

## Direct Cation- -Cation Interactions in Several Oxides\*

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It is pointed out that interactions between octahedral-site cations are cation-anion-cation interactions if the cation-occupied octahedra share a common corner, but may be primarily cation-cation (no anion intermediary) if the cation-occupied octahedra share either a common edge or a common face. It is further pointed out that cation- -cation interactions may be naturally classified as "strong" or "weak" since there is a critical cation separation below which the interacting electrons are best described by a collective-electron model, above which by a Heitler-London model. The characteristics of the different interactions under varying conditions are summarized. In the case of strong cation-cation interactions, covalent-type bonds may be formed at low temperatures. The resulting phase transitions are marked by the following features: (1) the transitions may be noncooperative (isolated cation-cation pairing introducing no symmetry change

to the structure) and extend over a considerable temperature interval ( $\Delta T \sim 100^\circ\text{C}$ ), or cooperative, occurring at a definite temperature and exhibiting thermal hysteresis. (2) Bonded cations are displaced from the center of symmetry of their anion interstice (in contrast to Jahn-Teller or spin-orbit distortions). (3) Bonding electrons are spin-paired so that they make no contribution to the atomic moment unless localized, unpaired  $d$  electrons are simultaneously present to weaken the covalent-type bond via intra-atomic exchange. (4) Bonding electrons cannot contribute to metallic-type conductivity so that if the bond-forming phase ties up all of the outer  $d$  electrons in covalent-type bonds, the transition is semiconducting  $\rightleftharpoons$  metallic. The physical properties of several compounds that illustrate the importance of the cation- -cation interactions are discussed.

### I. INTRODUCTION

SEVERAL oxides containing transition-element cations have physical properties that suggest the existence of cation-cation interactions via direct overlap of cation  $d$ -electron wave functions. Such interactions are to be distinguished from those that occur via an anion intermediary. They have been independently proposed to account on the one hand for certain magnetic interactions,<sup>1</sup> on the other for some interesting electrical properties.<sup>2</sup> The purpose of this paper is to strengthen the argument for these interactions by describing the several interactions that may occur or compete with one another in predominantly ionic crystals given different crystallographic configurations and cations with varying numbers of outer  $d$  electrons, by pointing out some of the physical consequences to be anticipated from these interactions, and by comparing these consequences with the properties of several pertinent transition-metal compounds. These latter comparisons are found to support the hypothesis that cation- -cation (to be contrasted with cation-anion-cation) interactions may be significant if octahedral-site cations have the outer-electron configuration  $3d^m$  ( $m \leq 5$ ) and the occupied octahedra share either a common face or a common edge.

But first it is necessary to establish a nomenclature by which the cation-cation interactions via direct overlap of cation wave functions can be distinguished from those that occur via an anion intermediary. The conventional distinction of direct vs indirect interactions

has been rendered ambiguous by a recent publication of Anderson<sup>3</sup> in which he has proposed the nomenclature "superexchange," "direct exchange," and "indirect exchange" for the various contributions to a given cation-anion-cation interaction. In an attempt to avoid confusion, those interactions that do not involve an anion intermediary will be referred to as cation- -cation interactions, those that do as cation-anion-cation interactions.

From a theoretical point of view, the only satisfactory single-electron wave functions in a solid-state problem are running waves, whereas experimentally the cation outer electrons are frequently found to have the character of isolated  $d$ -type electrons. Mott<sup>4</sup> has argued that, if the intercation distance is large, the Heitler-London approximation is appropriate and an integral number of electrons are localized on each cation; that, if the intercation distance is small, it is necessary to use a collective-electron model in which the electrons are delocalized, metallic-type conduction occurring should the corresponding zone, or band of energy states, be only partially filled. Further, Mott has pointed out that an abrupt transition with intercation distance should be anticipated. Anderson<sup>3</sup> has chosen to call the localized electronic charges "isolated spin quasi-particles." This spin quasi-particle concept isolates the one-electron effects from the polarization effects that determine the sign of the coupling between localized spins of neighboring cations. In this paper the Mott distinction between materials having localized electrons (quasi-particles) and those having delocalized electrons (collective-electron model) is maintained in the characterization of weak vs strong cation- -cation interactions. Further, the various quasi-particles (and the delocalized electrons as well) are assumed to occupy bands that

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<sup>1</sup> D. G. Wickham and J. B. Goodenough, *Phys. Rev.* **115**, 1156 (1959).

<sup>2</sup> F. J. Morin, *Phys. Rev. Letters* **3**, 34 (1959); *Bell System Tech. J.* **37**, 1047 (1958).

<sup>3</sup> P. W. Anderson, *Phys. Rev.* **115**, 2 (1959).

<sup>4</sup> N. F. Mott, *Proc. Phys. Soc. (London)* **A62**, 416 (1949).

TABLE I. Spin-spin interactions between high-spin-state, octahedral-site cations.  $\Lambda$  symbolizes relative orientations of anion octahedra about interacting cations: No. 1=common octahedral face; No. 2=common octahedral edge;  $\alpha$ =common octahedral corner with cation-anion-cation angle  $\alpha$ . The two cations have outer-electron configurations  $nd^{m_1}$ ,  $nd^{m_2}$ , and  $J$  is the exchange constant, + indicating ferromagnetic coupling, - antiferromagnetic coupling, 0 no (or paramagnetic) coupling. The estimated magnetic-ordering temperature  $T_{N,C}$  is for oxides of transition elements of the first long period as obtained from empirical data: these are to be modified in accordance with the qualifying remarks.  $R$  and  $Z$  are the cation-cation separation and cation atomic number, respectively.

| $\Lambda$               | Interaction <sup>a</sup> | $m_1$  | $m_2$  | $J$                        | $T_{C,N}$ [°K]  | Remarks  |
|-------------------------|--------------------------|--|--|----------------------------|---|--|
| No. 1<br>or<br>No. 2    | Cat- -Cat                | 0<br>$\leq 5$<br>$5 < m < 8$<br>$8 \leq m \leq 10$                   | $\leq 10$<br>$\leq 5$<br>$\leq 8$<br>$\leq 10$                             | 0<br>-<br>+<br>0           | 0<br>$\leq 500$<br>$< 50^c$<br>0                      | $T_{C,N}$ decreases with increasing $R, Z$ . "Strong" interactions may form "bonded" cation pairs below $T_N$ with physical consequences given in Table II. Cat-An-Cat ( $\alpha=90^\circ$ ) weak and -if $4 \leq m_1 \leq 8$ while $m_2 \leq 5$ , + otherwise.          |
| $\alpha=180^\circ$      | Cat-An-Cat               | 0<br>$\leq 3$<br>$4 \leq m \leq 8$<br>$4$<br>$4 \leq m \leq 8$<br>10 | $\leq 10$<br>$\leq 3$<br>$\leq 3$<br>$4$<br>$5 \leq m \leq 8$<br>$\leq 10$ | 0<br>-<br>+<br>b<br>-<br>0 | 0<br>$\sim 100$<br>$\leq 300$<br>b<br>$\sim 750$<br>0 | $T_N \sim (z/27k)[(S+1)/S](\Delta^2/U)\xi$ if $5 \leq m_{1,2} \leq 8$ and spin-orbit coupling negligible; $T_{N,C}$ reduced by about factor of 10 if $m_1$ or $m_2 \leq 3$ . <sup>d</sup> Both $\sigma$ and $\pi$ bonding symmetric about anion. Cat- -Cat cannot occur. |
| $\alpha \sim 135^\circ$ | Cat-An-Cat               | 0<br>$\leq 3$<br>$4 \leq m \leq 8$<br>$4$<br>$4 \leq m \leq 8$<br>10 | $\leq 10$<br>$\leq 3$<br>$\leq 3$<br>$4$<br>$5 \leq m \leq 8$<br>$\leq 10$ | 0<br>-<br>-<br>b<br>-<br>0 | 0<br>$\sim 100$<br>$\leq 300$<br>b<br>$\sim 750$<br>0 | Similar to case $\alpha=180^\circ$ except that bonding on opposite sides of cation is no longer symmetric. <sup>e</sup>  |

<sup>a</sup> Table assumes degenerate  $t_{2g}$  level. If octahedral site distorted by electron ordering within  $t_{2g}$  or  $e_g$  levels, degeneracy is removed and each interaction (i.e., along different crystallographic directions) must be considered separately, though according to the same principles.

