PHYSICAL REVIEW VOLUME 128, NUMBER 3 NOVEMBER 1, 1962

Anisotropic Spin-Orbit Coupling of d^3 and d^8 Solutes in Corundum

HIROSHI KAMIMURA*
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received June 5, 1962)

The g shifts and the zero-field splittings of the ground states of the transition metal ions Cr^{3+} (a d^3 solute) and Ni^{2+} and Cu^{3+} (d^8 solutes) in corundum are studied within the expanded crystalline field framework, in which each d electron is considered to itinerate between the transition metal ion and ligands. It is shown that two types of the distortion of the wave function by the trigonal field play very important roles in the production of the observed g shifts and the zero-field splitting, if the transition metal ions are assumed not to move abnormally. One type is the distortion of the covalent π bonds, and another is due to the configuration mixing effect by the trigonal field. The former operates favorably to explain the experimental facts in both cases of the d^3 and d^8 solutes, while the latter acts favorably in the case of the d^3 solutes and unfavorably in the case of the d^8 solutes.

These effects of distortions make the matrix element of the spin-orbit coupling between the excited T_2 state and the ground state an anisotropic one. It is concluded that π bonding is very important in the case of the d^8 solutes. The parameter v which measures the splitting of a single t_2 electronic level by the trigonal field is found to be 740 cm^{-1} in Ni^{2+} and 760 cm^{-1} in Cu^{3+} in good agreement with the values found for other ions such as Cr^{3+}, Co^{2+}, V^{3+}, and Ru^{3+}.

1. INTRODUCTION

THERE has been considerable experimental work on magnetic and optical properties of $3d$-group transition metal ions in corundum, Al_2O_3.[1–10] The interpretation of the experimental facts has been done in terms of crystal-field theory. It is, however, important to investigate these experimental results from the unified standpoint of different transition metal impurities in the same host crystal. Recently, Geschwind and Remeika[11] have made such an attempt. In their survey of experimental results, they have paid attention to (1) the strength of the cubic crystal field, (2) the magnitude and the sign of the trigonal crystal field, and (3) the Jahn-Teller effect in the ground-state spin resonance. As to the trigonal crystal field they have found that the sign of the trigonal field obtained in cases of Ni^{2+} and Cu^{3+} is opposite to the one obtained in cases of V^{3+}, Cr^{3+}, Ru^{3+}, and Co^{2+}, if the perturbation theory of Pryce[12] is applied.

Table I shows the value of the trigonal splitting of a one-electron t_2 level, v, obtained by applying the perturbation theory of Pryce to the experimental results of electron spin resonance for transition metal impurities in corundum. One possible explanation of this change of sign might be ascribed to a displacement of equilibrium position of the impurity ion from that previously occupied by the host lattice ions.[13] It is, however, not very easy to understand why only the Ni^{2+} and Cu^{3+} ions should behave differently from other impurities. Geschwind and Remeika have also suggested configuration mixing as an explanation for this reversal in sign. In this paper we will explore these alternative explanations of the experimental observation and propose a new explanation as well.

The Ni^{2+} and Cu^{3+} impurities which substitute for the Al^{3+} ions of Al_2O_3, are situated on the threefold axis of corundum and are coordinated to six oxygens, which are located at the corners of a deformed octahedron. The ground state for these impurities, which reside in a nearly cubic crystalline field, is $^3A_2$, which is orbitally nondegenerate. Therefore, the g shift and the zero-field splitting of the ground state are caused by the mixing of orbital angular momentum from excited electron states into the ground state by the spin-orbit coupling. For the d^8 systems in a cubic field

TABLE I. Trigonal field splitting parameter v in Al_2O_3, from electron spin resonance data.

Solute	v (cm^{-1})	Reference
Ru^{3+}	$+850$	11
Co^{2+}	$+750$	3
	$+852$	4
V^{3+}	$+870$	5, 6
	$+361$	10
Cu^{3+}	-1030	11
Ni^{2+}	-1100	11

---

* On leave from the Department of Physics, University of Tokyo, Tokyo, Japan.

[1] S. Geschwind and J. P. Remeika, Bull. Am. Phys. Soc. **6**, 116 (1961); J. Eisinger, W. E. Blumberg, and S. Geschwind, *ibid.* **6**, 117 (1961).

[2] S. A. Marshall, Bull. Am. Phys. Soc. **5**, 158 (1960).

[3] G. M. Zverev and A. M. Prokhorov, Soviet Phys—JETP **12**, 41 (1961).

[4] J. E. Geusic, Bull. Am. Phys. Soc. **4**, 261 (1959); Report No. 3, Solid-State Maser Research, Bell Telephone Laboratories, March 20, 1961 (unpublished).

[5] G. M. Zverev and A. M. Prokhorov, Soviet Phys.—JETP **11**, 330 (1960).

[6] S. Foner and W. Low, Phys. Rev. **120**, 1585 (1960).

[7] M. H. L. Pryce and W. A. Runciman, Discussions Faraday Soc. **26**, 34 (1958).

[8] S. Sugano and I. Tsujikawa, J. Phys. Soc. Japan **13**, 899 (1958).

[9] A. A. Manenkov and A. M. Prokhorov, J. Exptl. Theoret. Phys. (U.S.S.R.) **28**, 762 (1955) [translation: Soviet Phys.—JETP **1**, 611 (1955)].

[10] D. K. Rei, Soviet Phys.—JETP **3**, 1606 (1962).

[11] S. Geschwind and J. P. Remeika, Suppl. J. Appl. Phys. **33**, 370 (1962).

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

[13] H. A. Weaklem and D. S. McClure, Suppl. J. Appl. Phys. **33**, 347 (1962).

whose ground state is $^3A_2$, group theoretical considerations show that in first approximation, only the excited states, $^3T_2$ and $^1T_2$, determine the zero-field splitting. Liehr and Ballhausen[14] have shown that the $^1T_2$ state yields only a small contribution to the zero-field splitting, as it is energetically much further removed from the ground state than is the $^3T_2$ state. To avoid unnecessary complexity, we shall ignore all effects due to the $^1T_2$ electronic state perturbation. Thus, we have only to consider the excited $^3T_2$ state in our discussion of the g shifts and the zero-field splittings of impurity ions in corundum.

