ (cm^{-1})
$(\Phi_e\|h\|\Phi_e)$	+0.1201	-3580
$(\Phi_t\|h\|\Phi_t)$	+0.1364	
$(\Phi_e\|h\|\Psi_e)$	-0.1510	+16 320
$(\Phi_t\|h\|\Psi_t)$	-0.0559	
$(\Psi_e\|h\|\Psi_e)$	-0.3300	-7470
$(\Psi_t\|h\|\Psi_t)$	-0.0847	
Calculated $10Dq$		+5270
Observed $10Dq$		+7250[a]

[a] K. Knox, R. G. Shulman, and S. Sugano, Bull. Am. Phys. Soc. 5, 415 (1960).

Table II. Separate contributions to the nickel diagonal terms of the components of V_L.

	V_L^0	V_L^K	V_L^E
$(\Phi_e\|V_L\|\Phi_e)$	1.58687	-0.03017	-0.02396
$(\Phi_t\|V_L\|\Phi_t)$	1.58055	-0.02069	-0.01082
Difference	0.00632	-0.00948	-0.01314

and $\chi_t = \psi_t$ are the normalized appropriate linear combinations of fluoride ion $2p_\sigma$, $2s$, and $2p_\pi$ orbitals, respectively. The fluoride ion $2s$ and $2p$ atomic orbitals were Froese's Hartree-Fock functions.[4] The fluorine $1s$ functions were shrunk into the nuclei. The augmentation parameters for Ψ_e of $\lambda_e\mu_{\sigma e} \equiv \lambda_\sigma$ and $\lambda_e\mu_{se} \equiv \lambda_s$ were determined from the nuclear magnetic resonance measurements[1] of the F^{19} nucleus in a single crystal of $\mathrm{KNiF_3}$. The values[5] were $(\lambda_e\mu_{\sigma e})^2 = 3\times 0.0369$ and $(\lambda_e\mu_{se})^2 = 3\times 0.00451$.

The first order Hartree-Fock Hamiltonian employed in (1) is

$$h = -\tfrac{1}{2}\Delta + V_M + V_L, \tag{4}$$

in which Δ is the kinetic energy operator and V_M is the Coulomb and exchange potential of all the Ni^{++} electrons and nucleus. The contribution of the ligands is

$$V_L = V_L^0 + V_L^K + V_L^E, \tag{5}$$

in which

$$V_L^0 = \sum_{i=1}^{6} \frac{1}{|r - R_i|}$$

is the point-charge potential of six ligands centered at R_i;

$$V_L^K = \sum_{i=1}^{6} -\frac{8}{|r-R_i|} + \int d\tau_2 r_{12}^{-1} \sum_{k=2s,2p} |\Phi_{ik}(2)|^2$$

is Kleiner's correction[6] of the point-charge potential which arises from the imperfect screening of the fluorine nuclei by their electrons whose atomic orbitals are Φ_{ik}; finally

$$V_L^E = -\sum_{i=1}^{6} \int d\tau_2 r_{12}^{-1} \sum_{k=2s,2p} \Phi_{ik}^*(2)\Phi_{ik}(1)P_{12}$$

is the exchange interaction introduced in the previous paper,[2] where P_{12} is the permutation operator of electrons 1 and 2. All the two-center integrals were calculated on an IBM-7090 with Switendick and Corbató's program.[7] The results are presented in Table I.

The nickel diagonal term makes a negative contribution to $10Dq$. This term represents the approximation in which the effects of the ligands are treated as perturbations upon the nickel ion energy levels. The separate contributions to this term of V_L^0, V_L^K, and V_L^E are shown in Table II. Although the individual exchange terms are small, they make a larger contribution than the total Coulomb interaction because of the cancellation[8] of the contributions from V_L^0 and V_L^K which allows the difference between exchange terms for e and t_2 to dominate. In Table II, the difference between N_t and N_e is not taken into account because its effect is negligible.

In order to calculate the contributions of the transfer integral and fluorine diagonal terms to $10Dq$, it is necessary to know the value of λ_t since the nuclear magnetic resonance measurements only determine λ_σ and λ_s. λ_t may be determined nonempirically by minimizing the corresponding bonding orbital energy. Such a nonempirical method can be also applied to the determination of λ_σ and λ_s, and a comparison between their calculated and observed values would be very interesting.

In the present calculation, however, we employed the following method in order to avoid the tedious calculation of important three-center integrals of the type $(\Phi_{3d}|V_{jL}|\Phi_{ik})$ appearing in the transfer integrals; a three-center integral for the e orbital was determined so that the observed λ_e minimizes the e bonding orbital energy. Then, using the calculated overlap integrals to relate the three-center integral for the t_2 orbital to that for the e orbital, λ_t was determined by minimizing the energy, with the result that $\lambda_t = 0.286$. The large value of λ_t is consistent with our previous findings.[1] Furthermore, the values of the three-center integrals thus determined were found to be reasonable. The three-center integrals are being evaluated independently so that we will be able to compare calculated and observed values of λ_σ and λ_s. However, the reasonable values derived for the three-center integrals in the above-mentioned procedure confirm the observed values of λ_σ and λ_s. It is interesting to observe that the $V_L{}^E$ term makes an important contribution to the $10Dq$ in the transfer integral also.

In all energy determinations we have assumed a potential well model in which the $NiF_6{}^{-4}$ 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. All of these assumptions, calculations, and additional refinements will be discussed more fully in future publications.

In conclusion we can say:

(1) The traditional concept of the cubic crystal field should be changed: The nickel diagonal term gives a negative contribution to the crystal field splitting. Its contribution comes mainly from the exchange interaction between d electrons and ligand electrons. The transfer integral term is the only term which makes a positive contribution to $10Dq$. Roughly speaking, this contribution is reduced by a factor of ~50% by the negative contribution of the fluorine diagonal term. Although this relation is found in our specific problem numerically, it is generally applicable. This will be discussed in the future.

(2) The molecular orbital model is successful in explaining both the nuclear magnetic resonance experiments and the cubic crystal field parameter in a consistent way. The value of $10Dq$ calculated from this model is 5300 cm^{-1}, in reasonable agreement with the observed value of 7250 cm^{-1}.

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[2] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan 11, 864 (1956).

[3] R. E. Watson, Phys. Rev. 118, 1036 (1960).

[4] C. Froese, Proc. Cambridge Phil. Soc. 53, 206 (1957).

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[7] A. C. Switendick and F. J. Corbató, Quarterly Progress Report, October 15, 1959, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts (unpublished).

[8] A. J. Freeman and R. E. Watson, Phys. Rev. 120, 1254 (1960), have calculated $V_L{}^0$ and $V_L{}^K$ in $Cr(H_2O)_6{}^{+3}$ with Hartree-Fock functions and have shown their combined effect to be very small.