PHYSICAL REVIEW VOLUME 171, NUMBER 2 10 JULY 1968

Spin-Orbit-Coupling Effects in Transition-Metal Compounds

John B. Goodenough

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts*

(Received 27 December 1967)

Crystal-field splittings in a high-symmetry phase may leave an orbitally degenerate ground state. Three types of degeneracies are considered: (1) a twofold degeneracy that carries no orbital angular momentum, (2) a twofold degeneracy that carries an orbital angular momentum, and (3) a threefold degeneracy that carries an azimuthal angular momentum $M_L=0, \pm 1$. In the first type, there is a competition between ferromagnetic superexchange coupling that stabilizes dynamic Jahn-Teller vibrational modes and a static Jahn-Teller distortion that introduces anisotropic superexchange interactions. In the second type, spin-orbit coupling removes the degeneracy, and the usual empirical rules for the sign of the superexchange coupling are applicable provided that the transfer integrals with near-neighbor ions take account of the geometrical modification of the orbitals by spin-orbit coupling. In the third type, there is a competition between (a) a magnetostrictive static distortion that enhances the spin-orbit-coupling stabilization below a magnetic-ordering temperature, and (b) a pure Jahn-Teller static distortion. However, from a knowledge of the structure the orbital configurations and their transfer integrals are known, and the usual empirical rules for superexchange coupling can be applied. Further, if the transfer integrals are $b>b_c$, where b_c is sharply defined, it is necessary to use a collective-electron band model. For narrow bands, spin-orbit-coupling energies may be large enough to split degenerate bands of collective-electron orbitals. This latter splitting appears to be illustrated by NbS_2 and WS_2, where the cationic occupation of trigonal-bipyramidal interstices optimizes spin-orbit-coupling stabilization. Ferromagnetic superexchange via dynamic Jahn-Teller correlations is illustrated by high-temperature $LaMnO_3$. The competition between spin-orbit-coupling and Jahn-Teller stabilizations is dramatically illustrated by the system $NiFe_tCr_{2-t}O_4$. Whereas superexchange energies maintain a Jahn-Teller stabilization below T_c in $CuCr_2O_4$, despite collinear Cu^{2+}-ion spins, magnetostrictive distortions below T_N occur in FeO and CoO. Elastic restoring forces favor trigonal ($\alpha>60°$) symmetry for octahedral-site Fe^{2+}, but tetragonal ($c/a<1$) symmetry for Co^{2+} and V^{2+}. In trigonal FeO, superexchange interactions also help stabilize the trigonal distortion, whereas in tetragonal CoO they do not. The compound $LaVO_3$ also has a spin-orbit coupling stabilization that is enhanced by a magnetostrictive distortion to tetragonal ($c/a<1$) symmetry below T_N. However, the isoelectronic compound $PbCrO_3$ shows no such distortion, presumably because it illustrates band antiferromagnetism together with spin-orbit-coupling stabilization. The low-spin ions Fe^{4+} and Co^{4+} also form collective d orbitals in oxides with perovskite structure; electric, magnetic, and crystallographic data for $SrFeO_3$ and $LaSrCo_2O_6$ indicate collective d electrons having transfer integrals in the narrow range $b_c<b<b_m$, where b_m is the maximum transfer integral for spontaneous band magnetism.

I. INTRODUCTION

THERE are two limiting descriptions of the atomic outer electrons after the atoms have been brought together to form a crystal: crystal-field theory and band theory. Crystal-field theory rests on the assumption that the outer electrons are localized at discrete atomic positions, whereas band theory rests on the assumption that each electron belongs collectively to all the atoms of a periodic array. Band electrons are described by Fermi-Dirac statistics and have as a characteristic feature a discontinuity in electron density versus energy at an energy surface in momentum space, the Fermi surface. Electrons that are localized to different atomic positions, on the other hand, have no well-defined Fermi surface. Therefore, any physical property that depends upon the existence of a Fermi surface can serve as a criterion for distinguishing localized electrons from collective electrons. However, the most useful of these are those properties that are enhanced as the band of allowed collective-electron energies becomes narrower. Among these are spontaneous crystallographic distortions,[1] concentration of elastic energies into discrete vibrational modes via electron-phonon interactions,[2] and interatomic magnetic ordering via electron correlations.[3,4] From a series of studies on transition-metal oxides and sulfides,[5–10] it has been possible to demonstrate indirectly that the transition from localized to collective d electrons is sharp and depends upon the magnitude of the transfer integrals between crystal-field d orbitals on neighboring cations. (Where there is an energy difference between these orbitals, the transfer integral must be multiplied by the ratio of itself to the energy difference.) In one compound, $LaCoO_3$, a first-order electronic transition has been observed and interpreted as a localized-electron$\rightleftarrows$collective-electron transition.[11] This would

---

* Operated with support from the U.S. Air Force.

[1] J. B. Goodenough, Mater. Res. Bull. **2**, 37, 165 (1967).

[2] W. Kohn, Phys. Rev. Letters **2**, 393 (1959).

[3] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[4] A. W. Overhauser, Phys. Rev. Letters **3**, 414 (1959); J. Phys. Chem. Solids **13**, 71 (1960).

[5] J. B. Goodenough, "Metallic Oxides," in *Progress in Solid-State Chemistry*, Vol. 5, edited by R. Reiss (to be published).

[6] D. B. Rogers, R. J. Arnott, A. Wold, and J. B. Goodenough, J. Phys. Chem. Solids **24**, 347 (1963).

[7] J. B. Goodenough, Bull. Soc. Chim. France **4**, 1200 (1965).

[8] J. B. Goodenough, J. Appl. Phys. **37**, 1415 (1966).

[9] J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience Publishers, Inc., New York, 1963).

[10] J. B. Goodenough, *Colloques Interantionaux du CNRS, No. 157, Orsay, 1965* (Centre Nationale de la Recherche Scientifique, Paris, 1967).

[11] P. M. Raccah and J. B. Goodenough, Phys. Rev. **155**, 932 (1967).

TABLE I. Lowest terms and ground-state wave functions for octahedral-site cations having n outer d electrons.

n	$t^{\xi}e^{\eta}$	V_{el}	V_{c}	V_{LS}	$V_{LS}+V_{\mathrm{nc}}(\delta<0)+H_{\mathrm{ex}}$	$V_{LS}+V_{\mathrm{nc}}(\delta>0)+H_{\mathrm{ex}}$
1	t^1e^0	^2D	$^2T_{2g}$	$J=\frac{3}{2}$	$\|+1,+\frac{1}{2}\rangle$	$a_1\|0,+\frac{1}{2}\rangle+a_2\|+1,-\frac{1}{2}\rangle$
2	t^2e^0	^3F	$^3T_{1g}$	$J=2$	$\|+1,+1\rangle$	$b_1\|+1,-1\rangle+b_2\|0,0\rangle+b_3\|-1,+1\rangle$
3	t^3e^0	^4F	$^4A_{2g}$	$J=\frac{3}{2}$	$\|0,+\frac{3}{2}\rangle$	$\|0,+\frac{3}{2}\rangle$
4	t^3e^1	^5D	^5E_g	$J=2$	$^5B_{1g}\|0,+2\rangle$	$^5A_{1g}\|0,+2\rangle$
	t^4e^0		$^3T_{1g}$	$J=0$	$b_1\|+1,-1\rangle+b_2\|0,0\rangle+b_1\|-1,+1\rangle$	$b_1'\|+1,-1\rangle+b_2'\|0,0\rangle+b_1'\|-1,+1\rangle$
5	t^3e^2	^6S	$^6A_{1g}$	$J=\frac{5}{2}$	$\|0,+\frac{5}{2}\rangle$	$\|0,+\frac{5}{2}\rangle$
	t^5e^0		$^2T_{2g}$	$J=\frac{1}{2}$	$a_1\|0,+\frac{1}{2}\rangle+a_2\|+1,-\frac{1}{2}\rangle$	$a_1'\|0,+\frac{1}{2}\rangle+a_2'\|+1,-\frac{1}{2}\rangle$
6	t^4e^2	^5D	$^5T_{2g}$	$J=1$	$a_1\|-1,+2\rangle+a_2\|0,+1\rangle+a_3\|+1,0\rangle$	$b_1\|+1,-1\rangle+b_2\|0,0\rangle+b_1\|-1,+1\rangle$
	t^6e^0		$^1A_{1g}$	$J=0$	$\|0,0\rangle$	$\|0,0\rangle$
7	t^5e^2	^4F	$^4T_{1g}$	$J=\frac{1}{2}$	$a_1\|-1,+\frac{3}{2}\rangle+a_2\|0,+\frac{1}{2}\rangle+a_3\|+1,-\frac{1}{2}\rangle$	$a_1'\|-1,+\frac{3}{2}\rangle+a_2'\|0,+\frac{1}{2}\rangle+a_3'\|+1,-\frac{1}{2}\rangle$
	t^6e^1		^2E_g	$J=\frac{1}{2}$	$^2B_{1g}\|0,+\frac{1}{2}\rangle$	$^2A_{1g}\|0,+\frac{1}{2}\rangle$
8	t^6e^2	^3F	$^3A_{2g}$	$J=1$	$\|0,+1\rangle$	$\|0,+1\rangle$
9	t^6e^3	^2D	^2E_g	$J=\frac{1}{2}$	$^2B_{1g}\|0,+\frac{1}{2}\rangle$	$2A_{1g}\|0,+\frac{1}{2}\rangle$

mean that there is a latent heat associated with the creation of a Fermi surface on passing from an "electron solid" to a "Fermi gas."

In developing a theory of the outer d electrons in transition-metal oxides and sulfides, it has proved convenient to start with a crystal-field model and to inquire how the assumption of localized electrons may break down.[1,5,8,10] In the region of narrow bands, where the localized-electron assumption just breaks down, the bandwidths appear to be smaller than the cubic-field splittings $10Dq\gtrsim1$ eV that are generally encountered for octahedral-site transition-metal ions in oxides and sulfides. Further, to make contact with the one-electron band theory, it is convenient to use a one-electron crystal-field model to which has been added only the intra-atomic exchange correlations responsible for splitting the orbitals of different spin. The interatomic superexchange interactions between localized-electron atomic moments on neighboring atoms, for example, have generally been discussed in terms of such one-electron localized orbitals. However, this procedure has been restricted to cations having no azimuthal orbital momentum. One purpose of this paper is to review the many-electron solutions, including spin-orbit coupling, for the crystal-field limit to see how the orbital geometries induced by multiplet splitting influence both the empirical rules for the signs of superexchange interaction and the spontaneous, cooperative crystallographic distortions that are induced by localized-electron ordering. The latter have already been anticipated[12] by physical arguments based on one-electron models. The former have never received explicit treatment, and this is necessary in order to remove an otherwise remaining ambiguity in the application of semiempirical rules for the signs of the superexchange interactions.[13,14] The second purpose of this paper is to introduce spin-orbit coupling into the one-electron band orbitals. Spin-orbit coupling may be large enough to split degenerate narrow bands into discrete bands, thereby making a semiconductor of a compound that otherwise would have been a metal. It is assumed that, for collective electrons, spin correlations and electron-phonon interactions can be treated separately.