For the g shift and the zero-field separations D, Geschwind and Remeika have used the spin Hamiltonian expression[12]

$$\tfrac{1}{3}D[3S_z^2-S(S+1)]+g_{\shortparallel}\beta S_zH_z+g_{\perp}\beta(S_xH_x+S_yH_y)$$

within the framework of the naive crystal-field theory. Thus,

$$\Delta g_{\shortparallel}\sim-8\lambda_e/\Delta_{\shortparallel},\quad \Delta g_{\perp}\sim-8\lambda_e/\Delta_{\perp}, \tag{1a}$$

$$D\approx\tfrac{1}{2}\lambda(g_{\shortparallel}-g_{\perp}). \tag{1b}$$

Here, λ_e is the effective spin-orbit coupling in the crystal and $\Delta_{\shortparallel}-\Delta_{\perp}$ is the splitting of the $^3T_2$ excited state by the trigonal field, as shown in Fig. 1. This is related to the trigonal splitting of a one-electron t_2 energy, v, by the formulas following Pryce and Runciman:[7]

$$\Delta_{\shortparallel}-\Delta_{\perp}=\tfrac{1}{2}v.$$

In the present case the z axis is taken along the trigonal axis.

In order to explain the experimental results for Ni^{2+} and Cu^{3+} shown in Table II with (1a) and (1b), v should be taken as having a negative value. This choice is opposite to that taken for the analogous V^{3+}, Cr^{3+}, Co^{2+}, and Ru^{3+} systems. Sugano and Tanabe[15] also have found that in the case of ruby the sign of the zero-field separation of the ground state is inconsistent with the correct sign of v which has been obtained from the splittings of the band spectra if the above-mentioned formulas are used, and then they have suggested that if the anisotropy of the spin-orbit coupling constant is taken into account in these formulas, the inconsistency is removed. The same suggestion is also applicable to the present cases of Ni^{2+} and Cu^{3+} in order to explain the experimental observation, and further to get the sign of v to be consistent with that obtained for other impurities. The purpose of the present paper is to make clear the main mechanisms which cause the anisotropic spin-orbit coupling in the cases of the d^8 and d^3 solutes in the trigonal field, and further to show whether the amount of anisotropy of the spin-orbit coupling constant needed to arrive at a positive v can be deduced from the theory.

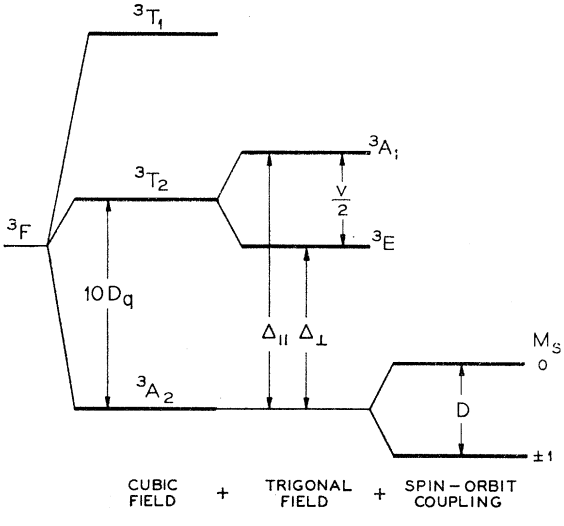

FIG. 1. The splitting of the free-ion ^3F level of the $(3d)^8$ solutes in corundum by a cubic field, trigonal field, and spin-orbit coupling.

TABLE II. Experimental results for Ni^{2+} and Cu^{3+}.

	Cu^{3+a}	Ni^{2+b}
$g_{\shortparallel}$	2.0788 ± 0.0005	2.196
$g_{\perp}$	2.0772 ± 0.0005	2.187
D	$-0.1884\ cm^{-1}$	$-1.312\ cm^{-1}$

[a] See reference 1.
[b] See reference 2,

It is shown in the present paper that two types of distortions of wave functions by the trigonal field play very important roles in making the spin-orbit coupling an anisotropic one.

One type is the distortion of the covalent π bond. In order to take account of the effect of this distortion, we shall adopt the molecular orbital model to describe the wave function of a single d electron. The trigonal field influences only the t_2 molecular orbitals, where t_2 refers to the transformation properties of the functions which are isomorphic with the t_{2g} irreducible representation. Consequently, the t_2 molecular orbital in the plane perpendicular to the c axis, $\varphi|t_2x_0\rangle$, is different from the other two t_2 molecular orbitals, $\varphi|t_2x_+\rangle$ and $\varphi|t_2x_-\rangle$. Therefore, we will distinguish $\varphi|t_2x_0\rangle$ from $\varphi|t_2x_+\rangle$ and $\varphi|t_2x_-\rangle$ throughout this paper. With a LCAO (linear combination of atomic orbitals) method, we can write three t_2 antibonding molecular orbitals in the following form:

$$\varphi|t_2x_0\rangle=(1/\sqrt{N_0})[\psi_{d\epsilon}|x_0\rangle-\rho\varphi_\pi|x_0\rangle], \tag{2a}$$

$$\varphi|t_2x_\pm\rangle=(1/\sqrt{N})[\psi_{d\epsilon}|x_\pm\rangle-\eta\varphi_\pi|x_\pm\rangle], \tag{2b}$$

where the $\psi_{d\epsilon}$'s refer to the $d\epsilon$ wave functions of the transition metal ions; the φ_π's are linear combinations of O^{2-} atomic orbitals π; x_+, x_0, and x_- are the trigonal basis of the t_2 representation; and N_0 and N are normalization factors.

---

[14] A. D. Liehr and C. J. Ballhausen, Ann. Phys. (New York) **6**, 134 (1959).

[15] S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **13**. 880 (1958).

Another type of distortion is due to the configuration mixing effect by the trigonal field of higher energy terms other than the ${}^3A_2$ and ${}^3T_2$ states on these two states. Assuming that the trigonal field has the symmetry T_2, the ${}^3T_1$ states with the $t_2{}^5e^3$ and $t_2{}^4e^4$ configurations are mixed into the ${}^3A_2$ and ${}^3T_2$ states.

These situations are shown pictorially in Fig. 2. The assumption of the trigonal field with symmetry T_2 seems reasonable to us because the trigonal fields with the other symmetries A_2 and T_1 arise from the sixth- and fourth-order terms in the expansion of the electron coordinates. These fourth- and sixth-order terms are considered weak.

The above-mentioned effects of the distortions of the wave functions make the matrix element of the spin-orbit coupling between ${}^3T_2$ and ${}^3A_2$ states an anisotropic one, in the calculation for the g shifts and the zero-field separations.

As shown in later sections, the distortion by the trigonal field of the covalent π bond is very important to an understanding of the experimental results for the d^8 solutes in corundum.

The theory is also applicable to the case of ruby, because the ground orbital level is nondegenerate and the excited state to be mixed into the ground state by the spin-orbit coupling is mainly T_2. It will be shown that both distortion effects, of wave functions due to the configuration mixing and of the covalent π bonds, play important roles.

