

Theory of Ionic Ordering, Crystal Distortion, and Magnetic Exchange Due to Covalent Forces in Spinel*

J. B. GOODENOUGH AND A. L. LOEB

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts

(Received September 1, 1954)

Elastic- and electrostatic-energy considerations are insufficient for an explanation of cation ordering between tetrahedral and octahedral sites in spinels. Tetrahedral, octahedral, and square covalent bonds are also important when cations are to be accommodated in these sites. The square bonds in octahedral sites can cause the tetragonal distortion observed in Mn_3O_4 , $\gamma\text{-Mn}_2\text{O}_3$, ZnMn_2O_4 , CuFe_2O_4 , CuCr_2O_4 , CaIn_2O_4 , CdIn_2O_4 , and metallic indium. A new magnetic exchange mechanism, "semicovalent exchange," which is consistent with the covalent model, is used to explain the magnetic properties of spinels.

I. INTRODUCTION

EXPERIMENTAL data on spinels indicate that the distribution of cations over tetrahedral and octahedral sites cannot be explained on the basis of electrostatic and elastic energies alone. Electronic bonding energies must be considered. Also, no explanation has yet been given for the difference between Fe_3O_4 , which alone transforms on cooling from a cubic to an orthorhombic spinel at a relatively low transition temperature, and other spinels, such as Mn_3O_4 , ZnMn_2O_4 , CuFe_2O_4 , which become on cooling tetragonal at a relatively high transition temperature. The tetragonality of metallic indium and of CaIn_2O_4 and CdIn_2O_4 have never been explained. For hausmannite there has been no definitive selection between the formulas $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ and $2\text{MnO} \cdot \text{MnO}_2$. The difference in resistivity discontinuities through the transition temperatures of Fe_3O_4 , on the one hand, and Mn_3O_4 and ZnMn_2O_4 , on the other, has not been explained. Neither has any explanation been given for the fact that Mn_3O_4 is paramagnetic at least down to 72°K despite the large magnetic moments of Mn^{2+} , Mn^{3+} , and Mn^{4+} ions. In this paper it is suggested that covalent forces are responsible for the above effects. A new magnetic-exchange mechanism, "semicovalent exchange," is proposed.

II. IONIC ORDERING

A. Description of Spinel

Many oxides consist of a face-centered cubic lattice of O^{2-} ions which is held together by interstitial cations. There are two kinds of interstices between the elements of such a lattice, tetrahedral interstices with four nearest neighbors and octahedral interstices with six nearest neighbors. If all the tetrahedral sites are empty and all the octahedral sites are filled, the crystal has the rock-salt structure; if only tetrahedral sites are occupied, the crystal has the zinc-blende structure. In oxides with the spinel structure there are cations in each type of interstice; twice as many octahedral as tetrahedral sites are occupied. The spinel lattice may be thought of as

an ordered mixture of the zinc-blende and rock-salt structure.

There are two general classes which have the spinel lattice, the 2-4 spinels with the formula $2\text{X}^{2+}\text{O} \cdot \text{Z}^{4+}\text{O}_2$ and the 2-3 spinels $\text{X}^{2+}\text{O} \cdot \text{Y}_2^{3+}\text{O}_3$. In order to describe the cation distribution, these formulas may be written as $\text{Z}(\text{X}_2)\text{O}_4$ or $\text{X}(\text{ZX})\text{O}_4$ and $\text{X}(\text{Y}_2)\text{O}_4$ or $\text{Y}(\text{XY})\text{O}_4$, where the ions within the parentheses occupy octahedral sites. If there is only one kind of cation in the octahedral sites, the spinel is called normal. If there are equal amounts of both kinds of cations in the octahedral sites, the spinel is inverse. If there is an unequal number of each kind of cation in the octahedral sites, the spinel is mixed.

B. Critique of Previous Work

Since the physical properties of any spinel depend not only on the kind of cations in the spinel but also on their distribution within the interstices, it is important to understand what forces are responsible for cation ordering within a lattice. Verwey and his co-workers¹⁻¹⁴ have made a study of the cation arrangement in oxides with spinel structure. A summary of the experimental determination of cation location is given in Table I.

Since the observed cation distributions do not always

¹ E. J. W. Verwey, *Z. Krist.* **91A**, 65 (1935).

² van Arkel, Verwey, and van Bruggen, *Rec. trav. chim.* **55**, 331 (1936).

³ Verwey, van Arkel, and van Bruggen, *Rec. trav. chim.* **55**, 340 (1936).

⁴ E. J. W. Verwey and J. H. de Boer, *Rec. trav. chim.* **55**, 531 (1936).