II. CRYSTAL-FIELD THEORY

A. Essential Features of Theory

The Hamiltonian for localized crystal-field orbitals has the form

$$\mathcal{H}=\mathcal{H}_0+V_{\mathrm{el}}+V_{\mathrm{c}}+(V_{LS}+V_{\mathrm{nc}})+V_{\lambda}+\mathcal{H}_{\mathrm{ex}},\qquad(1)$$

where $\mathcal{H}_0$ is the energy of a single electron moving in the spherical potential of the averaged positions of the nuclei and all other electrons. Solutions of $\mathcal{H}_0$ are the familiar hydrogenic wave functions. The angular-dependent parts of the orbitally $(2l+1)$-fold-degenerate d wave functions are

$$\Psi_0\sim r^{-2}\{(z^2-x^2)+(z^2-y^2)\}=3\cos^2\theta-1,\qquad(2)$$

$$\Psi_{\pm1}\sim r^{-2}(yz\pm izx)=\sin\theta\cos\theta\exp(\pm i\varphi),\qquad(3)$$

$$\Psi_{\pm2}\sim r^{-2}\{(x^2-y^2)\pm ixy\}=\sin^2\theta\exp(\pm i2\varphi).\qquad(4)$$

If an electron configuration d^n has $2\leq n\leq8$, then there is an intra-atomic electron-correlation correction V_{el} to the spherical approximation $\mathcal{H}_0$. This is responsible for Hund's highest-multiplicity rules for the free ion. On a one-electron model, it introduces a splitting $\Delta_{\mathrm{ex}}\sim1$ eV of orbitals of different spin α and β. In a crystal the fivefold d-orbital degeneracy is also split by the crystalline fields. The crystal-field energies $V_{\mathrm{c}}+V_{\mathrm{nc}}$ include covalent-mixing energies (excluding the superexchange energy $\mathcal{H}_{\mathrm{ex}}$) as well as electrostatic energies. Cations in an octahedral or a tetrahedral interstice have a dominant cubic-field term V_{c}, which splits by an energy $10Dq$ a one-electron D state into an orbitally threefold-degenerate T_{2g} level and a two-

---

[12] J. B. Goodenough, J. Phys. Soc. Japan **17**, Suppl. B-I, 185 (1962).

[13] J. B. Goodenough, Phys. Rev. **100**, 564 (1955); J. Phys. Chem. Solids **6**, 287 (1958).

[14] J. Kanamori, J. Chem. Phys. Solids **10**, 87 (1959).

TABLE II. Lowest terms and ground-state wave functions for tetrahedral-site cations having n outer d electrons.

n	$e^{\eta}t^{\xi}$	V_{el}	V_{c}	V_{LS}	$V_{LS}+V_{\text{nc}}(\delta<0)+H_{\text{ex}}$	$V_{LS}+V_{\text{nc}}(\delta>0)+H_{\text{ex}}$
1	e^1t^0	^2D	^2E_g	$J=\frac{1}{2}$	$^2B_{1g}\vert 0,+\frac{1}{2}\rangle$	$^2A_{1g}\vert 0,+\frac{1}{2}\rangle$
2	e^2t^0	^3F	$^3A_{2g}$	$J=1$	$\vert 0,+1\rangle$	$\vert 0,+1\rangle$
3	e^2t^1	^4F	$^4T_{1g}$	$J=\frac{5}{2}$	$\vert +1,+\frac{3}{2}\rangle$	$a_1\vert +1,-\frac{1}{2}\rangle+a_2\vert 0,+\frac{1}{2}\rangle+a_2\vert -1,+\frac{3}{2}\rangle$
	e^3t^0		^2E_g	$J=\frac{1}{2}$	$^2B_{1g}\vert 0,+\frac{1}{2}\rangle$	$^2A_{1g}\vert 0,+\frac{1}{2}\rangle$
4	e^2t^2	^5D	$^5T_{2g}$	$J=3$	$\vert +1,+2\rangle$	$b_1\vert +1,-1\rangle+b_2\vert 0,0\rangle+b_3\vert -1,+1\rangle$
	e^4t^0		$^1A_{1g}$	$J=0$	$\vert 0,0\rangle$	$\vert 0,0\rangle$
5	e^2t^3	^6S	$^6A_{1g}$	$J=\frac{5}{2}$	$\vert 0,+\frac{5}{2}\rangle$	$\vert 0,+\frac{5}{2}\rangle$
	e^4t^1		$^2T_{2g}$	$J=\frac{3}{2}$	$\vert +1,+\frac{1}{2}\rangle$	$a_1\vert 0,+\frac{1}{2}\rangle+a_2\vert +1,-\frac{1}{2}\rangle$
6	e^3t^3	^5D	^5E_g	$J=2$	$^5B_{1g}\vert 0,+2\rangle$	$^5A_{1g}\vert 0,+2\rangle$
	e^4t^2		$^3T_{1g}$	$J=2$	$\vert +1,+1\rangle$	$b_1\vert +1,-1\rangle+b_2\vert 0,0\rangle+b_3\vert -1,+1\rangle$
7	e^4t^3	^4F	$^4A_{2g}$	$J=\frac{3}{2}$	$\vert 0,+\frac{3}{2}\rangle$	$\vert 0,+\frac{3}{2}\rangle$
8	e^4t^4	^3F	$^3T_{1g}$	$J=0$	$b_1\vert +1,-1\rangle+b_2\vert 0,0\rangle+b_1\vert -1,+1\rangle$	$b_1'\vert +1,-1\rangle+b_2'\vert 0,0\rangle+b_1'\vert -1,+1\rangle$
9	e^4t^5	^2D	$^2T_{2g}$	$J=\frac{1}{2}$	$a_1\vert 0,+\frac{1}{2}\rangle+a_2\vert +1,-\frac{1}{2}\rangle$	$a_1'\vert 0,+\frac{1}{2}\rangle+a_2'\vert +1,-\frac{1}{2}\rangle$

fold-degenerate E_g level; it splits a two-electron F state into three: the orbitally threefold degenerate T_{1g} and T_{2g} states and a nondegenerate A_{2g} state. The orbitally twofold-degenerate E_g level and the two-electron, nondegenerate A_{2g} level contain the one-electron orbitals Ψ_0 and $(\Psi_{+2}+\Psi_{-2})/\sqrt{2}$, which carry no azimuthal angular momentum. Therefore these are not further split by the spin-orbit-coupling energy

$$V_{LS}=\sum_k \lambda_k \mathbf{l}_k\cdot\mathbf{s}_k=\lambda\mathbf{L}\cdot\mathbf{S}, \tag{5}$$

which vanishes if the one-electron, azimuthal angular momenta l_z vanish or if $L_z=\sum_k l_{zk}$ vanishes. However, the orbitally threefold-degenerate terms T_{1g} and T_{2g} carry azimuthal quantum numbers $M_L=0, \pm1$. Covalent mixing does not change the angular-dependent part of the wave functions, only the radial part. However, the larger radial extension reduces the atomic spin-orbit-coupling parameter λ by a multiplicative fraction k_c, which can be determined from paramagnetic-resonance data. Since atomic P states are transformed by cubic fields into T_{1g} states, there is mixing of the T_{1g} orbitals of a lower F state and a first-excited P state. However, this mixing can also be shown to only contribute to the multiplicative fraction k_c.[15] Spin-orbit coupling splits a level into states of different $|\mathbf{J}|=|\mathbf{L}+\mathbf{S}|$, each with a degeneracy $(2J+1)$.

In general, the perturbation V_{LS} cannot be considered separately from the noncubic crystal-field energy V_{nc} and the many-atom exchange energy $\mathcal{H}_{\text{ex}}$. Trigonal or tetragonal crystalline fields split the threefold-degenerate T_{1g} or T_{2g} levels by an energy δ into twofold-degenerate $M_L=\pm1$ and nondegenerate $M_L=0$ levels. Where this splitting is small, it is reasonable to assume conservation of energy of the T manifold, so that it is customary to define for these symmetries

$$V_{\text{nc}}=\delta(L_z^2-\tfrac{2}{3}), \tag{6}$$

where δ may be either positive or negative, depending upon the sign of the field and whether it splits a one-electron or a two-electron energy level. In a trigonal field the one-electron E_g levels are not split and the T_{2g} level becomes $A_{1g}{}^T+E_g{}^T$, having one-electron orbitals

$$a^T\sim3\cos^2\theta_T{}^{-1}, \tag{7}$$

$$e_{\pm}{}^T\sim c_1\sqrt{2}\sin^2\theta_T\exp(\mp i2\varphi_T)\pm c_2\sin\theta_T\cos\theta_T\exp(\pm i\varphi_T), \tag{8}$$

where θ_T and φ_T refer to the trigonal axis. Mixing of orbitals of E_g and $E_g{}^T$ symmetry makes the coefficients c_1 and c_2 vary with the sign and magnitude of the trigonal field. For cubic symmetry, with trigonal axis $\alpha=60°$, $c_1=c_2$, whereas $c_1<c_2$ for $\alpha>60°$ and $c_1>c_2$ for $\alpha<60°$.

For an integral number of d electrons per atom, the interatomic exchange interactions are given by superexchange theory, and therefore have the form[16,17]

$$\mathcal{H}_{\text{ex}}=-\sum_{ij}(J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j+\cdots)\approx-2J_p\langle S\rangle S_{z'}, \tag{9}$$

where the higher-order terms are neglected in the present discussion. In the molecular-field approximation, the parameter J_p is the sum of all the near-neighbor exchange parameters and can be determined from the temperature dependence of the paramagnetic susceptibility; $\mathbf{z}'$ is along the axis of the average spin $\langle S\rangle$ on the neighboring cations. Below the magnetic-ordering temperature, $\langle S\rangle$ increases with sublattice magnetization. This term contributes to the spectroscopic-splitting factor g, and hence to the net atomic moment (see Sec. VI and Tables I and II). However, in this paper, we shall only be concerned with the signs of the parameters J_{ij}.

Finally, the energy V_λ of Eq. (1) represents the elastic coupling energy between cationic interstices that

---

[15] J. Kanamori, Progr. Theoret. Phys. (Kyoto) **17**, 177 (1957); **17**, 197 (1957).

[16] R. K. Nesbet, Ann. Phys. (N.Y.) **4**, 87 (1958).

[17] P. W. Anderson, Phys. Rev. **115**, 2 (1959).