In Sec. 2, the perturbed wave functions of the ${}^3A_2$ and ${}^3T_2$ states by the configuration mixing are derived. In Sec. 3 the expressions for the g shift and zero-field separation of the ground state of the d^8 solutes are given and further the linear relation between the trigonal splitting and the anisotropy of the spin-orbit coupling of the single d electron is derived by the simple molecular orbital approach. The comparison with the experimental data observed by Geschwind and Remeika will be presented in Sec. 4. In Sec. 5 the theory will be applied to ruby.

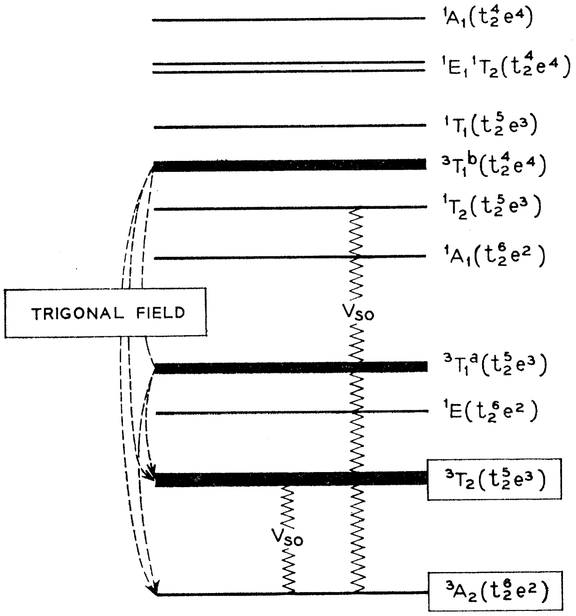

FIG. 2. Energy diagram for Ni^{2+} in corundum.

TABLE III. The matrix elements of the cubic field, the trigonal field, and the Coulomb interactions between the electrons for the ${}^3A_2$, ${}^3T_1{}^a(t_2{}^5e^3)$, and ${}^3T_1{}^b(t_2{}^4e^4)$ states.

	${}^3A_2$ e_2	${}^3T_1{}^a(t_2{}^5e^3)$ a_0	${}^3T_1{}^b(t_2{}^4e^4)$ a_0
${}^3A_2$ e_2	$-12Dq$	$-2K'$	
${}^3T_1{}^a$ a_0	$-2K'$	$-2Dq+12B-K$	$-6B-4K'$
${}^3T_1{}^b$ a_0		$-6B-4K'$	$8Dq+3B$

2. THE CONFIGURATION MIXING EFFECT BY THE TRIGONAL FIELD

Now we shall consider the configuration mixing effect of the trigonal field on the ${}^3A_2$ and ${}^3T_2$ states. As we have assumed a trigonal field with symmetry T_2, the ${}^3A_2$ ground state and the ${}^3T_2$ excited state have matrix elements of the trigonal field only with the ${}^3T_1$ states of the configurations $t_2{}^5e^3$ and $t_2{}^4e^4$. The nonvanishing matrix elements are shown in Tables III and IV, where Dq denotes the strength of the cubic field, B measures the Coulomb interactions between the electrons, and K and K' are defined as

$$K=(t_2x_+|v(F_2)|t_2x_+), \tag{3a}$$

and

$$K'=-(1/\sqrt{2})(t_2x_+|v(F_2)|eu_+), \tag{3b}$$

in terms of the single electron operator of the trigonal field $v(F_2)$. (a_+,a_0,a_-) and (x_+,x_0,x_-) are the sets of the trigonal basis of the T_1 and T_2 states, respectively. In case the t_2 and e orbitals are constructed purely from $3d$ orbitals, we have $K=K'=-\frac{3}{4}v$.

As a result of this configuration mixing we can write the perturbed wave functions of the ${}^3A_2$ and ${}^3T_2$ states, Ψ_{A_2} and $\Psi_{T_2}(\gamma)$, in the following forms:

$$\Psi_{A_2}=a_1\Phi^0({}^3A_2)+a_2\Phi^0({}^3T_1(t_2{}^5e^3)a_0)+a_3\Phi^0({}^3T_1(t_2{}^4e^4)a_0), \tag{4a}$$

and

$$\Psi_{T_2}(x_\pm)=b_1\Phi^0({}^3T_2(t_2{}^5e^3)x_\pm)+b_2\Phi^0({}^3T_1(t_2{}^5e^3)a_\pm)+b_3\Phi^0({}^3T_1(t_2{}^4e^4)a_\pm), \tag{4b}$$

$$\Phi_{T_2}(x_0)=\Phi^0({}^3T_2(t_2{}^5e^3)x_0), \tag{4c}$$

where the $\Phi^0(\Gamma)$'s are the unperturbed eigenfunction of the Γ state; a_1 and b_1 are nearly equal to 1, while a_2, a_3, b_2, and b_3 are small.

As the energy difference between the ${}^3A_2$ state and the $t_2{}^4e^4$ ${}^3T_1$ state is much larger than the strength of the trigonal field, we may neglect the coefficient a_3, and further we can estimate the coefficient a_2 by using

TABLE IV. The matrix elements of the cubic field, the trigonal field, and the Coulomb interactions between the electrons for the $^3T_2$, $^3T_1{}^a(t_2{}^5e^3)$, and $^3T_1{}^b(t_2{}^4e^4)$ states.

	$^3T_2(t_2{}^5e^3)$ $x_\pm$	$^3T_1{}^a(t_2{}^5e^3)$ $a_\pm$	$^3T_1{}^b(t_2{}^4e^4)$ $a_\pm$
$^3T_2$ $x_\pm$	$-2Dq+(K/2)$	$\mp\frac{3}{2}iK$	$\mp 2K'$
$^3T_1{}^a$ $a_\pm$	$\pm\frac{3}{2}iK$	$-2Dq+12B+(K/2)$	$-6B+2K'$
$^3T_1{}^b$ $a_\pm$	$\mp 2K'$	$-6B+2K'$	$8Dq+3B-K$

the second-order perturbation in the following:

$$a_2=\frac{2K'}{\mathcal{E}(^3T_2(t_2{}^5e^3))-\mathcal{E}(^3A_2)}. \tag{5}$$

To determine the coefficients b_i $(i=1,2,3)$, we must solve the three-dimensional secular equation (refer to Table IV) to obtain their values.