<sup>b</sup> Two situations possible: (1) occupied  $e_g$  levels overlap conduction band giving ferromagnetism ( $T_C > 300^\circ\text{K}$ ) with  $\mu < 4\mu_B/\text{cation}$  and metallic-type conductivity; (2) cooperative Jahn-Teller distortion results in antiferromagnetic interactions between some cation pairs, ferromagnetic or negligible interactions between others. (See reference 8).

<sup>c</sup> Assumes weak interactions and degenerate  $t_{2g}$  levels.

<sup>d</sup> See reference 3.  $\Delta$  is ligand-field splitting,  $S$  cation spin,  $z$  number of coupled cation neighbors,  $k$  Boltzmann's constant,  $\xi$  a measure of the fraction of covalence in the cation-anion bond, and  $U$  is the intra-atomic Coulomb energy required to shift an electron from one cation to another given each cation initially has the correct number of electrons.

<sup>e</sup> Magnetic coupling follows from physical arguments set forth in reference 7 together with consideration of total geometric relationship.

reflect the symmetry properties of the atomic wave functions from which they are formed. Therefore the physical arguments are presented in terms of easily visualized atomic, or cation, orbitals. Although such arguments are inadequate for any quantitative description of a solid-state problem, they can be extremely useful for establishing the principal qualitative features that must be considered.

## II. VARIOUS CATION-CATION INTERACTIONS

In all of the materials under consideration, the transition-metal cation is in an octahedral (or distorted-octahedral) interstice of an anion sublattice. The electrostatic interactions between anion and cation electrons cause a splitting (ligand-field splitting of energy  $\Delta=10Dq$ ) of a cation  $nd$  level into a more stable, triply degenerate  $t_{2g}$  level ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  atomic orbitals directed away from neighboring anions) and a less-stable, doubly degenerate  $e_g$  level ( $d_{z^2}$ ,  $d_{x^2-y^2}$  atomic orbitals directed towards neighboring anions). In all of the materials under consideration in this paper, this splitting is smaller than the intra-atomic exchange energy  $E_{ex}$ , viz.,  $\Delta < E_{ex}$ , so that all cations are in a high-spin state.

The problem is to estimate the relative magnitudes of the various cation- -cation vs cation-anion-cation interactions that can occur in any given material. If the physical consequences of each mechanism can be unambiguously, even if only qualitatively, determined

from general physical arguments, comparison with experiment should enable a classification of relative interaction strengths as well as a check on the accuracy and completeness of the physical reasoning. The physical consequences can, as is discussed below, be qualitatively predicted and are listed in Tables I and II. The estimated strengths given in Table I ( $T_{N,C}$ ) are obtained empirically (although order of magnitudes of various cation-anion-cation interactions also follow from theoretical considerations<sup>5</sup>), and subsequent comparisons with experiment in Sec. III provide a consistency argument for the existence of cation- -cation interactions.

There are two factors that determine the sign of the spin-spin interaction between any pair of cations: the relative orientations of their anion octahedra, and the number of cation outer electrons. Anderson<sup>5</sup> first pointed out that if the cation-anion-cation angle is  $90^\circ$ , the cation-anion-cation interactions are weak: it is assumed in this paper that they are negligibly small.<sup>6</sup> It follows that, if two cation-occupied octahedra share a common face or a common edge, the resulting cation-anion-cation interactions are to be neglected. However, these geometries are favorable for cation- -cation interactions, since the  $t_{2g}$  orbitals may be directed towards the octahedral edges (atomic  $d_{yz}$ ,  $d_{zx}$ ,  $d_{xy}$ ) or through

<sup>5</sup> P. W. Anderson, Phys. Rev. **79**, 350 (1950).

<sup>6</sup> If the weak cation- -cation interactions are negligible, this assumption can no longer be valid since  $90^\circ$  cation-anion-cation interactions, though weak, do exist.

TABLE II. Comparison of physical properties to be associated with cation-anion-cation vs cation- -cation interactions between octahedral-site cations.  $T$  is temperature,  $T_C$  Curie temperature,  $\mu_{\text{eff}}$  effective paramagnetic cation moment,  $S$  net cation spin,  $\mu_B$  Bohr magneton,  $\mu$  ferromagnetic or antiferromagnetic cation moment,  $\Delta$  ligand-field splitting,  $E_{\text{ex}}$  exchange splitting, and  $n_{2g}$  is number of  $t_{2g}$  electrons per cation.

| Property                  | Cation-anion-cation  | Weak cation- -cation  | Strong cation- -cation   |
|---------------------------|--|---|--|
| Magnetic order            | (1) Cations on opposite sides of an anion antiferromagnetic<br>(2) Ferromagnetism (see Table I)  | (1) Nearest-neighbor cations antiferromagnetic if $n_{2g} \leq 3$<br>(2) Ferromagnetism (very low $T_C$ ) if $n_{2g} > 3$ and $t_{2g}$ level degenerate | (1) Spin pairing between bonded cation pairs if $n_{2g} \leq 3$ (or $n_{2g} \leq 5$ and bonding removes degeneracy).<br>(2) Ferromagnetism if unpaired $e_g$ electrons simultaneously present with (a) $n_{2g} > 3$ and degenerate $t_{2g}$ level, or (b) $5 < n_{2g} < 6$ . |
| Electrical conductivity   | Semiconductor (or insulator) <sup>b</sup>  |   | Metallic. May become semiconductor at low $T$ . <sup>c</sup>   |
| Cation magnetic moment    | $\mu_{\text{eff}}^2 \propto S(S+1)\mu_B^2$ ; $\mu \propto S\mu_B$ with $S$ the same at low and high $T$ and predictable from knowledge of occupation of isolated-cation $d$ levels, $\Delta$ , and $E_{\text{ex}}$ .   |   | $\mu_{\text{eff}}^2 \propto S(S+1)\mu_B^2$ ; $\mu \propto S'\mu_B$ with $S > S'$ , where $S'$ is net cation spin in low- $T$ phase. <sup>d</sup>   |
| Phase change <sup>a</sup> | Jahn-Teller or spin-orbit type. Possible if $m=1, 2, 4, 6, 7, 9$ ( $m=4, 9$ are Jahn-Teller and the strongest). <i>Characteristic</i> : alteration of anion-octahedron symmetry, but cation in center of symmetry. Jahn-Teller type independent of $T_{C,N}$ , spin-orbit type correlated with $T_{C,N}$ . |   | Bond-formation type. Possible if $n_{2g} \leq 5$ . <i>Characteristic</i> : cation-cation pairing that shifts cation from center of symmetry of anion interstice.   |

<sup>a</sup> Cooperative if lattice symmetry changed; noncooperative transitions may extend over a range of temperature ( $\Delta T \sim 100^\circ\text{C}$ ).

<sup>b</sup> Exceptions: (1) If cations of same element, but different valence, are simultaneously present, material may have a metallic-type  $\sigma - T$  character below a ferromagnetic Curie temperature. (2) If  $m=4$ , the occupied  $e_g$  levels may overlap the conduction band.

<sup>c</sup> If all available  $t_{2g}$  electrons participate, at low  $T$ , in covalent-type cation-cation bonds, semiconductor. If no bond formation or if not all half-filled  $t_{2g}$  orbitals participate in bond formation, remains metallic at low  $T$ .