⁵ J. H. de Boer and E. J. W. Verwey, *Proc. Phys. Soc. (London)* **49A**, E59 (1937).

⁶ Verwey, Haayman, and Heilmann, *Philips Tech. Rev.* **9**, 185 (1947).

⁷ E. J. W. Verwey and E. L. Heilmann, *J. Chem. Phys.* **15**, 174 (1947).

⁸ Verwey, Haayman, and Romeijn, *J. Chem. Phys.* **15**, 181 (1947).

⁹ Verwey, de Boer, and van Santen, *J. Chem. Phys.* **16**, 1091 (1948).

¹⁰ de Boer, van Santen, and Verwey, *J. Chem. Phys.* **18**, 1032 (1950).

¹¹ J. H. van Santen, *Philips Research Repts.* **5**, 282 (1950).

¹² E. W. Gorter, *Compt. rend.* **230**, 192 (1950); *Nature* **165**, 798 (1950).

¹³ E. J. W. Verwey *et al.*, *Z. physik. Chem.* **198**, 6 (1951).

¹⁴ F. C. Romeijn, *Philips Research Repts.* **8**, 304 (1953).

* The research in this document was supported jointly by the Army, Navy, and Air Force under contract with the Massachusetts Institute of Technology.

TABLE I. Observed cation distributions in some oxides with the spinel structure.^a

X ²⁺	Y ³⁺ or Z ⁴⁺ Ionic radius ^b	Al ³⁺ 0.57	V ³⁺ 0.66	Cr ³⁺ 0.64	(Mn ³⁺) 0.70	Fe ³⁺ 0.67	Rh ³⁺ 0.69	Ga ³⁺ 0.62	In ³⁺ 0.92	Ge ⁴⁺ 0.44	Sn ⁴⁺ 0.74	Ti ⁴⁺ 0.64	Si ⁴⁺ 0.39	V ⁴⁺ 0.61
Mg ²⁺	0.78	N ^c	N ^d	N ^e		I ^{†f}	N ^g	I ^{†h}	I ^{†i}	O ^c		I ^c	O ⁱ	I ^g
Mn ²⁺	0.91	N ^c	N ^d	N ^e	(N) ^e	I ^e								
Fe ²⁺	0.83	N ^c	N ^d	N ^e		I ^e								
Co ²⁺	0.82	N ^c		N ^e		I ^e								
Ni ²⁺	0.78	$\frac{1}{2}N\frac{3}{4}I^e$		N ^e		I ^e				N ^c	I ^e	I ^c		
Cu ²⁺	(0.70?)	[N] ^j		I ^k		I ^{†e}				N ^c				
Zn ²⁺	0.83	N ^c	N ^d	N ^g	(N) ^e	N ^e	N ^g	[N] ^l			I ^f	I ^c	P ⁱ	
Cd ²⁺	1.03	N ^c		N ^e		N ^e		N ^g	[N] ^j					
Li ⁺	0.78	Al(Li ₁ Al ₁)O ₄ ^e		Fe ₃ Li ₃ (Cr ₂)O ₄ ^e				Fe(Li ₁ Fe ₁)O ₄ ^e						

^a [N] means normal structure inferred, cation distribution not experimentally established. Distributions marked with daggers are not entirely inverse; the number of divalent ions in the tetrahedral sites are temperature-dependent. The letters N, I, O, P refer to normal-spinel, inverse-spinel, olivine, and phenacite structures, respectively.

^b Atomic Radii: *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, 1953-1954), thirty-fifth edition. Goldschmidt values wherever available.

^c F. C. Romeijn, Philips Research Repts. 8, 304 (1953).

^d G. H. B. Lovell, Trans. Brit. Ceram. Soc. 50, 315 (1951).

^e E. J. W. Verwey and E. L. Heilmann, J. Chem. Phys. 15, 174 (1947).

^f T. F. W. Barth and E. Posnjak, Z. Krist. 82, 325 (1932).

^g W. Rüdorff and B. Reuter, Z. anorg. Chem. 253, 177, 194 (1947).

^h F. Machatschki, Z. Krist. 82, 348 (1932).

ⁱ A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, London, 1950), second edition.

^j L. Passerini, Gazz. chim. ital. 60, 389, 754 (1930).

^k McGuire, Howard, and Smart, Ceram. Age 60, 22 (1952).

^l F. Buschendorf, Z. physik. Chem. (B) 14, 297 (1931).

coincide with their predictions, which were based only on the electrostatic and elastic forces in a purely ionic model, Verwey and Heilmann⁷ suggested that the anomalies could be accounted for by the stability of the tetrahedral covalent bonds which form about certain cations when located in tetrahedral interstices.