3. THE CALCULATION OF THE ANISOTROPIC SPIN-ORBIT COUPLING OF THE SINGLE *d* ELECTRON BY THE SIMPLE MOLECULAR ORBITAL APPROACH

In this section, first of all we shall derive the expressions for the g shift and the zero-field separation by using the wave functions (4a), (4b) and (4c). A perturbing Hamiltonian for the ground state is given by

$$\mathcal{H}'=\mathbf{V}_{\text{so}}+\mu_B\mathbf{H}\cdot(\mathbf{T}+2\mathbf{S}). \tag{6}$$

Here, $\mathbf{V}_{\text{so}}$ denotes the spin-orbit coupling.

The off-diagonal matrix elements of $\mathbf{V}_{\text{so}}$ between the $^3T_2$ state and the ground state, $^3A_2$, together with those of $\mathbf{T}$ are given in Tables V and VI, where, neglecting the terms of not less than second power with respect to the trigonal field, $(\beta_\parallel,\beta_\perp)$ and $(\gamma_\parallel,\gamma_\perp)$ are given by the following equations:

$$\beta_\parallel=[a_1+(a_2/2)(\zeta/\zeta')-a_3], \tag{7a}$$

$$\beta_\perp=[a_1-(a_2/4)(\zeta/\zeta')+\tfrac{1}{2}a_3]b_1, \tag{7b}$$

and

$$\gamma_\parallel=[a_1+(a_2/2)(k/k')-a_3], \tag{8a}$$

$$\gamma_\perp=[a_1-(a_2/4)(k/k')+\tfrac{1}{2}a_3]b_1, \tag{8b}$$

and

$$\zeta=(\zeta_\parallel+\zeta_\perp)/2, \tag{9a}$$

$$\zeta'=(\zeta_\parallel{}'+\zeta_\perp{}')/2, \tag{9b}$$

$$k=(k_\parallel+k_\perp)/2, \tag{9c}$$

and

$$k'=(k_\parallel{}'+k_\perp{}')/2. \tag{9d}$$

The two sets of anisotropic spin-orbit constants $(\zeta_\parallel,\zeta_\perp)$ and $(\zeta_\parallel{}',\zeta_\perp{}')$ are defined as

$$\begin{aligned}\zeta_\parallel&=-2(t_2x_+\tfrac{1}{2}|v_{\text{so}}|t_2x_+\tfrac{1}{2}),\\ \zeta_\perp&=-\sqrt{2}(t_2x_+\tfrac{1}{2}|v_{\text{so}}|t_2x_0-\tfrac{1}{2}),\end{aligned} \tag{10a}$$

and

$$\begin{aligned}\zeta_\parallel{}'&=-\sqrt{2}(t_2x_+\tfrac{1}{2}|v_{\text{so}}|eu_+\tfrac{1}{2}),\\ \zeta_\perp{}'&=-(t_2x_0-\tfrac{1}{2}|v_{\text{so}}|eu_-\tfrac{1}{2}),\end{aligned} \tag{10b}$$

in terms of the single-electron spin-orbit operator v_{so}. The two sets of anisotropic orbital angular momentum reduction factors $(k_\parallel,k_\perp)$ and $(k_\parallel{}',k_\perp{}')$ are defined as

$$\begin{aligned}k_\parallel&=-(t_2x_+|l_z|t_2x_+),\\ k_\perp&=(t_2x_+|l_+|t_2x_0),\end{aligned} \tag{11a}$$

and

$$\begin{aligned}k_\parallel{}'&=-(1/\sqrt{2})(t_2x_+|l_z|eu_+),\\ k_\perp{}'&=(1/\sqrt{2})(t_2x_0|l_+|eu_-),\end{aligned} \tag{11b}$$

in terms of the single-electron orbital angular momentum $\mathbf{l}$.

According to the scheme given by Pryce,[12] we obtain the following expressions for the g shifts and the zero-field splitting D:

$$\Delta g_\parallel=-8p^2\beta_\perp\gamma_\perp\lambda'k'/\Delta_\parallel, \tag{12a}$$

$$\Delta g_\perp=-8\beta_\perp\gamma_\perp\lambda'k'/\Delta_\perp, \tag{12b}$$

and

$$D=-4(\beta_\perp\lambda')^2(p^2/\Delta_\parallel-1/\Delta_\perp) \tag{13}$$

where

$$\lambda'=-\zeta'/2$$

and

$$p=(\beta_\parallel/\beta_\perp)(\zeta_\parallel{}'/\zeta_\perp{}')=(\gamma_\parallel/\gamma_\perp)(k_\parallel{}'/k_\perp{}').$$

It is seen in (12a), (12b), and (13) that the distortion effects of the wave functions by the trigonal field can be expressed by one quantity p.

In applying the theory to experimental results, we will use the approximation that $\zeta=\zeta'$, $k=k'$, and $K=K'$. This approximation is not exactly valid, since we have taken the molecular orbital approach for a single-electron wave function. We can, however, expect from the following discussion that this approximation is not too bad. It has been pointed out that the σ bonds are stronger than the π bonds in the ionic complexes because of larger overlap of e orbitals with the ligands.[16] In order to take account of this fact, Koide and Pryce[17] have introduced the phenomenological parameter ϵ in the evaluation of the Coulomb and exchange integrals so that the amplitude of each e orbital is diminished by the factor $(1-\epsilon)^{1/2}$ as compared to the amplitude of each t_2 orbital. Sugano and Peter have extended this idea to the evaluation of ζ, etc., in the case of ruby, putting $\zeta'=(1-\epsilon)^{1/2}\zeta$ and so on.[18] By using the semi-

TABLE V. The off-diagonal matrix elements of $\mathbf{V}_{\text{so}}$: $(^3\Psi_{A_2}M_s|\mathbf{V}_{\text{so}}|^3\Psi_{T_2}\gamma M_s{}')$.

γ	x_+			x_-			x_0		
$M_s \diagdown M_s{}'$	-1	0	$+1$	-1	0	$+1$	-1	0	$+1$
-1					$-i\beta_\perp\zeta'$		$i\beta_\parallel\zeta_\parallel{}'$		
0	$i\beta_\perp\zeta'$					$-i\beta_\perp\zeta'$		0	
$+1$		$i\beta_\perp\zeta'$							$-i\beta_\parallel\zeta_\parallel{}'$

---

[16] J. Owen, Proc. Roy. Soc. (London) **A227**, 183 (1955).
[17] S. Kiode and M. H. L. Pryce, Phil. Mag. **3**, 607 (1958).
[18] S. Sugano and M. Peter, Phys. Rev. **122**, 381 (1961).

TABLE VI. The off-diagonal matrix elements of $\mathbf{T}$: $({}^3\Psi_{A_2}|\mathbf{T}_{\gamma'}|{}^3\Psi_{T_2}\gamma)$.