<sup>d</sup> If low- $T$  phase a semiconductor,  $S' \rightarrow 0$  (unless unpaired  $e_g$  electrons are present); if low- $T$  phase a metal,  $(S - S') = nf$  where  $f$  = fraction ( $\sim 0.5$ ) and  $n$  = number of electrons per cation participating in bond formation. Only at high  $T$  ( $T \gg T_N$ ) is entropy sufficiently important to induce  $S$  to approach the value predicted from a knowledge of  $d$ -level occupation,  $\Delta$ , and  $E_{\text{ex}}$ .

the octahedral faces (hybridized  $d_{yz}$ ,  $d_{zx}$ ,  $d_{xy}$ ). Therefore the predominant interactions between neighboring cations whose anion octahedra share a common face or edge are assumed to be cation- -cation interactions. On the other hand, if the cation-occupied octahedra share a common corner, there can be no direct overlap of neighboring cation orbitals and therefore no cation- -cation interactions whether the cation-anion-cation angle  $\alpha$  be  $180^\circ$  or as small as  $\sim 120^\circ$ . Therefore the interactions between neighboring cations whose anion octahedra share a common corner are cation-anion-cation interactions, and this interaction is optimal if  $\alpha = 180^\circ$ . Finally it is to be noted that although only one mechanism contributes significantly to the spin-spin coupling of any cation pair, a given cation usually has several neighbors, some of which are coupled via a common octahedral corner and others via a common octahedral face or edge. Therefore the two mechanisms may compete one against another, and it is necessary to have some estimate of their relative magnitudes if predictions about low-temperature magnetic order are to be made. For a consideration of the signs of the various interactions, it is usually only necessary to consider the number of cation outer electrons. The magnitudes of the various interactions then depend upon a number of additional factors such as the magnitude of the ligand-field splitting, the degree of covalency in the anion-cation bond, the ratio of cation-cation separation to radial extension of the cation  $d$  wave functions.

The case of cation-anion-cation interactions has been considered by several workers.<sup>3,5,7-9</sup> The principal results of these considerations are simply tabulated in Table I. It will be noted that a degenerate  $e_g$  or  $t_{2g}$  level that is less than half-filled is considered to give interactions of the same sign, though smaller magnitude, as half-filled levels. However, the degeneracy of such less-than-half-filled levels may be removed by a distortion of the octahedral-site symmetry: in such an event the interactions that involve the resulting more stable, half-filled orbitals must be considered separately from these involving the resulting less stable, empty orbitals. The distinction between the case  $\alpha = 180^\circ$  (symmetrical bonding on either side of anion) and  $\alpha \sim 135^\circ$  (possible nonsymmetrical bonding on either side of anion) follows directly from previous considerations.<sup>7</sup> The situation  $m_1 = m_2 = 4$  invariably constitutes a special case:<sup>8</sup> either there is a cooperative distortion of the cation-occupied octahedra, or (as in several NIA-type structures) there is an apparent overlap of the partially filled  $e_g$  level and the conduction band that results in metallic-type conductivity and ferromagnetism. A principal point to notice is that for  $4 \leq m \leq 8$  ( $e_g$  levels degenerate) the cation-anion-cation interactions must predominate; but that if  $m \leq 3$ , the cation- -cation interactions may be as strong as, or stronger than, the cation-anion-cation interactions. This tendency is enhanced by the fact that

<sup>7</sup> J. B. Goodenough, J. Phys. Chem. Solids **6**, 287 (1958).

<sup>8</sup> J. B. Goodenough, J. phys. radium **20**, 155 (1959).

<sup>9</sup> J. Kanamori, J. Phys. Chem. Solids **10**, 87 (1959).

an absence of  $e_g$  electrons allows a minimal separation of cations sharing a common anion-octahedron face or edge.<sup>10</sup>

As mentioned in the introduction, it is convenient to distinguish those cation-cation interactions in which the cation electrons may be considered localized, quasi-particles (cation-cation separation  $R > R_c$ ) from those in which the cation electrons are delocalized ( $R < R_c$ , where the critical cation-cation separation  $R_c$  is sharply defined). The first class of interactions will be called "weak" cation-cation interactions; the second, "strong" cation-cation interactions. In either case it is necessary to distinguish the interactions between cations having half-or-less-filled cation orbitals from those between cations having more than half-filled cation orbitals.

Imagine two neighboring, octahedral-site cations that have overlapping  $t_{2g}$  orbitals. Optimum binding occurs for that configuration of  $t_{2g}$ -electron spins that permit the maximum amount of electronic charge in the overlapping region midway between the positive cation cores. If the electrons have parallel spins, they exclude one another from this region: therefore an antiferromagnetic correlation between electrons on neighboring cations stabilizes the binding. If the overlapping orbitals are half-or-less filled and if it is possible to propagate antiferromagnetic order throughout the sublattice of interacting cations, the antiferromagnetic correlation can be perfect and the binding optimal. If the interacting  $t_{2g}$  orbitals are more than half-filled, the bonding should be analogous to that in a hypothetical  $Z_2$  molecule in which each Z atom has a nuclear charge of  $+(3/2)e$ . Such a molecule would be ferromagnetic with an atomic moment of  $0.5\mu_B$  per atom, the total ferromagnetic moment coming from the electrons in excess of one electron per atomic orbital participating in the molecular orbitals. Thus a crystal with more than half-filled, degenerate  $t_{2g}$  orbitals and strong cation-cation interactions should be ferromagnetic with a cation moment equivalent to the number of electrons in excess of one per  $t_{2g}$  orbital or to the number of  $t_{2g}$  holes, whichever is smaller. These interactions are important for transition metals and metallic-type alloys.<sup>11</sup> However, the degeneracy of the  $t_{2g}$  states is usually not maintained if the number of  $t_{2g}$  electrons is  $n_{2g} < 5$ . Thus  $t_{2g}$  holes order to permit near-neighbor bonding with as many near neighbors as possible. Weak cation-cation interactions are expected to be negligibly small if the  $t_{2g}$  orbitals are more than half-filled.

These considerations lead to the following rules for the physical manifestations of cation-cation interaction.

(1) **Weak interactions.**—Weak cation-cation interactions give rise to (a) semiconductivity or insulation; (b) a paramagnetic susceptibility characteristic of cation moments equivalent to those of the free

cations subject to the crystalline fields; (c) antiferromagnetic exchange between near-neighbor cations if  $n_{2g} \leq 3$ .

(2) **Strong interactions.** (a) *Degenerate  $t_{2g}$  states.*—Strong cation-cation interactions give rise to (i) metallic-type conductivity; (ii) a paramagnetic susceptibility approaching at highest temperatures that characteristic of weak interactions, approaching at lowest temperatures that characteristic of weak Pauli paramagnetism.

(b) *Nondegenerate  $t_{2g}$  states.*—Strong cation-cation interactions may be stabilized at low temperatures by the removal of any  $t_{2g}$  degeneracy through covalent-type bond formation between cation pairs. Covalent-type cation-cation bond formation gives rise to (i) a phase transition that may be noncooperative (involves isolated cation pairs and introduces no symmetry change) or cooperative, the noncooperative transitions extending over a finite temperature interval ( $\Delta T \sim 100^\circ\text{C}$ ) and the cooperative transitions occurring at a definite temperature, but exhibiting thermal hysteresis; (ii) spin pairing of the bonding electrons, the bonding electrons contributing  $0\mu_B$  if no unpaired  $d$  electrons remain or  $\sim 0.5\mu_B$  if unpaired  $d$  electrons are simultaneously present at the cations to weaken the bonding via intra-atomic exchange; (iii) antiferromagnetic correlation between bonded cations if cation moments are present; (iv) no contribution to metallic-type conductivity from the bonding electrons (semiconducting if all  $t_{2g}$  electrons participate in covalent-type bonding).

Further, these bond-formation phase changes can be distinguished from Jahn-Teller and spin-orbit phase changes by the following unambiguous criterion: (a) the cations remain close to the center of symmetry of their anion interstices in a Jahn-Teller or spin-orbit transition, (b) the cations are shifted from the center of anion-interstice symmetry by the formation of cation-cation pairs in a bond-forming transition. (Jahn-Teller transitions are cooperative transitions in which the octahedral interstice is distorted so as to minimize cation-anion core-core repulsions, to optimize cation-anion bonding.<sup>8,12</sup> Similarly transitions associated with  $T_N$  as a result of a cooperative spin-orbit coupling, as in FeO and CoO, are the result of cation-anion interactions.)