Romeijn¹⁴ has suggested that ions with a noble-gas outer-electron-shell structure, such as Mg²⁺, Al³⁺, and Ti⁴⁺, are less compressible than ions with a full or half-filled *d*-shell, such as Zn²⁺, Cd²⁺, Ga³⁺, In³⁺, Ge⁴⁺, Sn⁴⁺, Mn²⁺, and Fe³⁺, so that the latter group is more easily accommodated in tetrahedral sites than is the former. It is not obvious why a full or half-filled *d* shell should be more compressible than a noble-gas shell. However, since the outer electron shells in noble-gas structures are separated from the next higher energy levels by a considerable energy gap, they do not provide empty orbitals for the formation of covalent bonds. In transition metals the *nd* and (*n*+1)*s* orbitals differ very little in energy. Covalent bonds are therefore easily formed, and since covalent bonds involve orbital overlap, they are shorter than electrovalent bonds. Therefore the ions with outer *d* shell appear more compressible than those with outer noble-gas shell.

Finally Romeijn¹⁴ and van Santen and van Wieringen¹⁵ considered the effect on electronic binding energies of crystalline fields in ionic crystals of cubic symmetry. They stated that the *d* shell splits in such a field into two set of orbitals, one extending along the <111> directions, the other in the <100> directions.¹⁶ Van Santen and van Wieringen assumed that the former is more stable when the outer electron configuration of the cation is *d*³ or *d*⁸ (as in Mn⁴⁺, Cr³⁺, and Ni²⁺), but that

the latter is more stable for the configuration *d*² or *d*⁷ (as in V³⁺ and Co²⁺). An ion with a stable <111> electron configuration would, according to van Santen and van Wieringen's express assumption of electrovalent bonding, fit more easily into an octahedral site where the electron charges of the cation can fit between the directed anion *p* orbitals without appreciable overlap. An ion with a stable <100> electron configuration would fit more easily into a tetrahedral site for an analogous reason.

The assumption regarding the relative stabilities of the *d*-shell bonds has never been substantiated. What is more important, however, is that the result of the overlapping of the filled oxygen *p* orbitals with the empty cation orbitals has been ignored. Such an overlap gives rise to coordinate covalence which reduces the polarity of the cation-anion bond, stabilizes the system, and reduces the effective anion radius. The influence of electrostatic and elastic energies on cation ordering is reduced. It will be shown below that if covalent considerations are used to supplement and modify the electrostatic and geometric considerations of the purely ionic model, the cation distributions in the spinel lattice can be readily accounted for without recourse to an assumption either with regard to the *d*-shell splitting of various atoms or to the compressibility of the *d* shell.

The cation distribution in a crystal is determined by its minimum free energy $A = E - TS$, where *T* is its absolute temperature, *S* is its entropy, and *E*, its internal energy, is the sum of an electrostatic contribution *E_i*, an elastic (Born-repulsion) contribution *E_r*, and an electronic-bonding and exchange contribution *E_e*. In the spinel lattice, covalence effects *E_i*, *E_r*, and *E_e*. In the absence of covalence *E_e* approximately equals zero. Covalent bonding makes *E_e* appreciably negative

¹⁵ J. H. van Santen and J. S. van Wieringen, Rec. trav. chim. 71, 420 (1952).

¹⁶ H. A. Bethe, Ann. Physik 3, 133 (1929).

and, by decreasing the ionic charge and bond length, alters the influence of E_i and E_r . Since disorder corresponds to high entropy and the entropy contribution (TS) increases with temperature, high temperatures tend to disturb ordering.

III. COVALENT BONDS

A. Introduction

It was pointed out in Sec. IIA, above, that spinels are an ordered mixture of the zinc-blende and rock-salt structures. It is expected that those metals whose oxides form the zinc-blende structure tend to occupy tetrahedral sites in spinels as they do in the oxides. Similarly metals whose oxides are of the rock-salt type tend to occupy octahedral sites. Frequently the relative stabilities of the two metals in a given interstice in the spinels must be compared before an actual prediction about their distribution over the two types of sites can be made.

The zinc-blende interionic bond is predominantly covalent if the cation is large. Purely ionic forces would place the cation in the interstices with the largest anion coordination, *viz.*, the octahedral position. The metals whose oxides have the zinc-blende structure are therefore expected to be covalently bound to tetrahedral sites when in a spinel lattice.

The octahedrally coordinated cations of the rock-salt structure may be either electrovalently or covalently bound to their near-neighbor anions. The relative strength with which a metal, whose simple oxide has the rock-salt structure, is held to an octahedral interstice in the spinel lattice depends upon the relative charge, size, and covalent-bonding of the competing cations. Cations which are more stable in octahedral sites in the simple oxides tend to go into octahedral sites, but may be forced into tetrahedral sites in the spinel lattice. Therefore both electrovalence and covalence may be found in each type of interstice. To distinguish between electrovalence and covalence, the valence of the former is written in Arabic numerals (e.g., Mg^{2+}), of the latter, in Roman numerals (e.g., Zn^{II}).