$\gamma' \backslash \gamma$	x_+	x_-	x_0
a_+		$-2ik'\gamma_\perp$	
a_-	$-2ik'\gamma_\perp$		
a_0			$2ik'_{\parallel}\gamma_{\parallel}$

empirical value of ϵ obtained by them, ζ' is roughly equal to 0.9ζ. This result indicates that the approximation of $\lambda=\lambda'$, $k=k'$, and $K=K'(=-\frac{3}{4}v)$ is a reasonable one. By this approximation, we can obtain $\beta_{\parallel}=\gamma_{\parallel}$ and $\beta_\perp=\gamma_\perp$ from (7a), (7b), (8a), and (8b).

Thus, p is expressed by

$$p=\frac{(1+\frac{1}{2}a_2/a_1-a_3/a_1)}{b_1(1-\frac{1}{4}a_2/a_1+\frac{1}{2}a_3/a_1)}q, \tag{14}$$

where $q=\zeta_{\parallel}'/\zeta'$.

In (14) we can see that p consists of two factos S and q, where

$$S=\frac{1+\frac{1}{2}a_2/a_1-a_3/a_1}{b_1(1-\frac{1}{4}a_2/a_1+\frac{1}{2}a_3/a_1)}. \tag{15}$$

The factor S expresses the effect of configuration mixing while q describes the effect of the distortion of the t_2 molecular orbitals. If we put ρ and η in (2a) and (2b) equal to each other, then q is equal to one. As mentioned before, we shall neglect the coefficient a_3 in the factor S. Then it is easily seen from (5) and (15) that S is larger than one for negative v (positive K') and smaller than one for positive v.

The variation of the g shifts and the zero-field splitting as a function of p indicates that when p becomes slightly larger than one, $\Delta g_{\parallel}$ becomes larger than $\Delta g_\perp$ and D is negative even for positive v as well as for negative v. Therefore we can conclude that p must be taken to be larger than one in order to explain the experimental result and moreover to obtain a consistent positive sign for v.

As already mentioned, the factor due to the configuration mixing, S, is larger than one only for negative v. This fact tells us that the configuration mixing effect operates unfavorably to obtain a consistent sign for v.

Thus, the problem must proceed to the stage of taking account of the contribution due to the distortion of the covalent π bonds. In first approximation, q is written in the following form:

$$q=2/1+(N_0/N)^{1/2}, \tag{16}$$

by using the wave functions (2a), (2b), and (10b). As the difference between N_0 and N is determined by v, q should be determined self-consistently with v.

Although it is difficult to do this quantitatively, we can derive in first approximation a linear relation between q and v by means of a simple molecular orbital approach. In this approach the coefficients η and ρ in (2b) and (2a) are approximately expressed in the following forms:

$$\eta=-\tfrac{1}{2}(t_1+t_2/\mathcal{E}_{d\epsilon}-\mathcal{E}_{p\pi}), \tag{17a}$$

and

$$\rho=-\tfrac{1}{2}(2t_2/\mathcal{E}_{d\epsilon}-\mathcal{E}_{p\pi}), \tag{17b}$$

where $\mathcal{E}_{d\epsilon}$ and $\mathcal{E}_{p\pi}$ are energy levels of a single $d\epsilon$ electron on the transition metal ion and of a single $p\pi$ electron on the attached oxygen ion, respectively, and t_1 and t_2 are the resonance integrals between the $d\epsilon$ electron and the $p\pi$ electron in the plane including the c axis and perpendicular to it, respectively. In deriving (17a) and (17b), we have assumed the energy difference $\mathcal{E}_{d\epsilon}-\mathcal{E}_{p\pi}$ is larger than the intergrals t_1 and t_2. Remembering that the energy difference of the single t_2 electron between states corresponding to $\varphi(t_2x_0)$ in (2a) and $\varphi(t_2x_\pm)$ in (2b) is equal to v, v is given by

$$v=-(t_1+2t_2)(t_1-t_2)/(\mathcal{E}_{d\epsilon}-\mathcal{E}_{p\pi}), \tag{18}$$

in terms of the resonance integrals t_1 and t_2. Thus, we can obtain the following approximate relation between q and v, starting from (16);

$$q=1+\frac{v}{4[(\mathcal{E}_{d\epsilon}-\mathcal{E}_{p\pi})+4t_2^2/(\mathcal{E}_{d\epsilon}-\mathcal{E}_{p\pi})]}. \tag{19}$$

As the t_2 molecular orbitals in (2a) and (2b) have been assumed to be antibonding, the difference $\mathcal{E}_{d\epsilon}-\mathcal{E}_{p\pi}$ is positive. It is, therefore, easily seen from (19) that q must be larger than one for positive v, while smaller than one for negative v. This can be explained intuitively as follows. Since a positive v means an elongation of the octahedron composed by six oxygens along the c axis, the resonance integral t_2 is larger than t_1 for positive v. Therefore, the normalization factor N_0 in (2a) is smaller than N in (2b). Thus, we can find in (16) that q is larger than one for positive v.

We see from the above-mentioned result how the distortion of the covalent π bonds can explain the experimental results for Cu^{3+} and Ni^{2+} in terms of a positive v, consistent with the sign of v found for the orbitally degenerate ground states. Further, as the resonance integral t_2 is larger for the transition metal impurity which has the stronger covalency, we can expect that the deviation of q from one becomes smaller for such an impurity.

In order to get the order of magnitude of q, we may estimate q by replacing (19) by the expression

$$q=1+\tfrac{1}{4}v/10Dq. \tag{20}$$

4. DISCUSSION AND COMPARISON WITH EXPERIMENT

It is of interest to consider what further experiments might be performed to check the theory. In this section we shall treat q as a semiempirical parameter

TABLE VII. The values of Dq, B, and v in the cases of Ni^{2+} and Cu^{3+}, together with numerical values of the coefficients a_i and b_i obtained for these values.

	Cu^{3+}	Ni^{2+}
Dq (cm^{-1})	2100	1000
B (cm^{-1})	1030	870
v (cm^{-1})	760	740
a_1	0.9999	0.9997
a_2	−0.0153	−0.0246
a_3	−0.0018	−0.0047
b_1	0.9982	0.9950
b_2	0.0490	0.0723
b_3	0.0341	0.0691

which is to be determined from the experimental facts because it is difficult to calculate the quantitative value of q as seen in (16) and (19). We shall denote the semiempirical q by q_s. In the last section the semiempirical values of q will be compared with the quantitative values estimated by (20).