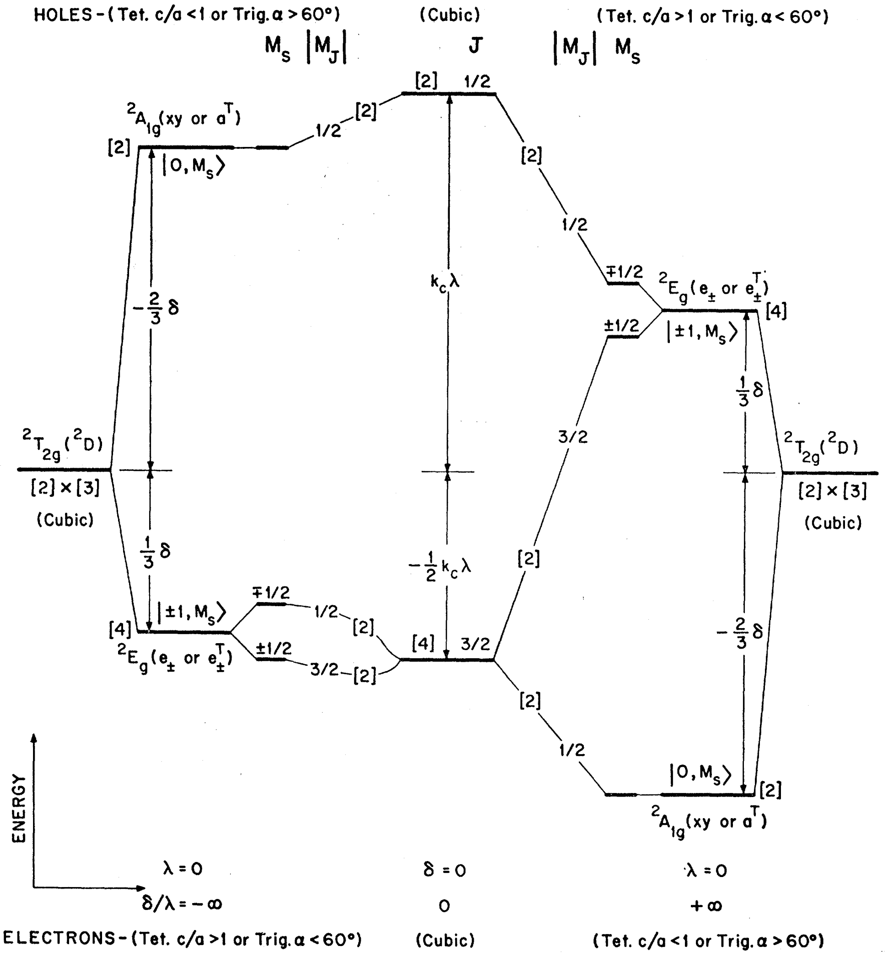

FIG. 1. Schematic $^2T_{2g}$-level splittings by perturbation $V_{\rm nc}+VV_{LS}$ versus δ/λ. Numbers in brackets give degeneracies; $\lambda>0$ for a single α-spin electron and $\lambda<0$ for a single β-spin hole. For tetragonal ($c/a<1$) and trigonal ($\alpha>60°$) distortions, $\delta>0$ for a single α-spin, octahedral-site electron or for a single β-spin, tetrahedral-site hole.

are distorted to lower symmetry by an ordering of electrons among localized-electron orbitals. In a crystal the net energy per transition-metal atom to be gained by a spontaneous distortion to lower symmetry depends critically upon the elastic energy, and hence upon whether these distortions can be cooperative. Cooperative distortions of the cationic interstices reflect a many-atom energy term.

B. Application

Application of these ideas is summarized in Tables I and II for various octahedral-site and tetrahedral-site transition-metal ions having n outer d electrons with configurations $t^\xi e^\eta$, where t and e refer to cubic-field one-electron orbitals having $T_{2g}(xy,\ yz,\ zx)$ or $E_g(x^2-y^2,\ 2z^2-x^2-y^2)$ symmetry. For octahedral-site cations the T_{2g} term is lower than the E_g term, and for tetrahedral-site cations this order is inverted. Therefore, for octahedral-site cations there is an ambiguity in the distribution within $(\xi+\eta)=n$, where $4\leq n\leq 7$, high-spin ions having $\Delta_{\rm ex}>10Dq$ (smaller ξ) and low-spin ions having $\Delta_{\rm ex}<10Dq$ (larger ξ). For tetrahedral-site cations the ambiguity occurs where $3\leq n\leq 6$. Under each individual perturbation, the corresponding lowest term is shown. For the combined perturbation

$$V_{LS}+V_{\rm nc}+\mathcal{H}_{\rm ex}$$

the ground-state wave functions are shown. These contain all components $|M_L,\ M_S\rangle$ of equal $M_J=M_L+M_S$. The coefficient of these components as well

TABLE III. Lowest terms and ground-state wave functions for cations in trigonal bipyramidal interstices.

d^n	$V_{\rm el}$	V_T	V_{LS}	Remarks
d^1	^2D	$^2E_g{}^T$	$J=\frac{3}{2}$	$E(J=\frac{5}{2})-E(J=\frac{3}{2})=2k_c\lambda$; $\Psi_g=\lvert\pm2,\mp\frac{1}{2}\rangle$
d^2	^3F	$^3A_{2g}{}^T$	$J=0$	$E(J=1)-E(J=0)=2k_c\lambda-\Delta_{\rm ex}$; $\Psi_g=\lvert 0,0\rangle$; $\Delta_{\rm ex}<2k_c\lambda$
			$J=1$	$E(J=0)-E(J=1)=\Delta_{\rm ex}-2k_c\lambda$; $\Psi_g=\lvert\pm2,\mp1\rangle$; $\Delta_{\rm ex}>2k_c\lambda$

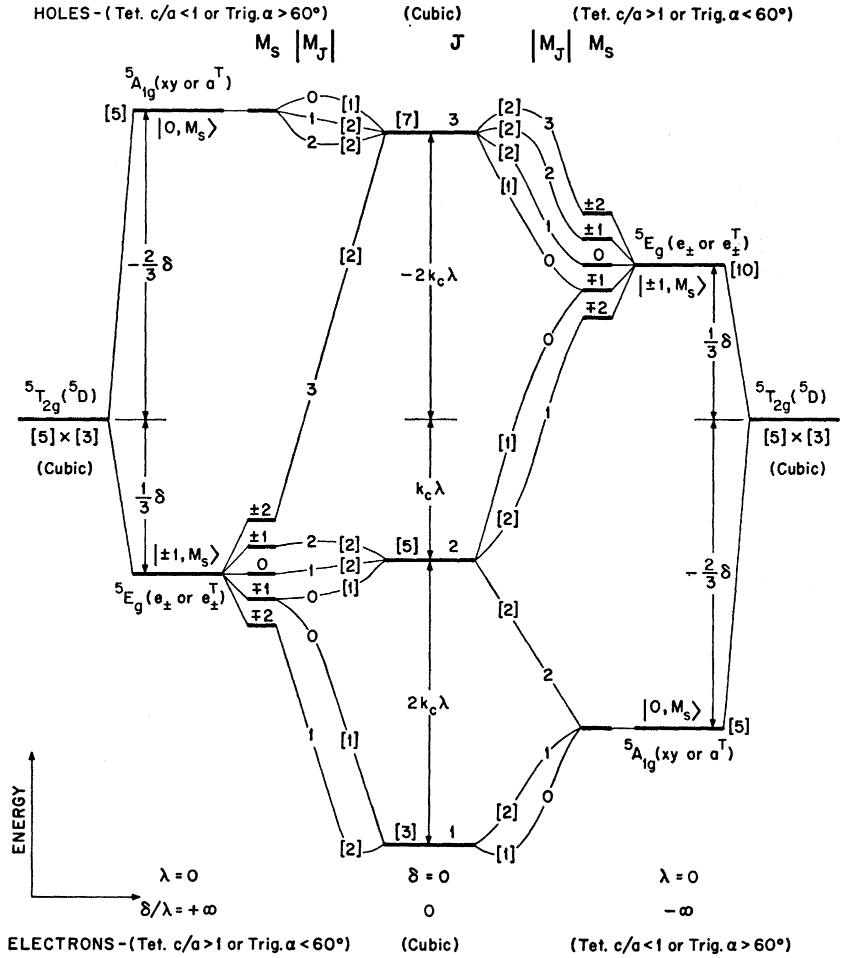

FIG. 2. Schematic $^5T_{2g}$-level splittings by perturbation $V_{nc}+V_{LS}$ versus δ/λ. Numbers in brackets give degeneracies; $\lambda<0$ for a single β-spin electron and $\lambda>0$ for a single α-spin hole. For tetragonal $(c/a<1)$ and trigonal $(\alpha>60°)$ distortions, $\delta>0$ for a single β-spin, octahedral-site electron or for a single α-spin, tetrahedral-site hole.

as the splittings schematically illustrated in Figs. 1–4 are determined from the secular equations for $V_{LS}+V_{nc}+\mathcal{H}_{ex}$. (Zeeman splittings of Kramers doublets by molecular fields are not shown in Figs. 1–4.) The first-order spin-orbit-coupling splittings shown can be obtained from conservation of energy of the T_{1g} or T_{2g} terms and the Landé interval rule

$$E_J-E_{J-1}=(ak_c\lambda)\,J, \tag{10}$$

where the parameter

$$a=-1 \text{ for } T_{2g}, \qquad a=-\tfrac{3}{2} \text{ for } T_{1g} \tag{11}$$

is introduced to account for the isomorphism between atomic P states and T_{2g} or T_{1g} states. (All the matrix elements of the orbital-momentum operator $\mathbf{L}$ within the states of T_{2g} or T_{1g} symmetry are exactly the same as those of $a\mathbf{L}$ within states of P symmetry.[18]) Note that the order of terms for hole wave functions is inverted and that $\lambda>0$ for a less than half-filled shell and $\lambda<0$ for a more than half-filled shell. For high-spin-state ions, each half-shell is treated separately, so that there is never more than a two-electron or a two-hole problem.

In Table III, these ideas are applied similarly for the case of transition-metal cations in trigonal-bipyramidal interstices. In these interstices the trigonal component of the field is very large, so that $c_2\approx 0$ in Eq. (8). This is in contrast to the octahedral-site cations of Table I, where trigonal-field components are so small that $c_1\approx c_2$. Given localized electrons, two solutions of the two-electron problem d^2 are possible, depending upon the relative magnitudes of the spin-orbit-coupling splitting $2k_c\lambda$ and the intra-atomic-exchange splitting Δ_{ex} of orbitals of different spin.

III. SUPEREXCHANGE THEORY

The superexchange perturbation energy $\mathcal{H}_{ex}$ of Eq. (9) describes the coupling between localized-electron spins on neighboring atoms. The localized crystal-field orbitals for octahedral-site cations have the form

$$\Psi_t=N_\pi(f_t+\lambda_\pi\Phi_\pi+\lambda_c\Phi_c), \tag{12}$$

$$\Psi_e=N_\sigma(f_e+\lambda_\sigma\Phi_\sigma), \tag{13}$$

where f_t and f_e are the cationic d orbitals of T_{2g} and E_g

---

[18] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951). A clear exposition is given by J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, London, 1961).