These predictions for the physical consequences of cation-cation interactions vs cation-anion-cation interactions are summarized in Tables I and II. Since the predictions are usually quite distinct, it should be possible to determine the predominant mechanism operative in any given compound by an inspection of its physical properties. In the next section, the physical properties of several pertinent compounds are presented. There appears to be convincing evidence that cation-cation interactions often play a decisive role in pre-

<sup>10</sup> J. H. Van Santen and J. S. Van Wieringen, *Rec. trav. chim.* **71**, 420 (1952).

<sup>11</sup> J. B. Goodenough, Lincoln Laboratory Technical Report TR 208 (Sept. 1, 1959).

<sup>12</sup> J. B. Goodenough and A. L. Loeb, *Phys. Rev.* **98**, 391 (1955).

dominantly ionic compounds. The possibility of cation-cation covalent-type bonding also provides an interpretation of several experimental findings that have not been interpretable by previous investigators who have considered cation-anion-cation interactions alone.

### III. APPLICATION OF MODEL

#### A. Rocksalt-Type Compounds

In the rocksalt-type structure, all of the octahedral interstices of the fcc anion sublattice are occupied by cations, and each anion octahedron shares both its corners and its edges with neighboring octahedra. Therefore both cation-anion-cation and cation-cation interactions can be simultaneously present in this structure. Table I states that if  $5 \leq m \leq 8$ , as in MnO,  $\alpha$ -MnS, FeO, CoO, and NiO, the cation-anion-cation interactions must be the stronger. It follows that there is antiferromagnetic coupling within any simple-cubic sublattice of the fcc cation array, a prediction that has been well verified by neutron-diffraction experiments.<sup>13</sup> The cation-cation interactions are not satisfied by this magnetic order; but as each cation has an equal number of near neighbors with + and - spins, these interactions do not influence  $T_N$ . However, the paramagnetic Curie temperature  $\theta$  [ $\chi = C/(T - \theta)$ ] is determined by the sum of all the exchange interactions. The strength of the cation-cation interactions should be strongest for MnO and drop off rapidly with increasing atomic number, falling to zero at NiO. They would also be greater in MnO than in  $\alpha$ -MnS. Since the Mn-Mn interactions are antiferromagnetic, they would decrease  $\theta$ . Therefore the fact that  $T_N(\alpha\text{-MnS}) > T_N(\text{MnO})$  whereas  $\theta(\text{MnO}) < \theta(\alpha\text{-MnS})$  supports the idea that Mn-Mn interactions are stronger in the oxide. Such an effect cannot be readily explained by 90° cation-anion-cation interactions since superexchange is expected to increase with a decrease in the electronegativity of the intermediate anion, as is reflected in  $T_N$ . Such an argument has already been suggested by Kanamori.<sup>9</sup>

TiO (if quenched from  $T > 900^\circ\text{C}$ ),<sup>14</sup> VO, and CrN also crystallize in the rocksalt-type structure. These materials contain cations with  $m \leq 3$ : they therefore represent a situation in which cation-cation interactions may be stronger than cation-anion-cation interactions. Each of these materials is characterized by metallic-type conductivity at and above room temperature. Therefore Table II immediately suggests that each of these compounds contains strong cation-cation interactions. This inference is identical with Morin's<sup>2</sup> suggestion for the origin of the metallic-type conductivity in TiO and VO. However, if this inference is correct, then it follows that any low-temperature antiferromagnetic order is not necessarily characterized by antiferromagnetic order within simple-cubic cation

sublattices. Rather, any Néel point that may occur at lower temperatures is characteristic of a martensitic phase transformation that introduces cation-cation bonding, and the low-temperature phase exhibits the physical properties outlined in Table II.

A recent neutron diffraction study<sup>15</sup> of CrN reveals a phase change below  $0^\circ\text{C}$ . The low-temperature phase is antiferromagnetic with ordering of the fourth kind (improved ordering of the second kind) in which (110) cation planes are ferromagnetic and the ordering of these planes on moving along the  $[\bar{1}10]$  direction is  $\dots + + - - + + - - \dots$ . The structure is no longer cubic: the  $[\bar{1}10]$  axis is shortened, the  $[\bar{1}\bar{1}0]$  axis is lengthened, and alternate (001) planes are shifted plus and minus along the  $[\bar{1}10]$  direction so that antiparallel cations are nearest neighbors, parallel cations have a greater separation. This distortion suggests bonding via  $d_{yz}$ ,  $d_{zx}$  orbitals, but no bonding of the  $d_{xy}$  electrons. Further, bonding appears to be effective with two of the four cation near neighbors overlapped by a  $d_{yz}$  or  $d_{zx}$  orbital in the cubic phase. Such bonding cannot be a simple electron pairing such as is envisaged in a conventional covalent-type bond: nevertheless, it is undoubtedly similar, though weaker and less effective in pairing than is found in the single-pair bond. Such a covalent-type bond will be called a "multiple-pair" bond. Evidence, then, for cation-cation interaction is found both in the magnetic order and in the fact that the cations are shifted from the center of anion-interstice symmetry in a manner which cannot be explained on the basis of a Jahn-Teller or spin-orbit effect. However, it should be noted that the magnetic ordering in CrN probably represents a compromise between cation-anion-cation and cation-cation interactions. In the (001) planes where the N atom is located near the center of the cation pseudo-square, the antiferromagnetic cation-anion-cation interactions are also satisfied: it is only along the  $[001]$  axis that the cation-anion-cation interactions are ferromagnetic.

Further evidence for cation-cation bonding in the low-temperature phase is the fact that  $\mu^{\text{Cr}} = 2.36\mu_B$  for antiferromagnetic CrN, whereas the high-temperature paramagnetic susceptibility data gives a spin-only value for  $\text{Cr}^{3+}$  in the cubic phase. There is a sharp drop in  $\chi$  on cooling through  $T_N$  that is suggestive of electron pairing below the transition. However, complete electron pairing of  $d_{yz}$ ,  $d_{zx}$  electrons would reduce  $\mu^{\text{Cr}} \rightarrow 1\mu_B$ ; the residual moment then inducing some contribution from the paired electrons to give  $\mu^{\text{Cr}} \sim 1.5 - 2.0\mu_B$ . This is considerably smaller than the observed value. Since all other features of the transition are suggestive of cation-cation bond formation, it appears that in the multiple-pair bonds there is electron pairing equivalent to only  $\sim 0.3\mu_B$  per bonding electron. CrN

<sup>13</sup> C. G. Shull, J. phys. radium **20**, 169 (1959).

<sup>14</sup> A. D. Pearson, J. Phys. Chem. Solids **5**, 316 (1958).

<sup>15</sup> L. M. Corliss, N. Elliott, and J. M. Hastings, "The Antiferromagnetic Structure of CrN," Brookhaven National Laboratory Report BNL 4294.

remains metallic through the transition:<sup>16</sup> this is compatible with the cation-cation-bonding model since the  $d_{xy}$  electrons are not bonded.

Stoichiometric VO has a sharp ( $\Delta\rho \sim 10^6$  ohm-cm) semiconducting  $\rightleftharpoons$  metallic transition at 114°K on cooling, at 121°K on heating.<sup>2</sup> Clearly cation-cation bond forming is again suggested. Although  $V^{2+}$  is isoelectric with  $Cr^{3+}$ , the semiconductor character of low-temperature VO indicates a phase in which all these  $t_{2g}$  electrons participate in bonding. One possible configuration for this phase can be imagined easily: it consists of paired (111) cation sheets, the distance between sheets varying alternately on going along a  $[111]$  axis. In such a phase the cation moment would be  $\mu^V \rightarrow 0\mu_B$ . Such a prediction can be checked by neutron-diffraction and magnetic-susceptibility measurements.

The rocksalt phase of TiO ( $Ti^{2+}$  has  $3d^2$ ) remains metallic at all temperatures.<sup>2,14</sup> This behavior is similar to that of isoelectric VN which becomes superconducting below 8.2°K.<sup>17</sup> Apparently conditions are not favorable for phase stabilization via bond formation. However, it probably also follows that there is no Néel temperature, the cation moment gradually decreasing with temperature as the entropy term in the free energy becomes less significant.