From (12b), we find that $\Delta g_\perp$ is independent of p. Thus, we can determine a value of $(\beta_\perp^2 k'\lambda')$ from the experimental value of $g_\perp$; then we adjust q and v so as to get good agreement with the experimental values of $\Delta g_{\parallel}$ and D. Best agreement is obtained by taking $q_s = 1.03$, $\lambda' = -215$ cm^{-1}, and $v = 760$ cm^{-1} for Cu^{3+} and $q_s = 1.07$, $\lambda' = -235$ cm^{-1}, and $v = 740$ cm^{-1} for Ni^{2+}. Here, we have put approximately $k' = 1$. In this process it is also necessary to know the values of Dq and B. For these we have used the values obtained from the observed optical absorption spectrum for Cu^{3+} in corundum.[11] On the other hand, for Ni^{2+}, since optical data for Ni^{2+} in Al_2O_3 have not been reported, we have used for B the value of Ni^{2+} in MgO,[19] and for Dq a slightly larger value than the one in MgO, taking the smaller metal-oxygen distance in corundum into account. These values are shown in Table VII, together with those of the coefficients a_i and b_i $(i = 1,2,3)$ in (4a) and (4b) obtained for these values of Dq, B, and v.

The values of v obtained for Ni^{2+} and Cu^{3+} are nearly the same as those obtained for the cases of Ru^{3+}, Co^{2+}, V^{3+} and Cr^{3+} in corundum. The near constancy of v for these ions indicates that they all enter into essentially the same positon as the Al^{3+} ions. The values of the average spin-orbit coupling constant λ' deduced for Cu^{3+} and Ni^{2+} are depressed by as much as 50% and 30%, respectively, from the free-ion values. The free-ion value for Ni^{2+} is -322 cm^{-1} and for Cu^{3+} it is -415 cm^{-1}. Such a big reduction is considered to be due to the so-called covalency effect, to which the e molecular orbitals give a greater contribution than the t_2 molecular orbitals. It should be born in mind that the previously mentioned distortion effect of the t_2 molecular orbitals is essentially different from the mechanism which cause the reduction of the average spin-orbit coupling constant in crystals.

Finally, in order to obtain more accurate semiempirical values of q, we shall take all crystal field levels which arise from the d^8 configuration into account and solve the complete 45×45 secular equation which involves the trigonal field and the spin-orbit coupling as well as the cubic field and the Coulomb interaction. In constructing the secular determinant, Tanabe and Kamimura's table[20] was used. Double-barred matrices of the trigonal field and the angular momentum operator are listed in Appendixes I and II, while Tanabe[21] has recently calculated the double-barred matrices of the spin-orbit coupling.

The qualitative features mentioned in the present paper are not changed by this complete calculation. This fact means that the effects of the states neglected in the present work are very small. The values of q_s determined so as to give the observed zero-field splitting are 1.10 for Ni^{2+} and 1.05 for Cu^{3+}. They are a little larger than those obtained by the simple calculation. The values of the parameters used in the calculation are listed in Table VIII.

5. THE APPLICATION OF THE THEORY TO THE CASE OF RUBY

Detailed calculations for the zero-field splitting of ruby have been developed by Sugano and Tanabe[15] and by Sugano and Peter.[18] Therefore, we will not pursue this problem in detail. It is the purpose of this section to point out that both of the previously mentioned types of distortion of the wave functions play very important roles in the ground state of ruby.

The ground state of ruby is $^4A_2$. The excited states which can be mixed in by the spin-orbit coupling are $^4T_2$ and $^2T_2$. If we assume that the main perturbation of the ground state originates in the interaction with the $^4T_2$ state, the calculation is very similar to the one for nickel. The same expressions (12a), (12b), and (13) for the g shift and the zero-field separation are also used in the case of ruby, except that $2D$ is equal to the separation of the two Kramers doublets $M_s = \pm\frac{3}{2}$ and $M_s = \pm\frac{1}{2}$ of the ground quartet, $W(\pm\frac{3}{2}) - W(\pm\frac{1}{2})$, and that $\lambda' = \zeta'/3$. The total anisotropy of the spin-orbit coupling, p, is also expressed by (14) in this case. The

TABLE VIII. The values of the parameters used in the calculation.

	Cu^{3+}	Ni^{2+}
Dq	2100 cm^{-1}	1000 cm^{-1}
B	1030 cm^{-1}	870 cm^{-1}
C $(=4B)$	4120 cm^{-1}	3480 cm^{-1}
K	570 cm^{-1}	555 cm^{-1}
K' $(=K)$	570 cm^{-1}	555 cm^{-1}
ζ	430 cm^{-1}	470 cm^{-1}
ζ' $(=\zeta)$	430 cm^{-1}	470 cm^{-1}
k	1.0	1.0
k' $(=k)$	1.0	1.0

---

[19] W. Low, Phys. Rev. **109**, 247 (1958).

[20] Y. Tanabe and H. Kamimura, J. Phys. Soc. Japan **13**, 394 (1958).

[21] Y. Tanabe, Suppl. Progr. Theoret. Phys. (Kyoto) **14**, 17 (1960).

coefficient a_2, however, no longer has the same form as the one given in (5). Instead of expression (5) for the d^8 solutes, a_2 is given by the following expression:

$$\begin{aligned} a_2 &= -K'/[\mathcal{E}(^4T_1(t_2{}^2e)) - \mathcal{E}(^4A_2)] \\ &= \tfrac{3}{4}v/[\mathcal{E}(^4T_1(t_2{}^2e)) - \mathcal{E}(^4A_2)]. \end{aligned} \tag{21}$$

Besides the denominator, the only difference between (5) and (21) lies in the sign. This difference arises from the relation between particles and holes. It should be noted that we must take the minus sign for the d^3 solutes instead of the plus sign which was taken for the d^8 solutes.

In order to explain the experimental fact of negative D for ruby, it is also shown that p must be larger than one for positive v. Neglecting again the coefficient a_3 in this case, it is easily seen in (15) that the factor S, caused by the configuration mixing effect, is larger than one for positive v while smaller than one for negative v. Thus, in the case of the d^3 solutes, the configuration mixing effect as well as the effect due to the distortion of the covalent π bonds operate favorably to explain the experimental facts. This is the reason why Sugano and Peter[18] have succeeeded in explaining the correct sign of the zero-field splitting of the ground state for ruby by the configuration interaction effect. However, their result was not satisfactory to get good quantitative agreement with the experimental result. The difference in magnitude between their result and the experimental one, however, may be explained by the distortion effect of the covalent π bonds.