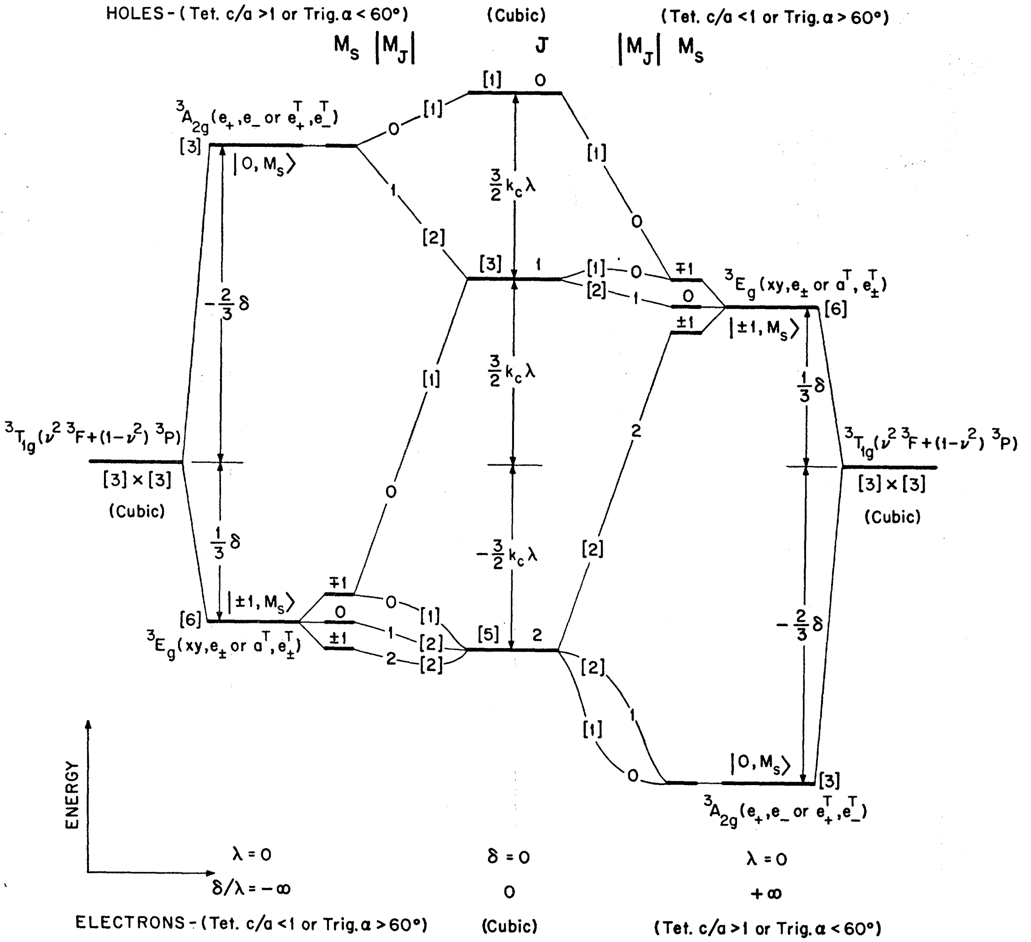

FIG. 3. Schematic $^3T_{1g}$-level splittings by perturbation $V_{\text{nc}}+V_{LS}$ versus δ/λ. Numbers in brackets give degeneracies; $\lambda>0$ for two α-spin electrons and $\lambda<0$ for two β-spin holes. For tetragonal ($c/a>1$) and trigonal ($\alpha<60°$) distortions, $\delta>0$ for two α-spin, octahedral-site electrons or for two tetrahedral-site, β-spin holes.

symmetry, and λ_π, λ_σ, and λ_c are covalent-mixing parameters. Here Φ_π represents the near-neighbor-anion p_π orbitals that π-bond via f_t, Φ_c all near-neighbor cationic s and p orbitals that σ-bond via f_t, and Φ_σ the anionic s and p_σ orbitals that σ-bond via f_e.

The essential physical idea behind superexchange theory is that the occupied, localized orbitals are stabilized by the inclusion of excited states that involve either the transfer of electrons from one cation to another or a simultaneous transfer of two anionic electrons, one each to the two coupled cations. This latter represents an electron-correlation correction to the covalent mixing. Formally,[16,17] this leads to Eq. (9), with exchange parameters

$$J_{ij}=(1/4S^2)\{C-D-E\}_{ij}, \tag{14}$$

where

$$C_{ij}\equiv\int d\tau_1\int d\tau_2\frac{e^2}{r_{12}}\Psi_i^*(r_1)\Psi_j(r_1)\Psi_j^*(r_2)\Psi_i(r_2) \tag{15}$$

is the usual direct exchange, which is positive definite for orthogonal orbitals, and

$$C\ll|D+E|. \tag{16}$$

The terms D and E refer, respectively, to the correlation correction to covalent mixing and to electron transfer between cations. If the correlation correction involves a single anionic orbital,[19] the signs of the two terms each depend in the same manner upon the occupancies of the interacting orbitals, so that it is possible to obtain rules for the signs of the superexchange parameters J_{ij} from simple physical arguments[9]:

(i) Two half-filled orbitals couple antiferromagnetically, giving

$$D+E=2b^2/U_T,\qquad U_T=(2U_D)^{-1}+U_E^{-1}. \tag{17}$$

---

[19] This condition is fulfilled in 180° cation-anion-cation superexchange interactions and σ-bond to π-bond 90° cation-anion-cation superexchange interactions, but not in σ-bond to σ-bond 90° interactons. A double transfer from two different anionic orbitals would transfer two electrons having parallel rather than antiparallel spins because of J^{intra} on the anion.

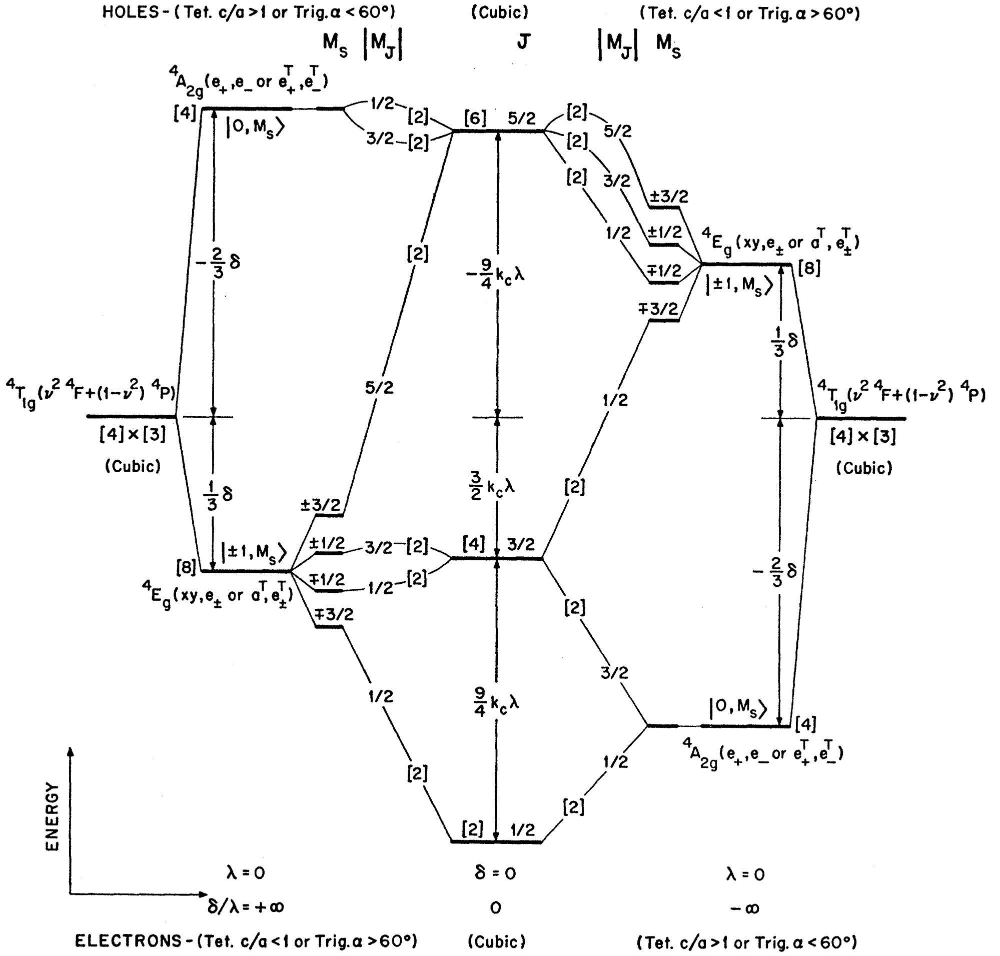

FIG. 4. Schematic $^4T_{1g}$-level splittings by perturbation $V_{\rm nc}+V_{LS}$ versus δ/λ. Numbers in brackets give degeneracies; $\lambda<0$ for two β-spin electrons and $\lambda>0$ for two α-spin holes. For tetragonal $(c/a>1)$ and trigonal $(\alpha<60°)$ distortions, $\delta>0$ for two octahedral-site, β-spin electrons or for two tetrahedral-site, α-spin holes.

(ii) An empty and a half-filled orbital (or a full and a half-filled orbital) couple ferromagnetically, provided that there is a net moment on the cation having an empty (or a full) interacting orbital, and

$$D+E=-2b^2\Delta_{\rm ex}/U^2, \qquad U^{-2}=(\sqrt{2}U_D)^{-2}+U_E^{-2}. \qquad (18)$$

Here $b_{ij}=(\Psi_i, h\Psi_j)$ is a one-electron transfer integral, U_D is the electrostatic energy required to transfer two electrons simultaneously from an anion to two nearest-neighbor cations, and U_E is the energy required to transfer an electron from one cation to another. Because the transfer integrals are $b_{ij}\sim\epsilon_0\Delta_{ij}$, where $\Delta_{ij}=(\Psi_i, \Psi_j)\sim\lambda_\sigma^2$, λ_π^2, or $\lambda_\sigma\lambda_\pi$ for cation-anion-cation superexchange, the numerators of the J_{ij} vary as λ_σ^4, λ_π^4, or $\lambda_\sigma^2\lambda_\pi^2$. Further, the energies U_D and U_E also decrease with increasing b_{ij}, so that J_{ij} increases sensitively with the covalent-mixing parameters λ_σ, λ_π. It follows that for large λ_σ and/or λ_π the interatomic interactions become too large to sustain localized d orbitals, and the assumption on which crystal-field theory rests breaks down. Although the breakdown from localized to collective electrons appears to be sharply defined,[5,11] the intra-atomic-exchange splitting $\Delta_{\rm ex}$ does not collapse to zero at the localized-electron$\rightleftarrows$collective-electron transition, and there is a small domain of collective-electron bandwidths over which there is a spontaneous band magnetism.[20] In the band regime the low-temperature magnetic order is dependent upon the Fermi surface, so that simple extrapolation of the predicted magnetic order from the rules for superexchange among localized orbitals must be modified, and the magnetic order is not necessarily continuous on passing through a localized-electron$\rightleftarrows$collective-electron transition.