The compounds  $LiVO_2$  and  $NaVO_2$  have a structure that is closely related to the rocksalt-type structure: it is rocksalt with an ordering of  $Li^+$  and  $V^{3+}$ , or  $Na^+$  and  $V^{3+}$ , ions on alternate (111) cation planes. This order introduces a unique  $\langle 111 \rangle$  axis and rhombohedral symmetry.<sup>18,19</sup> In a perfectly ordered structure any cation-anion-cation interactions are  $V^{3+}-O^{2-}-(Li^+$  or  $Na^+)$  interactions, and therefore nonexistent. It follows that any magnetic interactions are of the type  $V^{3+}-V^{3+}$ . Bongers<sup>19</sup> has examined the paramagnetic susceptibility of both  $LiVO_2$  and  $NaVO_2$ . Both samples have a high-temperature susceptibility that approaches the spin-only value for  $V^{3+}$ . The  $LiVO_2$  sample showed an abrupt susceptibility change at 450°K. ( $\chi = 0.210 \times 10^{-3}$  emu at 433°K;  $\chi = 0.794 \times 10^{-3}$  emu at 491°K.) Such a variation indicates spin pairing via cation-cation bond formation, and a corresponding phase transformation is anticipated. Although a crystallographic study through the transition region has not been performed, a comparison of  $c/a$  (hexagonal basis) for  $LiNiO_2$  ( $c/a = 4.930$ )<sup>20</sup> and  $LiVO_2$  ( $c/a = 5.22$ )<sup>21</sup> appears to support the suggestion of bonding in the basal plane of  $LiVO_2$ . The susceptibility measurements of the  $NaVO_2$  sample indicate a transition between 300°K and 380°K, but no abrupt change in  $\chi$ . Such an

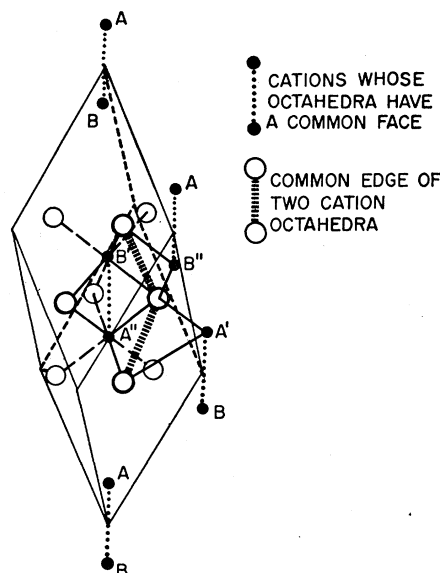


FIG. 1. Corundum-type structure.  $A-B$   $c$ -axis pairs share a common octahedral face,  $A-A$  and  $B-B$  basal-plane neighbors share a common octahedral edge, and there are  $A'-B'$  cation-anion-cation couplings between adjacent cation, basal, "puckered" planes.

observation is not inconsistent since the larger atomic radius of  $Na^+$  vs  $Li^+$  certainly means a weaker cation-cation interaction in  $NaVO_2$ . It would be interesting to study these transitions further to determine whether the other physical properties of  $LiVO_2$  and  $NaVO_2$  correspond, respectively, to strong vs weak cation-cation interactions.

## B. Corundum-Type Compounds

The corundum structure has a unique threefold axis. Along this axis are pairs of distorted, cation-occupied octahedra that share a common face. In the basal plane these octahedra share a common edge with three similar octahedra. The strongest cation-cation interactions occur along the  $c$  axis through the common octahedral face, but similar interactions may also occur perpendicular to the  $c$  axis. Cation-anion-cation interactions are also present: cation-occupied octahedra share a common corner with one of the cation-occupied octahedra belonging to a neighboring  $c$ -axis pair. The cation-anion-cation angle is  $\sim 135^\circ$ . (See Fig. 1.)

The compounds  $Ti_2O_3$ ,  $V_2O_3$ ,  $Cr_2O_3$ , and  $\alpha-Fe_2O_3$  have the corundum structure. Of these,  $Ti_2O_3$  behaves like a low-energy-gap, intrinsic semiconductor and  $V_2O_3$  like a metal at high temperatures;  $Cr_2O_3$  and  $\alpha-Fe_2O_3$  are insulators. This indicates strong  $Ti^{3+}-Ti^{3+}$  and  $V^{3+}-V^{3+}$  interactions, weak  $Cr^{3+}-Cr^{3+}$  and  $Fe^{3+}-Fe^{3+}$  interactions. Of these compounds, only  $\alpha-Fe_2O_3$  has strong cation-anion-cation interactions ( $m = 5$  vs  $m \leq 3$ ).

If strong cation-cation interactions are present in  $Ti_2O_3$  and  $V_2O_3$ , as is inferred by their metallic conduc-

<sup>16</sup> A. Wold (unpublished research, Lincoln Laboratory).

<sup>17</sup> G. F. Hardy and J. K. Hulm, Phys. Rev. **93**, 1004 (1954).

<sup>18</sup> L. D. Dyer, D. S. Borie, Jr., and G. P. Smith, J. Am. Chem. Soc. **76**, 1499 (1954).

<sup>19</sup> P. F. Bongers, Thesis, University of Leiden (July 4, 1957).

<sup>20</sup> J. B. Goodenough, D. G. Wickham, and W. L. Croft, J. Phys. Chem. Solids **5**, 107 (1958).

<sup>21</sup> D. G. Wickham and R. J. Arnott (unpublished research, Lincoln Laboratory).

tivity at high temperatures, then cation-cation bond formation with the physical characteristics outlined in Table II is likely at low temperatures. Further, in the corundum structure there are two types of cation-cation bonding that can occur: bonding of  $c$ -axis pairs and bonding within the basal planes. Formation of  $c$ -axis pairs must be the more stable interaction because these share a common octahedral face (shorter cation-cation separation). Also,  $c$ -axis bonding does not introduce a change in the lattice symmetry. Therefore it is possible for the pairs to bond independently of one another, or for the transition from nonbonded to completely bonded pairs to be noncooperative. Such a noncooperative transition would extend over a finite temperature interval. On the other hand, if basal-plane bonding takes place, it probably concentrates the electronic charge in a single cation-cation pair: in such an event the lattice symmetry is changed by an abrupt, cooperative transition.

### 1. $Ti_2O_3$

In the case of  $Ti_2O_3$  ( $Ti^{3+}$  has  $3d^1$ ), only the noncooperative transition can occur. Above the transition, intrinsic semiconduction with a small energy gap can occur as the crystalline-field splitting of the  $t_{2g}$  levels is fairly weak and cation-cation interactions can occur perpendicular as well as parallel to the  $c$  axis. Below the transition the  $d$  electrons would be paired so that there would be no atomic moment. Bonding of  $c$ -axis pairs would also reduce the  $c/a$  ratio since reduction of pair separation can be accomplished without reduction in the pucker that exists in the basal plane of anions. Since the transition is noncooperative, lack of stoichiometry would not influence appreciably the initial transition temperature. However, the presence of  $Ti^{4+}$  ions would guarantee the presence of unpaired  $Ti^{3+}$  electrons and therefore induce donor levels and localized, paramagnetic moments into the low-temperature phase.