Now we shall proceed to get the semiempirical value of q in this case by the same procedure as in the previous section. However, since the calculation is not complete as will be shown in the following, the obtained semiempirical value of q is not so accurate as those for Ni^{2+} and Cu^{3+}. In this case we adjust q and λ' so as to get good agreement with experimental values of $\Delta g_{\parallel}$, $\Delta g_{\perp}$, and D,[9] because we use for Dq, B, v, and k' the values obtained by Sugano and Peter.[17] Further, the mixing coefficients of the $^4T_1$ state with the configurations $t_2{}^2e$ and t_2e^2 into the $^4T_2$ state are taken to be zero. The best agreement between experiment and theory is found for $\lambda' = 63$ cm^{-1} and $q = 1.11$ with $Dq = 1667$ cm^{-1}, $B = 700$ cm^{-1}, $v = 1050$ cm^{-1}, and $k' = 0.62$.

6. CONCLUDING REMARKS

In the present paper we have pointed out two mechanisms which are very important in understanding the magnetic properties of the ground state of d^3 and d^8 systems in the trigonal crystal field whose ground states are orbitally nondegenerate. It has been shown that, among these, the distortion effect of the covalent π bonds always operates favorably to explain the experimental facts. On the other hand, the configuration mixing effect acts favorably in the case of the d^3 solutes and unfavorably in the case of d^8 solutes. This indicates that the experimental facts for Ni^{2+} and Cu^{3+} in Al_2O_3 cannot be explained by the naive crystal field theory which is based on the ionic model, as long as we assume that the impurity ions do not move abnormally. Thus, we can conclude that the itineracy of the t_2 electrons between the metal ion and ligands plays the important role especially in the case of the d^8 solutes in corundum. From this standpoint, we should like to remark that Shulman and Sugano[22] have recently pointed out the important role of the π bonds in $KNiF_3$.

TABLE IX. The semiempirical values of p and q_s and the calculated values of S and q, together with Dq, v, and λ' obtained from the experimental results.

	Cr^{3+}	Ni^{2+}	Cu^{3+}
p	1.14	1.05	1.02
q_s	~1.11	1.07(1.10)	1.03(1·05)
S	~1.03	0.98	0.99
q	1.02	1.02	1.01
Dq (cm^{-1})	1667	1000(?)	2100
v (cm^{-1})	1050	740	760
λ' (cm^{-1})	63	− 235	− 215
$\lambda'/\lambda_{\text{free}}$[a]	0.73	0.73	0.52

[a] λ_{free} means the over-all spin-orbit coupling constant of the free ion. The numerical values of q in parenthesis are more accurate ones obtained by solving the 45 × 45 secular determinant.

In Table IX the semiempirical values of p and q_s and the calculated values of q and S are listed for Cr^{3+}, Ni^{2+}, and Cu^{3+} together with the values of Dq, v, and λ' obtained from comparison of theory with experiments. The value of S has been calculated by means of (15), using the values of a_i and b_i tabulated in Table VII. The quantitative value of q has been estimated by the approximate expression (20).

Looking at Table IX, we find that the semiempirical values of q are reasonable, though the agreement between q_s and q is not satisfactory. In the present paper, we have not considered the effect of the intra-atomic spin-spin interaction which gives an appreciable contribution to the intervals of multiplets in the atomic spectra of transition metal ions.[23] In addition to the fact that we must calculate q more precisely in order to remove the discrepancy between the calculated and semiempirical values of q, the effect of the intra-atomic spin-spin interaction might contribute to remove this discrepancy.

ACKNOWLEDGMENTS

I would like to thank S. Geschwind for his many helpful discussions. The early part of this paper is based on his experimental work and has been helped by discussing his experimental results prior to publication. I also wish to thank R. E. Dietz, C. Herring, A. D. Liehr, M. Peter, and J. C. Phillips for their stimulating discussions and helpful comments on the manuscript and R. L. Kornegay for his help with the computations on the IBM 7090.

---

[22] R. G. Shulman and S. Sugano, Phys. Rev. Letters, **7**, 157 (1961).

[23] R. E. Trees, Phys. Rev. **82**, 683 (1951).

APPENDIX I

Double-barred matrices of the trigonal field $(\alpha S\Gamma\|V(T_2)\|\alpha' S\Gamma')$ within the $t_2{}^4e^4$, $t_2{}^5e^3$, and $t_2{}^6e^2$ configurations. Unlisted matrices are zero. K' and K are defined in Eqs. (3b) and (3a), respectively.

$\alpha S\Gamma$	$\alpha' S\Gamma'$	The values
$t_2{}^6e^2\ {}^3A_2$	$t_2{}^5e^3\ {}^3T_1$	$2\sqrt{3}K'$
$t_2{}^6e^2\ {}^1E$	$t_2{}^5e^3\ {}^1T_1$	$2\sqrt{3}K'$
$t_2{}^6e^2\ {}^1E$	$t_2{}^5e^3\ {}^1T_2$	$-2\sqrt{3}K'$
$t_2{}^6e^2\ {}^1A_1$	$t_2{}^5e^3\ {}^1T_2$	$2\sqrt{3}K'$
$t_2{}^5e^3\ {}^3T_2$	$t_2{}^5e^3\ {}^3T_2$	$-\frac{3}{2}\sqrt{2}K$
$t_2{}^5e^3\ {}^3T_2$	$t_2{}^5e^3\ {}^3T_1$	$\frac{3}{2}(\sqrt{6})K$
$t_2{}^5e^3\ {}^3T_2$	$t_2{}^4e^4\ {}^3T_1$	$-2(\sqrt{6})K'$
$t_2{}^5e^3\ {}^3T_1$	$t_2{}^5e^3\ {}^3T_1$	$-\frac{3}{2}\sqrt{2}K$
$t_2{}^5e^3\ {}^3T_1$	$t_2{}^4e^4\ {}^3T_1$	$6\sqrt{2}K'$
$t_2{}^5e^3\ {}^1T_2$	$t_2{}^5e^3\ {}^1T_2$	$-\frac{3}{2}\sqrt{2}K$
$t_2{}^5e^3\ {}^1T_2$	$t_2{}^5e^3\ {}^1T_1$	$\frac{3}{2}(\sqrt{6})K$
$t_2{}^5e^3\ {}^1T_2$	$t_2{}^4e^4\ {}^1T_2$	$-2(\sqrt{6})K'$
$t_2{}^5e^3\ {}^1T_2$	$t_2{}^4e^4\ {}^1E$	$8K'$
$t_2{}^5e^3\ {}^1T_2$	$t_2{}^4e^4\ {}^1A_1$	$-4\sqrt{2}K'$
$t_2{}^5e^3\ {}^1T_1$	$t_2{}^5e^3\ {}^1T_1$	$-\frac{3}{2}\sqrt{2}K$
$t_2{}^5e^3\ {}^1T_1$	$t_2{}^4e^4\ {}^1T_2$	$-6\sqrt{2}K'$
$t_2{}^4e^4\ {}^3T_1$	$t_2{}^4e^4\ {}^3T_1$	$-3\sqrt{2}K$
$t_2{}^4e^4\ {}^1T_2$	$t_2{}^4e^4\ {}^1T_2$	$3\sqrt{2}K$
$t_2{}^4e^4\ {}^1T_2$	$t_2{}^4e^4\ {}^1E$	$-2\sqrt{3}K$
$t_2{}^4e^4\ {}^1T_2$	$t_2{}^4e^4\ {}^1A_1$	$2(\sqrt{6})K$