The signs of the superexchange interactions, summarized in Eqs. (17) and (18), follow immediately from the Pauli exclusion principle, the presence of a $\Delta_{\rm ex}$, and the assumption that electrons are transferred

---

[20] J. B. Goodenough, J. Appl. Phys. 39, 403 (1968).

without a change of spin. Although these rules lead to unambiguous predictions of the signs of the magnetic couplings, nevertheless, application of these rules can be confusing if splitting by the principal component of the crystalline fields leaves an orbital degeneracy. This is illustrated below, where several types of orbital degeneracies are considered.

IV. TWOFOLD ORBITAL DEGENERACIES WITH $M_L=0$

The principal component of the crystalline field acting on an octahedral-site or a tetrahedral-site cation is cubic. As pointed out above, an E_g term, which occurs in Tables I and II for a single electron or a single hole in a half-shell, is orbitally twofold-degenerate. The degenerate one-electron e orbitals are

$$e_1 \equiv \Psi_0 \quad \text{and} \quad e_2 \equiv (\Psi_{+2}+\Psi_{-2})/\sqrt{2}. \qquad (19)$$

For each of these orbitals $m_l=0$, and there is no spin-orbit coupling. Typical ions having E_g ground terms are octahedral-site Mn^{3+} or Cr^{2+} $^5E_g(t^3e^1)$, Cu^{2+} $^2E_g(t^6e^3)$, and low-spin Ni^{3+} $^2E_g(t^6e^1)$; tetrahedral-site Fe^{2+} $^5E_g(e^3t^3)$; and eightfold-coordinated (double tetrahedral-site) Y^{2+} $^2E_g(e^1t^0)$. For compounds with three outer d electrons like Cr^{3+} or Mn^{4+}, a tetrahedral-site $^2E_g(e^3t^0)$ term has never been found to be competitive with octahedral coordination and a $^4A_{2g}(t^3e^0)$ ground term.

The sign of the superexchange interaction is ambiguous if coupling is via overlapping e orbitals. For example, near-neighbor octahedral-site Mn^{3+} ions in the perovskite $LaMnO_3$ are coupled via 180° cation-anion-cation interactions along the pseudocubic ⟨100⟩ axes. There are two sets of interactions in this case, relatively weaker ($\sim\lambda_\pi^4$) antiferromagnetic interactions via overlapping t orbitals and stronger ($\sim\lambda_\sigma^4$) interactions via overlapping e orbitals. The net sign of the interaction is dominated by the sign of the e-orbital superexchange. However, the e-orbital degeneracy leaves a potential ambiguity about the sign of this coupling.

Jahn and Teller[21] were the first to point out that if a localized-orbital degeneracy is present and there is no other perturbation (such as V_{LS}) to remove this degeneracy, then there is a spontaneous distortion of the interstice to some lower point symmetry that removes this degeneracy. For a large concentration of JT ions, elastic coupling between the distorted sites induces a cooperative distortion of the crystal to a lower space group. The term V_λ in Eq. (1) represents the elastic coupling energy, and indeed $LaMnO_3$ becomes cooperatively distorted at lower temperatures. From the low-temperature symmetry it is possible to identify the occupied and empty orbitals to predict the magnetic order. In this case, the electronic ordering introduces anisotropic Mn^{3+}–O^{2-}–Mn^{3+} interactions to stabilize ferromagnetic (100) pseudotetragonal planes coupled antiparallel to one another.[13,22,23] However, at high temperatures and/or dilute concentrations of JT ions, there is no static distortion of the interstices, and the problem is to decide whether the dominant e-electron transfer is to an empty or a half-filled e orbital.

If cubic symmetry is maintained, an e electron on one cation may transfer to either an empty or a half-filled e orbital on the other cation. Transfer to an empty e orbital requires only the electrostatic energy U_E associated with the creation of "polar" Mn^{4+} and Mn^{2+} ions. It leads to ferromagnetic coupling, but with an energy $\mathcal{H}_{ex}$ reduced by the multiplicative fraction Δ_{ex}/U_E according to Eq. (18). Transfer to a half-filled e orbital requires an additional energy Δ_{ex}. This gives *antiferromagnetic* coupling, but with an energy $\mathcal{H}_{ex}$ reduced by the multiplicative fraction $U_E/(U_E+\Delta_{ex})$. Since $\Delta_{ex}/U_E<0.62$ is anticipated in the localized-electron regime, where superexchange theory applies, the antiferromagnetic interactions should dominate. Nevertheless, experiment[24] shows that high-temperature $LaMnO_3$, where the symmetry is essentially cubic, has *ferromagnetic* Mn^{3+}–O^{2-}–Mn^{3+} interactions.

It may be argued that, because $\lambda_\sigma<\lambda_c$ approaches the critical value λ_c for the localized-electron$\rightleftarrows$collective-electron transition,[8] a $\Delta_{ex}/U_E>0.62$ is possible. Nevertheless, this discussion emphasizes the type of ambiguity that can occur in a practical application of the superexchange rules if the complete perturbation $(V_{LS}+V_{nc}+V_\lambda+\mathcal{H}_{ex})$ is not taken into account.

Several workers[23,25,26] have noted that the normal vibrational modes of an octahedral-site complex that remove the electronic degeneracy are themselves twofold-degenerate with symmetry E_g. A similar observation has been made for tetrahedral complexes.[27] This fact allows for a dynamic JT splitting of the e orbitals, where the strong electron-lattice coupling makes the electronic ground state a linear combination of e_1 and e_2 that varies dynamically with the vibrational configuration of the complex. In a crystal these complexes are coupled, and the elastic coupling energy is V_λ. Consequently, the vibrational modes of E_g symmetry about each JT ion are elastically coupled, so that only cooperative vibrational frequencies are enhanced by the electron-lattice coupling.

A static cooperative distortion at lower temperatures simply represents one frozen mode from those cooperative vibrational frequencies that are enhanced by the dynamic JT stabilization. Because the enhanced vibrational frequencies are cooperative, they correlate the occupancies of the e orbital at two cations on either

---

[21] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937).

[22] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

[23] J. Kanamori, J. Appl. Phys. Suppl. **31**, 14S (1960).

[24] G. H. Jonker, Physica **22**, 707 (1956).

[25] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

[26] H. C. Lonquet-Higgins, O. Öpik, M. H. L. Pryce, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958).

[27] J. B. Goodenough, J. Phys. Chem. Solids **25**, 151 (1964).

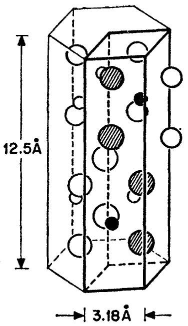

FIG. 5. Crystal structure of WS_2.

side of an intermediary anion. For example, two octahedral-site Mn^{3+} ions sharing a common corner, as in $LaMnO_3$, represent two magnetically coupled ions that, for most of the enhanced-vibration period, have a half-filled orbital coupled to an empty orbital. This introduces a weighting factor that makes the coupling unambiguously *ferromagnetic* via Eq. (18).[28]

V. TWOFOLD ORBITAL DEGENERACIES WITH $M_L \neq 0$

Several transition-metal compounds, like NbS_2 and WS_2, crystallize in the layer structure of Fig. 5, where the cations are in trigonal-bipyramidal anionic interstices and form close-packed layers that are separated by two close-packed anion layers. In this case, the principal crystal-field component is trigonal, and Table III is applicable. The niobium ion of NbS_2 has one outer $4d$ electron in the ground state $|\pm 2, \mp\frac{1}{2}\rangle$, which is split by V_{LS} from the state $|\pm 2, \pm\frac{1}{2}\rangle$ by $2k_c\lambda$:

$$\langle 2, \pm\tfrac{1}{2} \,|\, k_c\lambda \mathbf{L}\cdot\mathbf{S} \,|\, 2, \pm\tfrac{1}{2}\rangle = k_c\lambda\langle 2, \pm\tfrac{1}{2} \,|\, L_zS_z \,|\, 2, \pm\tfrac{1}{2}\rangle = \pm k_c\lambda. \qquad (20)$$

(The Landé interval rule is not applicable here, where there is no isomorphism with a free-ion state.) Since the ground-state orbital is nondegenerate and overlaps similar half-filled orbitals on each near-neighbor cation in its basal plane, any magnetic coupling is antiferromagnetic. (Half-filled bands as well as overlapping half-filled orbitals give rise to antiferromagnetic coupling of any spontaneous atomic moments.[20]) Actually, these interactions are so strong that the ground-state $4d$ orbitals are not localized in NbS_2, but form a half-filled narrow band of collective-electron orbitals. In fact, NbS_2 is metallic and Pauli paramagnetic,[29] the bandwidth being too large, apparently, to support even spontaneous band antiferromagnetism.

There are two outer $5d$ electrons per tungsten ion in WS_2, and the $^3A_{2g}{}^T$ level is split by spin-orbit coupling. Localized orbitals would have an intra-atomic-exchange splitting $\Delta_{\mathrm{ex}} > 2k_c\lambda$, and the triplet ground state ($J=1$) would contain the two one-electron orbitals $|\pm 2, \mp\frac{1}{2}\rangle$ and $|\mp 0, \mp\frac{1}{2}\rangle$. Again the orbitals would be half-filled, and any magnetic coupling would be antiferromagnetic. However, with strong W-W interactions the $5d$ electrons are not localized, as assumed by crystal-field theory, and collective-electron orbitals must be used. Since the electron-electron interactions responsible for spontaneous magnetism are weaker for collective electrons, the relationship $\Delta_{\mathrm{ex}} < 2k_c\lambda$ may be anticipated. In this event, the ground state is a singlet ($J=0$) and contains linear combinations of the two one-electron orbitals per tungsten $|+2, -\frac{1}{2}\rangle$ and $|-2, +\frac{1}{2}\rangle$. The narrow band of collective-electron energies is separated from the next higher band by the energy

$$E_g = 2k_c\lambda - \Delta_b, \qquad (21)$$

where Δ_b is the width of one of the narrow $5d$ energy bands. Thus WS_2 is expected to be a semiconductor, provided that $\Delta_b < 2k_c\lambda$. This has indeed been found to be the case.[29]

VI. THREEFOLD ORBITAL DEGENERACIES

A. Localized Electrons

Octahedral-site or tetrahedral-site cations having cubic-field ground-state terms T_{2g} or T_{1g} are orbitally threefold-degenerate, having azimuthal quantum numbers $M_L=0, \pm 1$. Here $V_{LS}\neq 0$, and it is necessary to consider the complete perturbation $V_{LS}+V_{\mathrm{nc}}+V_\lambda+\mathcal{H}_{\mathrm{ex}}$, where V_{nc} includes stabilization due to spontaneous distortions of the interstices to lower symmetry. Tables I and II show the general ground-state wave functions for a magnetically ordered phase having collinear atomic spins. The coefficients of the Kramers doublets a_1, a_2, a_3 and of the singlets b_1, b_2 all depend upon the relative magnitudes of the four perturbation terms.