Experimentally a transition is observed in  $Ti_2O_3$  near 200°C. Naylor<sup>22</sup> observed a change in specific heat characteristic of a second-order phase change. Foex and Loriers<sup>23</sup> reported a large change in the coefficient of thermal expansion and a resistivity change of two orders of magnitude through a temperature interval of about 200°C. Pearson<sup>14</sup> has examined the structural, conductivity, and magnetic-susceptibility changes through this transition. The predicted decrease in  $c/a$  with decreasing temperature through the transition was found. This observation has recently been checked by Newnham<sup>24</sup> who found that in his single-crystal sample the lattice-parameter change was spread over a wider temperature interval. Pearson found no sharp break in  $\rho$  on passing through the transition, but a distinct

break in  $\log \rho$  vs  $(1/T)$  was found near 200°C. The high-temperature resistivity of  $\sim 10^{-2}$  ohm cm increased to  $\sim 1$  ohm cm at  $\sim 220^\circ K$ . Absence of a larger resistivity change at the transition could easily be due to a lack of stoichiometry. Evidence for electron pairing also comes both from magnetic-susceptibility and neutron-diffraction measurements. Shirane and Pickart<sup>25</sup> found no noticeable magnetic peaks in their powder neutron data taken at 295°K and 4°K. The magnetic-susceptibility measurements of Pearson differed in absolute magnitude from earlier measurements by Foex and Wucher<sup>26</sup> and later measurements by Shirane and Pickart,<sup>25</sup> but all these sets of measurements indicate that  $\chi$  drops by a factor of two on passing through the transition, the low-temperature phase exhibiting a nearly temperature-independent susceptibility. Carr and Foner<sup>27</sup> have measured  $\chi_{11}$  and  $\chi_{\perp}$  on a single crystal of  $Ti_2O_3$  and found them both small and temperature independent below 250°K.<sup>28</sup>

### 2. $V_2O_3$

On the other hand,  $V_2O_3$  can have two transitions ( $V^{3+}$  has  $3d^2$ ): a noncooperative transition at higher temperatures due to  $c$ -axis pairing, and a cooperative transition at lower temperatures due to bonding in the basal plane. The high-temperature transition is predicted to have the following characteristics. (1) Below a critical temperature, bonding of the  $c$ -axis pairs sets in. Electrons participating in bonding contribute a reduced atomic moment and couple the atomic moments of the bonded pairs antiferromagnetically. However, the coupled antiferromagnetic pairs need not have any long-range magnetic order if the thermal energy is greater than the crystalline anisotropy. (2) As the temperature is lowered further, more pairs become coupled, the coupling of all pairs being virtually complete below some temperature interval of the order of 100°C. (3) Metallic-type conductivity occurs via the electrons in orbitals perpendicular to the  $c$  axis. However, the transition should be marked by a resistivity maximum near the upper transition temperature since at those temperatures electron scattering is large both because of the large vibrations between nearly bonded pairs and because of the disorder caused by some bonded, some unbonded pairs. At lower and higher temperatures, the cation positions become stabilized. (4) Contraction of the distance between  $c$ -axis pairs is accompanied by a reduction in the pucker of cation hexagons in a (111) pseudoplane as a result of the electrostatic interaction between the anions and the cation  $d$  electrons in orbitals perpendicular to the  $c$  axis. Such a simultaneous reduction in pucker could result in an increase in the  $c/a$  ratio on contraction of the  $c$ -axis pairs.

<sup>22</sup> B. F. Naylor, J. Am. Chem. Soc. **68**, 1077 (1946).

<sup>23</sup> M. Foex and J. Loriers, Compt. rend. **226**, 901 (1948).

<sup>24</sup> R. E. Newnham, Progress Report No. XXV, Laboratory for Insulation Research, Massachusetts Institute of Technology (1959), p. 38.

<sup>25</sup> G. Shirane and S. J. Pickart (private communication).

<sup>26</sup> M. Foex and J. Wucher, Compt. rend. **241**, 184 (1955).

<sup>27</sup> P. H. Carr and S. Foner, J. App. Phys. **31S**, April (1960).

<sup>28</sup>  $\parallel$  and  $\perp$  refer to the  $c$  axis.

The lowest-temperature phase is predicted to have the following characteristics: (1) a small magnetic susceptibility resulting from impurities or lack of stoichiometry (both  $V^{3+}$   $d$  electrons paired); (2) semiconducting properties; (3) distortion from hexagonal to orthorhombic symmetry<sup>29</sup>; all  $V^{3+}$ - $V^{3+}$  bonds perpendicular to the  $c$  axis being oriented in the same direction so as to minimize the elastic energy. This introduces one short axis within the original hexagonal plane, a compensating expansion occurring perpendicular to this axis within the plane. Any simultaneous change of the  $c$  axis should not, however, increase the separation of bonded  $c$ -axis pairs.

Powdered and polycrystalline samples of stoichiometric  $V_2O_3$  have been examined by several French workers,<sup>30</sup> and they have found evidence of both transitions. Specific-heat measurements of Jaffray and Lyand indicate a second-order phase change between 258 and 260°C that marks the onset (with decreasing temperature) of the first transition. They have interpreted their data between 70°C and 210°C as indicating a transition at 110 to 112°C, the specific heat showing a broad maximum at this point. Magnetic susceptibility measurements by Wucher indicate a temperature-independent susceptibility in the temperature range 110°C <  $T$  < 260°C. Comparison of these data with the model suggests that the first transition extends over the range of temperature 110°C <  $T$  < 260°C, the temperature-independent susceptibility reflecting the reduction in moment of the bonded pairs; and that below 110°C all  $c$ -axis pairs are bonded. Carr and Foner<sup>27</sup> have measured  $\chi_{11}$  and  $\chi_{\perp}$  for a single-crystal specimen.<sup>28</sup> In the range 170°K ≤  $T$  ≤ 300°K,  $\chi_{11}$  >  $\chi_{\perp}$  and both susceptibilities decrease with increasing temperature. The temperature dependence is not compatible either with a paramagnetic Curie-Weiss law or with normal antiferromagnetism. Foex has found that in the temperature range 110°C ≤  $T$  ≤ 250°C the thermal expansion coefficient is anomalously large. Newnham<sup>24</sup> has observed an increase in the  $c/a$  ratio through this same temperature interval. The first transition is also marked by a broad maximum in the electrical resistivity at about 235°C, the resistivity increasing from 10<sup>-1.72</sup> ohm cm at 25°C to 10<sup>-1.48</sup> ohm cm at 235°C. This is compatible with a low-mobility, metallic-type conductivity via cation- -cation interactions and a maximum uncertainty in the cation positions just below the transition temperature.

The low-temperature transition is a first-order transition,<sup>31</sup> the abrupt transition occurring at 168°K on heating, 150°K on cooling.<sup>27</sup> Through the transition the resistivity changes by over five orders of magnitude, the low-temperature phase being semiconducting, the

high-temperature phase metallic-type.<sup>2</sup> There is also an abrupt drop in  $\chi_{11}$  and  $\chi_{\perp}$ . Below the transition  $\chi_{11}$  and  $\chi_{\perp}$  are small and temperature independent.<sup>27</sup> Measurements<sup>30</sup> on a polycrystalline sample show a jump from 0.7 × 10<sup>-8</sup> emu to 1.1 × 10<sup>-8</sup> emu as the temperature is increased through the transition. These observations are compatible with a recent neutron-diffraction study by Paoletti and Pickart<sup>32</sup> that shows no positive evidence of antiferromagnetism in the low-temperature phase; and they all substantiate the hypothesis of electron pairing via cation- -cation bonding. Single crystals of  $V_2O_3$  cooled below the transition temperature crumbled on heating to room temperature.<sup>27</sup> This is compatible with the observation<sup>30</sup> of a discontinuous thermal expansion of a polycrystalline bar on cooling through the transition, which is suggestive of a phase transition to lower symmetry. Warekois<sup>33</sup> has recently verified that the low-temperature phase is monoclinic with dimensions compatible with the qualitative predictions based on  $V^{3+}$ - $V^{3+}$  bonding in the basal plane.

### 3. $Cr_2O_3$ and $\alpha$ - $Fe_2O_3$

It follows from Table I that  $\alpha$ - $Fe_2O_3$  ( $Fe^{3+}$  has  $3d^5$ ) should have a high  $T_N$  with antiferromagnetic coupling between cations whose octahedral interstices have a common anion corner (*viz.* + - - + along  $c$  axis), and that  $Cr_2O_3$  should have a relatively low  $T_N$  with weak, ambiguous cation-anion-cation and antiferromagnetic cation- -cation coupling (*viz.* + - + - along the  $c$  axis). In  $Cr_2O_3$  the cation- -cation (and perhaps also the cation-anion-cation) interactions are cooperative; in  $\alpha$ - $Fe_2O_3$  the weaker cation- -cation interactions in the basal plane are suppressed.