APPENDIX II

Double-barred matrices of the orbital angular momentum $(\alpha S\Gamma\|L\|\alpha' S\Gamma')$ within the $t_2{}^4e^4$, $t_2{}^5e^3$ and $t_2{}^6e^2$ configurations. Unlisted matrices are zero. k' and k are defined in Eqs. (9d) and (9c), respectively.

$\alpha S\Gamma$	$\alpha' S\Gamma'$	The values
$t_2{}^6e^2\ {}^3A_2$	$t_2{}^5e^3\ {}^3T_2$	$2\sqrt{3}ik'$
$t_2{}^6e^2\ {}^1E$	$t_2{}^5e^3\ {}^1T_1$	$-2\sqrt{2}ik'$
$t_2{}^6e^2\ {}^1E$	$t_2{}^5e^3\ {}^1T_2$	$2\sqrt{2}ik'$
$t_2{}^6e^2\ {}^1A_1$	$t_2{}^5e^3\ {}^1T_1$	$2\sqrt{3}ik'$
$t_2{}^5e^3\ {}^3T_2$	$t_2{}^5e^3\ {}^3T_2$	$-\frac{1}{2}(\sqrt{6})ik$
$t_2{}^5e^3\ {}^3T_2$	$t_2{}^5e^3\ {}^3T_1$	$\frac{3}{2}\sqrt{2}ik$
$t_2{}^5e^3\ {}^3T_2$	$t_2{}^4e^4\ {}^3T_1$	$-6\sqrt{2}ik'$
$t_2{}^5e^3\ {}^3T_1$	$t_2{}^5e^3\ {}^3T_1$	$\frac{1}{2}(\sqrt{6})ik$
$t_2{}^5e^3\ {}^3T_1$	$t_2{}^4e^4\ {}^3T_1$	$2(\sqrt{6})ik'$
$t_2{}^5e^3\ {}^1T_2$	$t_2{}^5e^3\ {}^1T_2$	$-\frac{1}{2}(\sqrt{6})ik$
$t_2{}^5e^3\ {}^1T_2$	$t_2{}^4e^4\ {}^1T_2$	$-6\sqrt{2}ik'$
$t_2{}^5e^3\ {}^1T_2$	$t_2{}^5e^3\ {}^1T_1$	$\frac{3}{2}\sqrt{2}ik$
$t_2{}^5e^3\ {}^1T_2$	$t_2{}^4e^4\ {}^1T_2$	$-6\sqrt{2}ik'$
$t_2{}^5e^3\ {}^1T_1$	$t_2{}^5e^3\ {}^1T_1$	$\frac{1}{2}(\sqrt{6})ik$
$t_2{}^5e^3\ {}^1T_1$	$t_2{}^4e^4\ {}^1T_2$	$2(\sqrt{6})ik'$
$t_2{}^5e^3\ {}^1T_1$	$t_2{}^4e^4\ {}^1E$	$-8ik'$
$t_2{}^5e^3\ {}^1T_1$	$t_2{}^6e^4\ {}^1A_1$	$-2\sqrt{2}ik'$
$t_2{}^4e^4\ {}^3T_1$	$t_2{}^4e^4\ {}^3T_1$	$-(\sqrt{6})ik$
$t_2{}^4e^4\ {}^1T_2$	$t_2{}^4e^4\ {}^1T_2$	$-(\sqrt{6})ik$
$t_2{}^4e^4\ {}^1T_2$	$t_2{}^4e^4\ {}^1E$	$2\sqrt{3}ik$

PHYSICAL REVIEW VOLUME 128, NUMBER 3 NOVEMBER 1, 1962

Magnetothermal Oscillations. The Oscillatory Dependence of Temperature on Magnetic Field

J. E. Kunzler, F. S. L. Hsu, and W. S. Boyle*
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received June 1, 1962)

Magnetothermal oscillations are a new low-temperature phenomenon. They result from quantum effects and can be employed as a useful tool for exploring the electronic band structure of metals. Magnetothermal oscillations show up experimentally as a reversible and cyclic variation of the temperature of a thermally isolated single crystal, such as bismuth, as either the magnitude or the direction of an externally applied magnetic field is changed in a uniform manner. The oscillatory temperature changes are periodic in $1/H$, and their variation with orientation is dependent on the detailed shape of the pertinent part of the Fermi surface in much the same manner as magnetic susceptibility oscillations. Of the oscillatory effects used for the study of Fermi surface shapes at moderate magnetic fields, magnetothermal oscillations have yielded the best resolution in bismuth. The high resolution obtained in the magnetothermal experiments made it possible to observe for the first time fine structure in de Haas-van Alphen oscillations due to electron spin. Data for bismuth, showing magnetothermal oscillations as a function of magnetic field strength or the field direction, are presented and discussed.

I. INTRODUCTION

EXPERIMENTALLY, magnetothermal oscillations are reversible changes in temperature of a thermally isolated single crystal, such as bismuth, as either the magnitude or direction of an externally applied magnetic field is slowly changed. The observed oscillatory temperature changes are periodic in $1/H$ as the magnitude of the magnetic field is varied while its orientation is fixed.[1–3] However, the relationship between the oscillations observed on changing the magnetic-field direction cannot be defined in such a simple manner. These temperature changes take the form of cooling peaks when the magnitude and orientation are in the

---

* Present address: Bellcom, Inc., Washington, D. C.

[1] J. E. Kunzler and W. S. Boyle, Bull. Am. Phys. Soc. 4, 168 (1959); J. E. Kunzler, *ibid.* 4, 319 (1959).

[2] W. S. Boyle, F. S. L. Hsu, and J. E. Kunzler, Phys. Rev. Letters 4, 278 (1960).

[3] J. E. Kunzler and F. S. L. Hsu, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, New York, 1960), p. 88.