1. $^2T_{2g}$ Configurations

With a single outer electron or hole, there is no intra-atomic-exchange splitting of states of different spin ($\Delta_{\mathrm{ex}}=0$). The secular equation for the combined perturbation $V_{LS}+V_{\mathrm{nc}}$ of Eqs. (5) and (6) separates into secular equations for different M_J, as shown in Fig. 1. The resulting energy changes are

$$E_{3/2} = \tfrac{1}{3}\delta - \tfrac{1}{2}k_c\lambda, \qquad (22)$$

$$E_{1/2}{}^{\pm} = -\tfrac{1}{6}\delta + \tfrac{1}{4}k_c\lambda \pm \tfrac{1}{2}\{\delta^2 + k_c\lambda\delta + (9/4)(k_c\lambda)^2\}^{1/2}, \qquad (23)$$

where the subscripts refer to M_J. For the case $\delta=0$ (or $V_{\mathrm{nc}}=0$) and $\lambda>0$, there is an orbital degeneracy ($E_{3/2}=E_{1/2}{}^{-}$). This degeneracy is removed by a JT stabilization, static or dynamic, so that in a crystal the complete problem must include not only V_{LS}, but also $V_{\mathrm{nc}}+V_\lambda$. In practice, however, $^2T_{2g,3/2}$ configurations having $\lambda>0$, as in octahedral-site Ti^{3+}, V^{4+}, or low-spin Co^{4+}, are metallic. Therefore this configuration is considered below as a collective-electron example.

---

[28] J. B. Goodenough, A. Wold, R. J. Arnott, and N. Menyuk, Phys. Rev. **124**, 373 (1961).

[29] A. Wold (private communication).

For the localized-electron case having $\delta=0$ and $\lambda<0$, which occurs in tetrahedral-site Cu^{2+} ions in oxides and halides, the ground-state doublet has the energy $E_{1/2}{}^{+}=-k_c|\lambda|$ and the coefficients in Table II are

$$a_1=a_1'=\sqrt{\tfrac{1}{3}} \quad \text{and} \quad a_2=a_2'=-\sqrt{\tfrac{2}{3}}. \tag{24}$$

Now, a distortion of the interstices to trigonal or tetragonal symmetry initially has $|\delta/\lambda|\ll 1$, so that to second order in $|\delta/\lambda|$

$$E_{1/2}{}^{+}=-|k_c\lambda|-\tfrac{4}{27}(\delta^2/|k_c\lambda|)-\tfrac{8}{243}[\delta^3/(k_c\lambda)^2]. \tag{25}$$

Since δ varies linearly with the atomic displacements, the elastic restoring forces are also proportional to δ^2; and addition of the one-ion elastic terms $q_2\delta^2-q_3\delta^3$ gives

$$E_{1/2}{}^{+}=-|k_c\lambda|-[(4|k_c\lambda|/27)-q_2]\delta^2 \\ -\{[8(k_c\lambda)^2/243]+q^3\}\delta^3, \tag{25'}$$

where $q_3>0$ because covalency, which stabilizes a $\delta>0$ can be assumed to dominate the anharmonic contribution to the elastic restoring forces. In a crystal, the magnitudes of q_2 and q_3 vary sensitively with the cooperative character of the distortion, and hence are related to the elastic constants via the elastic coupling energy V_λ. To determine whether a distortion from cubic symmetry ($\delta\neq 0$) stabilizes the ground state, it is first necessary to consider the additional perturbation $\mathcal{H}_{ex}$.

There are two temperature domains to be distinguished: $T>T_c$ and $T<T_c$, where T_c is the temperature below which the cationic spins are ordered collinearly. In the paramagnetic domain $T>T_c$, the molecular fields vanish ($\langle S\rangle=0$) and, from Eq. (9), $\mathcal{H}_{ex}=0$. Therefore in this domain Eq. (25′) is unaltered and a spontaneous distortion to $\delta>0$ may occur below a $T_t>T_c$ only if the condition $27|k_c\lambda|q_2<4$ is fulfilled. In the magnetically ordered state, on the other hand, there is an internal molecular field $\mathbf{H}_i$ at each atom, which produces a Zeeman splitting of the orbitals of different spin. The magnitude of this splitting depends upon the spectroscopic splitting factor **g**, which is defined by the relation

$$\mu_B\mathbf{H}_i\cdot\mathbf{g}\cdot\mathbf{S}'=\langle\Psi_g|\mathcal{H}_z|\Psi_g\rangle, \tag{26}$$

where the Zeeman energy is

$$\mathcal{H}_z=\mu_B\mathbf{H}_i\cdot(ak_c\mathbf{L}+2\mathbf{S}) \tag{27}$$

and $\mathbf{S}'$ is the effective spin of the ground state. For a T_{2g} state, $a=-1$ and

$$g_{||}=|2\langle\Psi_g|-L_z+2S_z|\Psi_g\rangle|=|2a_1^2-4a_2^2|, \tag{28}$$

$$g_\perp=\langle\Psi_g'|-L^-+2S^-|\Psi_g\rangle=2a_1^2-2\sqrt{2}a_1a_2, \tag{29}$$

where Ψ_g' is the same as Ψ_g of Table II except for an interchange of signs of each M_L, M_S. From Eq. (24) it follows that $g_{||}=g_\perp=2$ for $\delta=0$. Now, if $\delta\neq 0$, then from the secular equation for $V_{LS}+V_{nc}$

$$a_1^2=\tfrac{1}{3}+\tfrac{8}{27}(\delta/|k_c\lambda|)$$

and

$$a_2^2=\tfrac{2}{3}-\tfrac{8}{27}(\delta/|k_c\lambda|), \tag{30}$$

$$g_{||}=2-\tfrac{16}{9}(\delta/|k_c\lambda|)$$

and

$$g_\perp=2+\tfrac{8}{9}(\delta/|k_c\lambda|). \tag{31}$$

Therefore the Zeeman splittings in the molecular fields is maximized by making $\delta<0$ and having the spins parallel to the unique axis defined by δ. Further, this energy is linear in δ, so that a spontaneous distortion should occur for $T<T_c$.

In summary, a spontaneous distortion to tetragonal or trigonal symmetry can be anticipated below some transition temperature T_t, and the distortion corresponds to $\delta<0$ if $T_t\approx T_c$, but to $\delta>0$ if $T_t>T_c$.

This general argument has been made more crudely elsewhere.[12] It is consistent with the fact that the spinel $Cu^{2+}[Cr_2]O_4$ has a distortion to tetragonal ($c/a<1$) symmetry, corresponding to $\delta>0$, below a $T_t>T_c$. Although the magnetic order below T_c has a Yafet-Kittel[30] triangular-spin configuration with collinear Cu^{2+} spins,[31,32] nevertheless there is no reversal in the sign of the distortion below T_c. This is consistent with the contention that the relative magnitudes of T_t and T_c determine the sign of the distortions. In this case, for example, $\mathcal{H}_{ex}$ only stabilizes the observed triangular spin configuration in the presence of tetragonal ($c/a<1$) symmetry,[33] so that the cooperative superexchange only further stabilizes a $\delta>0$ below T_c. The elastic restoring forces q_2 are, presumably, especially small in the chromium spinels because the distortions $\delta>0$ permit the intermediary Cr^{3+} interstices to become more nearly octahedral,[31] thereby enhancing the crystal-field stabilization of the Cr^{3+} d electrons. Also, λ is relatively small, so that the required conditions for a $T_t>T_c$ are met.

In general, the interstices are not cubic below a magnetic-ordering temperature, particularly if the ordered spins are collinear. Either a spontaneous distortion has taken place below a $T_t>T_c$ or a spontaneous distortion of opposite sign occurs below T_c (or T_N). Given the unique axis, the ground-state wave functions active in superexchange coupling are defined by Table I. Even if competitive superexchange interactions stabilize a complex-spin configuration, local magnetostrictive distortions can be anticipated. In this event, prediction of the ground-state spin configuration must minimize $V_\lambda+\mathcal{H}_{ex}$, and the problem becomes very complex.

---

[30] Y. Yafet and C. Kittel, Phys. Rev. **87**, 290 (1952).

[31] E. Prince, Acta. Cryst. **10**, 554 (1957).

[32] R. Nathans, S. J. Pickart, and A. Miller, Bull. Am. Phys. Soc. **6**, 54 (1961).

[33] T. A. Kaplan, K. Dwight, D. M. Lyons, and N. Menyuk, J. Appl. Phys. Suppl. **32**, 13S (1961).

2. ${}^5T_{2g}$ *Configurations*

In the ${}^5T_{2g}$ configurations of octahedral-site Fe^{2+} or tetrahedral-site Mn^{3+} or Cr^{2+}, a $\Delta_{\mathrm{ex}}\neq 0$ splits localized-electron states of different spin. As shown in Fig. 2, the secular equation for $V_{LS}+V_{\mathrm{nc}}$ breaks up into secular equations for different M_J. Octahedral-site Fe^{2+} has $\lambda<0$, so that for $\delta>0$ there is a singlet ground term with energy $E_0{}^+$, for $\delta<0$ there is a doublet ground term with energy E_1, and for $\delta=0$ there is the degeneracy $E_0{}^+=E_1$. To first order in δ/λ the coefficients in Table I are

$$\begin{aligned} a_1&=\{\tfrac{3}{5}+0.23\delta/3k_c\lambda\}^{1/2},\\ a_2&=-\{\tfrac{3}{10}-0.20\delta/3k_c\lambda\}^{1/2},\\ a_3&=\{\tfrac{1}{10}-0.03\delta/3k_c\lambda\}^{1/2},\\ a_1{}'&=\{\tfrac{3}{10}+0.144\delta/3k_c\lambda\}^{1/2},\\ a_2{}'&=-\{\tfrac{2}{5}-0.288\delta/3k_c\lambda\}^{1/2}, \end{aligned} \tag{32}$$

and the spectroscopic splitting factor for $S'=1$ is

$$\begin{aligned} g_{\|}&=(3+\tfrac{1}{2}k_c)+0.52(1+\tfrac{1}{2}k_c)\delta/3k_c\lambda,\\ g_{\perp}&=(3+\tfrac{1}{2}k_c)-0.26(1+\tfrac{1}{2}k_c)\delta/3k_c\lambda. \end{aligned} \tag{33}$$

For $\delta<0$ (or $\delta/\lambda>0$) the coefficient a_1 increases with δ/λ at the expense of the other two, and $g_\perp\rightarrow 0$ while $g_{\|}$ increases. Conversely, a $\delta>0$ (or $\delta/\lambda<0$) stabilizes the singlet and increases $g_\perp$ at the expense of $g_{\|}$. The situation is therefore analogous to that described for the ${}^2T_{2g}$ configurations. Where $T_t\approx T_c$ (or T_N), a spontaneous distortion corresponding to $\delta<0$ can be anticipated. Dipole-dipole anisotropy is generally smaller than that given by Eq. (33). Further, a crystallographic symmetry change accompanying the magnetic ordering makes the transition first-order.