Experimentally this antiferromagnetic order has been confirmed by neutron-diffraction studies.<sup>34,35</sup> The Néel temperature of  $\alpha$ - $Fe_2O_3$  is 675°C,<sup>36</sup> of  $Cr_2O_3$  is ≈ 33°C.<sup>37</sup>

Although the  $Cr^{3+}$ - $Cr^{3+}$  and  $Fe^{3+}$ - $Fe^{3+}$  interactions are weak, it is interesting to enquire whether there is any evidence that the weak interactions between  $c$ -axis pairs have a different influence on some physical property than the other interactions, and whether this difference manifests itself as some type of compensation temperature. In this connection it is perhaps significant that between -20°C and 675°C  $\alpha$ - $Fe_2O_3$  exhibits a weak, parasitic ferromagnetism that is correlated with atomic moments in, or nearly in, the basal plane.<sup>34</sup> Below -20°C, the parasitic ferromagnetism disappears<sup>38</sup> and the magnetic axis is the  $c$  axis<sup>34</sup> just as it is in  $Cr_2O_3$ .<sup>35</sup> In  $Cr_2O_3$  antiferro-

<sup>29</sup> A. Paoletti and S. J. Pickart (private communication).

<sup>30</sup> E. P. Warekois, *J. App. Phys.* **31S**, April (1960).

<sup>31</sup> C. G. Shull, W. A. Strauser, and E. O. Wollan, *Phys. Rev.* **83**, 333 (1951).

<sup>32</sup> B. N. Brockhouse, *J. Chem. Phys.* **21**, 961 (1953).

<sup>33</sup> R. Chevallier, *J. phys. radium* **12**, 172 (1951).

<sup>34</sup> J. Jaffray and J. Viloteau, *Compt. rend.* **226**, 1701 (1948).

<sup>35</sup> F. J. Morin, *Phys. Rev.* **78**, 819 (1950).

<sup>29</sup> A simultaneous tilting of the  $c$  axis could reduce the symmetry to monoclinic.

<sup>30</sup> M. Foex, J. Jaffray, S. Goldsztaub, R. Lyand, R. Wey, and J. Wucher, *J. recherches centre natl. recherche sci. Labs. Bellevue (Paris)* **4**, 237 (1952).

<sup>31</sup> C. T. Anderson, *J. Am. Chem. Soc.* **58**, 564 (1936).



magnetic-resonance studies<sup>39</sup> suggest that the crystalline anisotropy may be varying with temperature in an unusual way in an interval of  $\sim 100^\circ\text{C}$  below  $T_N$ .

#### 4. Ilmenites

The ilmenite structure is similar to the corundum structure except that there is ordering of the two different cations into alternate (111) planes of the rhombohedral cell. In  $\text{MnTiO}_3$ ,  $\text{FeTiO}_3$ , and  $\text{NiTiO}_3$  the Ti cations appear to be  $\text{Ti}^{4+}$ . However, in  $\text{FeTiO}_3$  there are a few physical properties that suggest there is some degree of  $\text{Ti}^{3+}$  present. Since the  $\text{Fe}^{2+}$ - $\text{Ti}^{4+}$  pairs along a  $c$  axis share a common octahedral face, the possibilities of direct electron transfer may account for these properties.

Further, recent neutron-diffraction studies<sup>40,41</sup> show that the magnetic order in antiferromagnetic  $\text{FeTiO}_3$  and  $\text{NiTiO}_3$  is similar: ferromagnetic Fe or Ni (111) planes are alternately coupled antiferromagnetically. In the ilmenite structure, the indirect magnetic interactions are relatively weak as they involve two intervening oxygen atoms. Thus  $T_N$  for a natural crystal of  $\text{FeTiO}_3$  was found to be only  $68^\circ\text{K}$ .<sup>42</sup> The observed magnetic order is compatible with the expected antiferromagnetic cation-anion-anion-cation interaction. In the case of  $\text{Ni}(t_{2g}^6)$ , cation-cation interactions are negligibly small, and in the case of  $\text{Fe}^{2+}(t_{2g}^4)$  they are weak and ferromagnetic. However, in the case of  $\text{MnTiO}_3$  the  $t_{2g}$  orbitals are only half-filled so that antiferromagnetic Mn-Mn interactions within a (111) plane can compete with the indirect cation-anion-anion-cation interactions. The fact that  $\text{MnTiO}_3$  has a different magnetic order<sup>41</sup> in which near-neighbor Mn atoms within (111) planes are antiferromagnetic may indeed reflect cation-cation interactions that are stronger than cation-anion-anion-cation interactions.<sup>43</sup>

### C. Rutile-Type Compounds

The rutile structure has a body-centered tetragonal sublattice of octahedral-site cations, the octahedra sharing a common edge along the  $[001]$  axes and the body-centered octahedron sharing common corners with the corner octahedra via a cation-anion-cation angle  $\alpha \sim 135^\circ$ . It follows from the symmetry that the cation-cation and cation-anion-cation interactions can only be cooperative if the cation-cation interactions are ferromagnetic.

Rutile ( $\text{TiO}_2$ ) is an insulator. The  $\text{Ti}^{4+}$  ion has no

outer  $d$  electrons and is located at the center of its anion interstice. With no outer  $d$  electrons, neither direct nor indirect metallic-type conductivity is anticipated. With small additions of  $\text{Ti}^{3+}$ , however, electrical conductivity can occur both via the cation-cation interactions and via the  $\text{Ti}^{3+}$ -anion- $\text{Ti}^{4+}$  interactions.

The structure of  $\text{VO}_2$  ( $\text{V}^{4+}$  has  $3d^1$ ), on the other hand, is rutile-type only above  $340^\circ\text{K}$ . At room temperature the chains of octahedra along the  $[001]$  axis are puckered and the  $\text{V}^{4+}$  ions are shifted so as to form metal-metal pairs within the chains.<sup>44</sup> The bonded V-V pairs are separated by 2.65 Å whereas the other V-V distance along the chain is 3.12 Å. Such a low-temperature structure immediately suggests that cation-cation interactions have introduced covalent-type bonding between the vanadium pairs. (Crystallographic studies of several rutile-type systems have previously led Marinder and Magnéli<sup>45</sup> to propose metal-metal bonds along the  $c$  axis in these materials.) If this speculation is correct, then it follows from Table II that (1) above  $340^\circ\text{K}$   $\text{VO}_2$  is metallic and  $\mu_{\text{eff}} \approx 1.73\mu_B$  at  $T \gg 340^\circ\text{K}$ ; (2) at  $340^\circ\text{K}$  there is a semiconducting  $\rightleftharpoons$  metallic transition; (3) below  $340^\circ\text{K}$  the paramagnetic susceptibility is smaller and temperature independent as a result of electron pairing. Experimentally a first-order<sup>46</sup> semiconducting  $\rightleftharpoons$  metallic<sup>2</sup> transition is found with a  $10^\circ\text{C}$  thermal hysteresis about  $340^\circ\text{C}$ . The abrupt change in resistivity at the transition appears to be as great as  $10^4$  ohm cm in stoichiometric samples. The molar susceptibility increases discontinuously through the transition from a temperature-independent magnitude of  $0.1 \times 10^{-3}$  emu to a temperature-dependent magnitude of  $0.7 \times 10^{-3}$  emu.<sup>47,48</sup> The effective atomic moment increases above the transition to  $1.58\mu_B$  by  $466^\circ\text{K}$ .<sup>47</sup> Kasper<sup>49</sup> found no magnetic scattering in neutron-diffraction experiments below room temperature. The fact that  $\text{MoO}_2$ ,  $\text{WO}_2$ ,  $\text{TcO}_2$ , and  $\text{ReO}_2$  have a similar distorted rutile-type structure at room temperature<sup>44</sup> appears to eliminate the possibility that the Jahn-Teller effect is responsible for the distortions. So does the shift of the cations from the center of anion-interstice symmetry.