This situation is illustrated by the compound FeO, which becomes distorted to trigonal ($\alpha<60°$) symmetry corresponding to $\delta<0$, below the Néel temperature. This introduces a highly anisotropic g factor ($g_\perp\rightarrow 0$ and $g_{\|}\rightarrow 9$ for $\delta/\lambda\gg 1$ and an effective spin $S'=\frac{1}{2}$ of the doublet state) that aligns the atomic moment parallel to the trigonal axis, contrary to the dipole-dipole forces. Further, the strongest superexchange interactions are antiferromagnetic 180° cation-anion-cation interactions between half-filled e orbitals. Given these interactions and collinear spins along the trigonal axis, there are two possible spin configurations: (i) ferromagnetic (111) cationic planes coupled antiparallel to one another and (ii) two-thirds ferromagnetic, one-third antiferromagnetic near neighbors within (111) cationic planes and vice versa in neighboring (111) cationic planes. Although dipole-dipole interactions are minimized by the second alternative, the first alternative is found experimentally,[34] which suggests that the nearest-neighbor superexchange interactions are different within and between (111) planes. The question is whether this difference can be predicted from superexchange theory and a knowledge of the overlapping orbitals from Table I.

The nearest-neighbor superexchange interactions have two components: cation-cation and 90° cation-anion-cation interactions. With $\delta<0$, the coefficient $a_1\rightarrow 1$ for large $|\delta|$ and, in this limit, the occupied β-spin orbital is an $e_-{}^T$ orbital of Eq. (8). Therefore, within any (111) plane the $e_\pm{}^T$ orbitals are three-fourths filled. Consequently, any cation-cation interaction is *ferromagnetic*. There is also a predominantly *ferromagnetic* 90° cation-anion-cation superexchange within the plane via transfer of a β-spin $e_-{}^T$ electron to a half-filled e orbital. Between (111) planes, on the other hand, there is some overlap of half-filled a^T orbitals, which gives an *antiferromagnetic* interaction, and the 90° cation-anion-cation interactions contain less predominance of the ferromagnetic versus antiferromagnetic component. Thus the electron ordering manifest by a $\delta<0$ introduces an exchange striction that increases $|\delta|$ and stabilizes ferromagnetic (111) planes coupled antiferromagnetically to one another, as observed experimentally. Since exchange energies are much larger than dipole-dipole energies, the magnetic order is completely rationalized. The dipole-dipole forces introduce an additional magnetostrictive increase of $|\delta|$. Further, the structure is rationalized since a similar optimization of the superexchange energies cannot be achieved by a tetragonal ($c/a>1$) distortion. In addition, because of magnetostriction the elastic restoring forces are weaker for a trigonal ($\alpha<60°$) versus a tetragonal ($c/a>1$) distortion, whereas they are stronger for a trigonal ($\alpha>60°$) versus a tetragonal ($c/a<1$) distortion.

In the high-temperature cubic ($\delta=0$) phase of FeO, where $E_0{}^+=E_1$, only ferromagnetic nearest-neighbor interactions are anticipated.

3. ${}^3T_{1g}$ *Configurations*

The two-electron or two-hole ${}^3T_{1g}$ terms are split by spin-orbit coupling and noncubic crystalline fields as shown in Fig. 3, where the energies for different M_J values shown schematically in the figure have the analytic solutions

$$E_2=\tfrac{1}{3}\delta-\tfrac{1}{2}(3k_c\lambda), \tag{34}$$

$$E_1{}^{\pm}=-\tfrac{1}{6}\delta\pm\tfrac{1}{2}\{\delta^2+(3k_c\lambda)^2\}^{1/2}, \tag{35}$$

$$E_0{}^{\pm}=-\tfrac{1}{6}\delta+\tfrac{1}{4}(3k_c\lambda)\pm\tfrac{1}{2}\{\delta^2+(3k_c\lambda)\delta+(9/4)(3k_c\lambda)^2\}^{1/2}, \tag{36}$$

$$E_0=-\tfrac{1}{3}\delta+\tfrac{1}{2}(3k_c\lambda). \tag{37}$$

Thus for $\delta=0$ the ground state is orbitally either three-

---

[34] C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. **83**, 333 (1951).

fold-degenerate, as in octahedral-site V^{3+} $^3T_{1g,2}$, having $\lambda > 0$ and $E_2 = E_1^- = E_0^-$, or nondegenerate, as in tetrahedral-site Ni^{2+} $^3T_{1g,0}$ having $\lambda < 0$ and the ground term E_0^+.

In the case of octahedral-site V^{3+} ions, E_2 is the ground-state energy if $\delta < 0$ and E_0^- if $\delta > 0$. Expansion of E_0^- to second order in δ/λ gives

$$E_0^- = -\tfrac{1}{2}(3k_c\lambda) - \tfrac{4}{27}[\delta^2/(3k_c\lambda)] - \tfrac{8}{243}[\delta^3/(3k_c\lambda)^2]. \tag{38}$$

Therefore even for $T > T_t$ a distortion to $\delta < 0$ that stabilizes E_2 is energetically preferred to a distortion to $\delta > 0$ that stabilizes E_0^-. However, only below $T_t \approx T_c$ is there a long-range order of the spins that allows for a JT stabilization ($\delta < 0$) that enhances the spin-orbit coupling stabilization. It may therefore be unambiguously concluded that, given localized $3d$ electrons, octahedral-site V^{3+} ions should induce a spontaneous distortion of their interstices from cubic to tetragonal or trigonal symmetry below $T_t \approx T_c$, and the sign of the distortion must correspond to $\delta < 0$. For $\delta < 0$, elastic restoring forces are weaker and δ can be larger for tetragonal ($c/a < 1$) versus trigonal ($\alpha > 60°$) symmetry. This prediction is consistent with the observation of a spontaneous distortion to tetragonal ($c/a < 1$) symmetry in the perovskite $LaVO_3$ below its Néel temperature.[35] Finally, note that the two-electron orbital $|+1, +1\rangle$ of a V^{3+} ion below T_N contains the one-electron orbitals $\nu^2 t^2 + (1-\nu^2) t^1 e^1$, where ν^2 is a large fraction and the second term represents mixing from the ^3P state. In the strong-field limit $\nu^2 \rightarrow 1$, the two occupied t orbitals are $(\Psi_{+2} - \Psi_{-2})/i\sqrt{2}$ and Ψ_{+1} of Eqs. (3) and (4), so that in the perovskite structure, half-filled orbitals interact via π bonding with the intermediary anions along each of the $\langle 100 \rangle$ directions, and a simple type-G antiferromagnetic order can be predicted for $T < T_N$ in $LaVO_3$. [*Note added in proof.* At room temperature $LaVO_3$ is not quite cubic, but has a small distortion to O′-orthorhombic symmetry having $c/\sqrt{2} < a < b$. The fact that $c/\sqrt{2} < a$ occurs indicates the presence of a small JT stabilization above T_N. Below T_N this distortion increases sharply.]

The case of tetrahedral-site Ni^{2+} $^3T_{1g,0}$ is essentially identical to that of tetrahedral-site Cu^{2+} $^2T_{2g,1/2}$. It is only necessary to replace $k_c\lambda$ with $3k_c\lambda$ in Eq. (25) to have the small-δ/λ expansion for the ground term E_0^+, and it follows at once from the previous argument that a spontaneous distortion to tetragonal or trigonal symmetry can be anticipated below some T_t, the distortion corresponding to $\delta < 0$ if $T_t \approx T_c$ and to $\delta > 0$ if $T_t > T_c$. An interesting additional point is that long-range ordering of the crystallographic distortions is mediated through the elastic coupling energy V_λ, whereas long-range ordering of the spins is mediated through the exchange energy $\mathcal{H}_{ex}$. Thus the cooperative distortion temperature, which is T_t, can be varied oppositely to T_c by suitable chemical substitution. Since the ground state is determined by which transition temperature is the larger, it is possible to alter the sign of the distortion ($\delta > 0$ to $\delta < 0$) by changing the chemistry. Such a sign reversal as a function of composition has been observed[36] in the spinel system $Ni^{2+}_{2-t}Fe^{3+}_t[Ni^{2+}_tCr^{3+}_{2-t}]O_4$ in the range $0 < t < 1$. A subsequent study,[37] prompted by an earlier[12] assessment of the problem, used more homogeneous samples and found an even more dramatic reversal in the sign of the distortion as $T_t > T_c$ changed to $T_t < T_c$ as a function of t. (The fact that $T_t < T_c$ in this system is due to noncollinear A-site spins in the range $T_t < T < T_c$.)

4. $^4T_{1g}$ *Configurations*

Since cations with d^3 configuration, such as Cr^{3+} and Mn^{4+}, have an extreme preference for octahedral versus tetrahedral coordination, the $^4T_{1g,5/2}$ configurations do not occur, at least in concentrations large enough to be of interest to cooperative magnetism. However, the $^4T_{1g,1/2}$ configuration of octahedral-site Co^{2+} is common. There is a doublet ground state, as shown in Fig. 4, and the argument proceeds as in the case of the doublet ground state for $^2T_{2g,1/2}$. Again it may be concluded that there is a spontaneous distortion of the octahedral interstice from cubic to tetragonal or trigonal symmetry below a transition temperature T_t, and that for $T_t \approx T_c$ the sign of the distortion corresponds to $\delta < 0$ and for $T_t > T_c$ it corresponds to $\delta > 0$. Further, elastic restoring forces favor tetragonal ($c/a < 1$) versus trigonal ($\alpha > 60°$) symmetry below T_c.

This conclusion appears to be illustrated by the compound CoO, which is reported[38] to become tetragonal ($c/a < 1$) below its Néel temperature. Neutron-diffraction data[34] indicate ferromagnetic (111) cobalt planes coupled antiparallel, but a spin axis tilted somewhat from the [001] axis. Dipole-dipole forces set up effective internal fields in the (111) planes that must be added to those parallel to the [001] axis as a result of anisotropic g factors, and the resultant anisotropy field is tipped from the [001].

B. Collective Electrons

From studies[7–10] of oxides with rutile, perovskite, and perovskite-related structures, it appears that Ti^{3+} and most quadrivalent transition-metal ions in oxides do not have localized d electrons. Since collective-electron models are all one-electron models, the band

---

[35] D. B. Rogers, A. Ferretti, R. J. Arnott, and J. B. Goodenough, J. Appl. Phys. Suppl. **37**, 1431 (1966).

[36] T. R. McGuire and S. W. Greenwold, *Solid State Physics in Electronics and Telecommunications*, edited by M. Désirant and J. L. Michiels (Academic Press Inc., New York, 1960), Vol. 3, Pt. 1, p. 50.

[37] R. J. Arnott, A. Wold, and D. B. Rogers, J. Phys. Chem. Solids **25**, 161 (1964).

[38] H. P. Rooksby and N. C. Tombs, Nature **167**, 364 (1951).

orbitals of octahedral-site cations are linear combinations of the overlapping localized orbitals of a ${}^2T_{2g,3/2}$ configuration. The one-electron orbitals have energies defined by Eqs. (22) and (23), with $\lambda > 0$. In a cubic field, $\delta = 0$ and the energies are

$$E_{3/2} = E_{1/2}^- = E_{1/2}^+ - \tfrac{3}{2}k_c\lambda. \tag{39}$$

In a collective-electron model these levels are broadened into a narrow band of allowed energies, and the energy gap between the more stable d band, which contains $2J+1=4$ electronic states per cation, and the less stable d band, which has 2 electronic states per atom, is

$$E_g = \tfrac{3}{2}k_c\lambda - \Delta_b, \tag{40}$$

where Δ_b is a mean bandwidth. In the tight-binding approximation, this bandwidth is proportional to the transfer integral b_{ij} appearing in Eqs. (17) and (18) for the superexchange parameters J_{ij}. The sharp localized-electron$\rightleftarrows$collective-electron transition occurs at a critical value b_c of this transfer integral.[20]

In a cubic perovskite, orbitals of t_{2g} symmetry on neighboring cations interact via covalent mixing with the p_π orbitals of an intermediary anion. If there is no spontaneous band magnetism, then perovskites having cations with d^1, d^2, d^3, or d^5 outer-electron configurations would be metallic and Pauli paramagnetic, whereas those with d^4 cations would be semiconducting or semimetallic. Indeed, $LaTiO_3(d^1)$, $CaVO_3(d^1)$, $SrCrO_3(d^2)$, and $SrMoO_3(d^2)$ are metallic and Pauli paramagnetic. However, $PbCrO_3(d^2)$, $CaCrO_3(d^2)$, $CaMnO_3(d^3)$, and $LaSrCo_2O_6(d^{5.5})$ are magnetic. In these cases, supplementary criteria are needed to distinguish between localized-electron magnetism and collective-electron magnetism.[1,20]

1. Configuration d^2

With configuration d^2, the $J=\frac{3}{2}$ band of $PbCrO_3$ is half-filled, and for a narrow, half-filled band stabilization can be achieved by the creation of a Brillouin zone that circumscribes the Fermi surface.[1,10] This may be accomplished either by a distortion of the structure that increases the size of the unit cell or by electron correlations that tend to maintain two electrons at each cation, or by both simultaneously. The first mechanism, though dominant in the case of cation-sublattice d bands,[1] does not occur in a perovskite, where the interactions are transmitted via an anion intermediary and any stabilization is achieved by electron correlations with little or no associated distortions of the structure. The electron correlations are induced by the Coulomb energy $U_E \neq 0$ required to create "polar" states. It is the Coulomb energy appearing in Eqs. (17) and (18). For a small ratio b/U_E, where $b < b_c$, the d electrons are localized and the energies of cationic states of different formal valence are separated by U_E. Because the $J=\frac{3}{2}$ orbitals contain the $(\Psi_{+2}-\Psi_{-2})/i\sqrt{2}$ and $\Psi_{\pm 1}$ orbitals of Eqs. (3) and (4), creation of a "polar" state requires either U_E or $U_E' + \frac{3}{2}k_c\lambda$, where $U_E' \ll U_E$. In the interval $b_c < b < b_m$, where the conditions for localized electrons change to those for collective electrons exhibiting Pauli paramagnetism, U_E decreases rapidly with increasing transfer energy b, because of electron screening, and the energies for different formal cationic valence are broadened into narrow collective-electron bands of width Δ_b. However, as long as $b < b_m$, there is a discrete energy gap $E_g = U_E - \Delta_b$ (or $\frac{3}{2}k_c\lambda - \Delta_b$) at the Fermi surface, and the crystal is stabilized at a $T < T_N$ by a type-G antiferromagnetic order (all near neighbors antiparallel) that doubles the unit cell along all principal crystallographic directions. This magnetic order introduces a Brillouin zone that circumscribes the Fermi surface and therefore increases E_g. Since thermal excitations across E_g destroy this extra stabilization, the magnitude of T_N decreases with E_g, vanishing as b increases to b_m. This situation is presumably illustrated by the antiferromagnetic compounds $PbCrO_3$ and $CaCrO_3$. Indeed, the type-G magnetic ordering has been confirmed for $PbCrO_3$.[39] In these compounds, band antiferromagnetism can be distinguished from localized-electron antiferromagnetism because there is no crystallographic distortion to tegragonal $(c/a<1)$ symmetry below T_N. This is in sharp contrast to $LaVO_3$, which does exhibit the crystallographic distortion below T_N that is required by the localized-electron theory discussed above.

For broader d bands, where $\Delta_b > U_E$, there is only the introduction of a deep minimum at the Fermi energy in the density-of-states versus energy curve. Without a discrete energy gap, there may be no spontaneous band antiferromagnetism and the conductivity is metallic. This situation is presumably illustrated by the metallic, Pauli paramagnetic compounds $SrMoO_3$ and $SrCrO_3$.

The striking feature of this series of compounds, aside from the continuity in magnetic order on going from the localized-electron to the collective-electron regime, is the narrowness of the compositional range where spontaneous band antiferromagnetism is observed. It is completely spanned by $LaVO_3$ and $SrCrO_3$. Since the bandwidth is $\Delta_b \sim b \sim \epsilon_0 \lambda_\pi^2$, where λ_π is the covalent-mixing parameter of Eq. (12), this involves essentially the change in λ_π on going from V^{3+} to Cr^{4+}. (That λ_π is smaller in $CaCrO_3$ and $PbCrO_3$ than in $SrCrO_3$ is consistent with the more ionic character of the Sr^{2+} ion versus the Ca^{2+} and Pb^{2+} ions.[40])

(*Note added in proof.* Additional information on and discussion of these compounds is now available [J. B.

---

[39] W. L. Roth and R. C. DeVries, J. Appl. Phys. Suppl. **38**, 951 (1967).

[40] J. B. Goodenough, Phys. Rev. **164**, 785 (1967).

Goodenough, J. M. Longo, and J. A. Kafalos, Mater. Res. Bull. **3,** 471 (1968)]).

2. *Configuration d^3*

With configuration d^3 the larger Coulomb energy U_E is decisive. Where $U_E > \frac{3}{2}k_c\lambda + \Delta_b$, both the $J = \frac{3}{2}$ and the $J = \frac{1}{2}$ bands are half-filled. The empty $J = \frac{3}{2}$ band is separated from the $J = \frac{1}{2}$ band by the energy gap

$$E_g \approx U_E - \tfrac{3}{2}k_c\lambda - \Delta_b. \tag{41}$$

Provided that $E_g > 0$, the result would be a semiconducting antiferromagnet with type-G magnetic order. Since a semiconducting antiferromagnet with no spontaneous distortion is also anticipated for localized d electrons, it is not possible from this simple magnetic and structural information to characterize the electrons. However, a pressure experiment should be able to distinguish whether the electrons are collective or localized. Pressure would increase the transfer integrals b_{ij}, so that

$$dT_N/dP > 0 \quad \text{if} \quad b < b_c, \tag{42}$$

$$dT_N/dP < 0 \quad \text{if} \quad b > b_c. \tag{43}$$

Such pressure experiments have yet to be performed.

3. *$La_{1-x}Sr_xCoO_3$*

In the mixed system $La_{1-x}Sr_xCoO_3$ there is a critical value of x beyond which the compounds become metallic and ferromagnetic.[41] $LaSrCo_2O_6$ is representative. In this compound the number of d electrons per molecule is 11, and there is only half a hole per cobalt ion in the t_{2g} bands. Therefore, the upper $J = \frac{1}{2}$ band is three-quarters filled, and spontaneous band ferromagnetism becomes competitive with spontaneous band antiferromagnetism.[20] Since ferromagnetic order does not change the translational symmetry, it does not change the conductivity from metallic to semiconducting.

4. *Perovskites with Low-Spin d^4 Configurations*

The compounds $SrFeO_3$, $CaRuO_3$, and $SrRuO_3$ all have the low-spin d^4 configuration. All are metallic with spontaneous magnetism. The first two are antiferromagnetic[42,43] and $SrRuO_3$ is ferromagnetic.[43] The bandwidth Δ_b should increase on going from $SrFeO_3$ to $SrRuO_3$. With $U_E = 0$, Eq. (40) would be applicable and the compounds would be diamagnetic semiconductors. However, with spontaneous band magnetism, which manifests a $U_E > \frac{3}{2}k_c\lambda$ to split the $J = \frac{3}{2}$ and $J = \frac{1}{2}$ bands, both the $J = \frac{3}{2}$ and $J = \frac{1}{2}$ bands are partially filled. Saturation of the α-spin states occurs if $U_E > \frac{3}{2}k_c\lambda + \Delta_b$. With a half-filled $J = \frac{1}{2}$ band, spontaneous band antiferromagnetism is anticipated. On the other hand, if $\frac{3}{2}k_c\lambda - \Delta_b < \Delta_{ex} < \frac{3}{2}k_c\lambda + \Delta_b$, then one-quarter-filled $J = \frac{1}{2}$ and seven-eighths-filled $J = \frac{3}{2}$ bands occur, and ferromagnetism is competitive. The compound $SrRuO_3$, with reduced atomic moment $\sim 1.6\mu_B/$(Ru atom), apparently corresponds to this latter situation.[44] Whether $SrFeO_3$ and $CaRuO_3$ corresponds to the former has not yet been determined. The fact that $SrFeO_3$ is reported[42] to be cubic indicates that at least the β-spin electrons are collective in this compound.

---

[41] P. M. Raccah and J. B. Goodenough, J. Appl. Phys. **39,** 1209 (1968).

[42] J. B. MacChesney, R. C. Sherwood, and J. F. Potter, J. Chem. Phys. **43,** 1907 (1965).

[43] A. Callaghan, C. W. Moeller, and R. Ware, Inorg. Chem. **5,** 1572 (1966).

[44] J. M. Longo, P. M. Raccah, and J. B. Goodenough, J. Appl. Phys. **39,** 1327 (1968).