The rutile-type phase of  $\text{CrO}_2$  has strikingly different characteristics. Below  $T_c = 121^\circ\text{C}$  it is ferromagnetic with a chromium atomic moment of  $\mu^{\text{Cr}} = 2.07 \pm 0.03\mu_B$ .<sup>50</sup> Further, the ferromagnetic phase has

<sup>44</sup> A. Magnéli and G. Andersson, Acta Chem. Scand. 9, 1378 (1955).

<sup>45</sup> B. Marinder and A. Magnéli, Acta Chem. Scand. 11, 1635 (1957).

<sup>46</sup> J. Jaffray and A. Dumas, J. recherches centre natl. recherches sci. Labs. Bellevue (Paris) 5, 360 (1953-1954).

<sup>47</sup> W. Rudorff, G. Walter, and J. Stadler, Z. anorg. u. allgem. Chem. 29, 1 (1958).

<sup>48</sup> E. Hocheck and W. Klemm, Z. anorg. u. allgem. Chem. 242, 63 (1939).

<sup>49</sup> J. S. Kasper (private communication).

<sup>50</sup> G. Guillaud, A. Michel, J. Benard, and M. Fallot, Compt. rend. 219, 58 (1944).

<sup>39</sup> S. Foner, J. phys. radium 20, 336 (1959).

<sup>40</sup> G. Shirane, S. J. Pickart, R. Nathans, and Y. Ishikawa, J. Phys. Chem. Solids 10, 35 (1959).

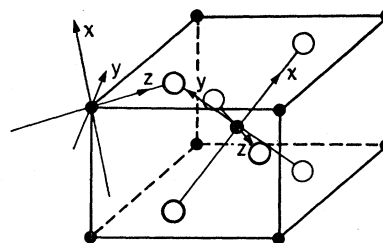
<sup>41</sup> G. Shirane, S. J. Pickart, and Y. Ishikawa, J. Phys. Soc. Japan 14, 1352 (1959).

<sup>42</sup> H. Bizette and B. Tsai, Compt. rend. 242, 2124 (1956).

<sup>43</sup> Similar arguments also hold for the series of anhydrous chlorides  $\text{MnCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{NiCl}_2$ . However, it should be noted that  $90^\circ$  cation-anion-cation interactions must also be significant since  $\theta = +68.2^\circ\text{K}$  in  $\text{NiCl}_2$  [C. Starr, F. Bitter, and A. R. Kaufmann, Phys. Rev. 58, 977 (1940)].

metallic-type conductivity ( $\rho \sim 10^{-2}$  ohm cm).<sup>51</sup> Although Cr-Cr interactions would be present if the  $t_{2g}$  level remains degenerate, the Néel temperature of  $\text{Cr}_2\text{O}_3$  ( $T_N \approx 33^\circ\text{C}$ ) shows that they would be weaker than the ferromagnetic interactions responsible for  $T_c = 121^\circ\text{C}$ . It follows that the ferromagnetism of low-temperature  $\text{CrO}_2$  is due to cation-anion-cation interactions. But ferromagnetic coupling is inconsistent with antiferromagnetic cation-cation interactions. This suggests that the degeneracy of the  $\text{Cr}^{4+}$  ion ( $m=2$ ) is removed by an ordering of the  $t_{2g}$  electrons that empties the orbitals parallel to the  $[001]$  axis (see Fig. 2). This would remove the competitive cation-cation interactions so as to permit a  $T_c$  as high as  $121^\circ\text{C}$ . Further, the asymmetric cation-anion interactions are characterized by overlap of half-filled cation orbitals on one side of the anion, empty orbitals on the other (see Fig. 2); and this asymmetry would result in ferromagnetic coupling.<sup>7</sup> A careful x-ray study to determine whether the individual cation-occupied interstices are slightly distorted to tetragonal symmetry would provide an important experimental check on this suggestion. The metallic-type conductivity below  $T_c$  may be due to two effects: (1) lack of stoichiometry; and (2) a maximum in the resistivity at  $T_c$ . It is difficult to prepare stoichiometric  $\text{CrO}_2$ , and a minimum electrical resistivity for cation-anion-cation interactions is expected with perfect ferromagnetic order.<sup>52</sup>

To complete the discussion of the rutile-type phases containing transition elements with  $m \leq 5$ , it is interesting to contrast the magnetic properties of  $\text{MnF}_2$  and  $\text{MnO}_2$ . In  $\text{MnF}_2$  ( $\text{Mn}^{2+}$  has  $3d^5$ ) the antiferromagnetic cation-anion-cation interactions are strong relative to the cation-cation interactions since the  $e_g$  orbitals are half-filled; in  $\text{MnO}_2$  ( $\text{Mn}^{4+}$  has  $3d^3$ ) the antiferromagnetic cation-anion-cation interactions are relatively weak as the  $e_g$  orbitals are empty (see Table I). This fact is also reflected in the respective lattice parameters 4.8734, 3.3103<sup>53</sup> and 4.44, 2.89.<sup>54</sup> The greater ionic character of  $\text{F}^-$  (smaller  $\zeta$  in Table I) plus the cation-cation competition must suppress  $T_N$  in  $\text{MnF}_2$ , and indeed  $T_N \sim 84^\circ\text{K}$ . In  $\text{MnO}_2$  the cation-cation separation along a  $[001]$  axis is considerably smaller so that cation-cation interactions are expected to be stronger and therefore to be comparable to the relatively



$d_{z^2}, d_{x^2-y^2}$  EMPTY;  $d_{xy}$  EMPTY;  $d_{yz}, d_{zx}$  HALF-FILLED

FIG. 2. Proposed electronic-order configuration for ferromagnetic  $\text{CrO}_2$ .

weak cation-anion-cation interactions. An antiferromagnetic ( $\alpha \sim 135^\circ$ ) cation-anion-cation interaction of comparable magnitude to the antiferromagnetic cation-cation interactions can lead to a complicated compromise magnetic order. Experimentally  $\text{MnF}_2$  has antiferromagnetic order between body-centered and corner  $\text{Mn}^{2+}$  ions<sup>55</sup> (as is predicted given stronger antiferromagnetic cation-anion-cation interactions<sup>56</sup>) and has properties that are reasonably quantitatively interpretable from the straightforward molecular-field theory of antiferromagnetism. On the other hand,  $\text{MnO}_2$  appears to have a screw-type order in which positive corner spins and negative body-centered spins are spiralled along the  $c$  axis with a screw-structure pitch  $3.5c$ , corresponding to  $J_2/J_1 = 1.60$ , where  $J_2$  is the antiferromagnetic (cation-cation) exchange interaction along the  $c$  axis,  $J_1$  is the antiferromagnetic (cation-anion-cation) exchange between corner and body-centered cations.<sup>56</sup> Further, Bizette's<sup>57</sup> observation of a resistivity maximum at  $T_N$  is attributed to effects similar to those referred to for  $\text{CrO}_2$ . A relatively low resistivity for  $\text{MnO}_2$  is attributed to the presence of some  $\text{Mn}^{3+}$  ions: Bizette points out that it is extremely difficult to obtain stoichiometric  $\text{MnO}_2$ .

#### D. NiAs-Type Compounds

There are many compounds with NiAs-type structure that have a complex magnetic behavior. Many of these properties appear to be complicated by the existence of cation-cation interactions. Discussion of this large class of compounds is deferred to a later publication.

<sup>51</sup> G. H. Jonker (private communication).

<sup>52</sup> R. R. Heikes, Phys. Rev. **99**, 1232 (1955).

<sup>53</sup> M. Griffel and J. W. Stout, J. Am. Chem. Soc. **72**, 4351 (1950).

<sup>54</sup> W. Zachariasen, Strukturbericht **1**, 213 (1931).

<sup>55</sup> R. A. Erickson, Phys. Rev. **9**, 779 (1953).

<sup>56</sup> A. Yoshimori, J. Phys. Soc. Japan **14**, 807 (1959).

<sup>57</sup> H. Bizette, J. phys. radium **12**, 161 (1951).