In spinel crystals the coordination of the close-packed-anion interstices limits the possible cation-anion bond types which can be formed. If the stable covalent-bond types which any cation forms can be independently determined, the anion interstices in which the steric constraints are compatible with stable covalent-bond formation are known. Measurements of the steric structure of complex ions containing a particular cation provide the necessary independent information since the complex-ion structure is primarily determined by the stable covalent-bond formation. Complex-ion structure is only secondarily effected by steric hindrance and the difference in the electronegativities of the components. The steric structure of complex ions can be determined by optical and by magnetic-sus-

ceptibility measurements.¹⁷ Thus a knowledge of complex-ion structure gives information about both the relative stabilities of a cation in octahedral vs tetrahedral coordination and the possible distortion of the steric constraints.

If covalent bonds are formed in the spinel lattice, both bonding electrons come from the anion, and the bond is coordinate-covalent. The near-neighbor anions perturb the cations so that they form stable, empty hybrid orbitals which overlap with the anion p orbitals. If the empty orbitals have energies which are nearly degenerate with the outermost filled orbitals, if the electronegativity difference between the ions is not too great, and if the orbital overlap is large, the empty cation orbitals interact with the full anion p orbitals to accept electrons from the anions. Then the anion p electrons are induced to share their time between the cation and the anion. If empty orbitals are not available for hybridization, half-filled orbitals can participate in covalence. However, filled cation orbitals obviously do not participate in covalent-bond formation.

B. The Oxygen Orbitals

The oxygen ion has the structure $1s^2 2s^2 2p^6$. The p orbitals are three mutually perpendicular dumbbells. In oxides with the spinel lattice each oxygen has four near-neighbor cations, of which three are in octahedral sites and the fourth is in a tetrahedral site. The three octahedral sites are situated along three mutually perpendicular directions from the oxygen; the tetrahedral site lies in the $\langle 111 \rangle$ direction away from the quadrant defined by the three octahedral sites. The oxygen can bond covalently with any or all of the octahedral-cation neighbors through its three p orbitals. In this case, however, there are no anion orbitals directed toward the tetrahedral site, and the tetrahedral-site cation-oxygen bond is ionic.

If the bond toward the tetrahedral site is covalent, the overlap of full oxygen orbitals with the empty orbitals of the octahedral-site cations is reduced since the oxygen p orbitals no longer point directly towards the cations. This reduction in orbital overlap reduces the strength of any covalent bonding in the octahedral sites.

Thus there is competition between the tetrahedral and octahedral sites for overlap with the full oxygen p orbitals. Unless strong covalence can occur simultaneously in both types of sites, there will be covalent bonding in, at most, one type of site only. If stable covalent bonds can be formed in both types of sites at once, hybrid (sp^3) orbitals, which point toward the four corners of a tetrahedron, may be admixed with the p^3 orbitals on the oxygen ion. Such orbitals do not overlap as much with the octahedral-cation orbitals as do the pure p^3 orbitals, and the strength of the octahedral-site

¹⁷ L. Pauling, *The Nature of the Chemical Bond* (Oxford University Press, London, 1948), second edition; J. Am. Chem. Soc. **53**, 1367 (1931).

covalent bond is reduced from the value it has when the tetrahedral-site bonds are ionic. A semiquantitative estimate of the proportionate reduction in octahedral-site covalent-bond strength due to simultaneous covalence in the tetrahedral sites is given later in Appendix I and Fig. 6.

C. Cation Hybrid Orbitals

There are three kinds of cation hybrid orbitals which are important in the spinel lattice where the steric constraints are due to the close packing about either tetrahedral or octahedral interstices. If either steric hindrance or too large differences in electronegativities prevent hybrid covalent-bond formation, ionic bonds are formed. The important cation hybrid orbitals have tetrahedral, octahedral, or square configurations.

1. Tetrahedral Orbitals

The tetrahedral orbitals result from the hybridization of (sp^3) orbitals.¹⁷ These point toward the four corners of a tetrahedron. They are predominantly formed in cations with a full d shell which is separated in energy by only a small interval from the next empty s and p shells. Tetrahedral coordination is common for Zn^{II} and Cd^{II} , for instance. The strength of these covalent bonds decreases with increasing atomic number of the cation and decreasing atomic number of the anion in any one column of the periodic table.

There is some evidence that Fe^{3+} and Mn^{2+} , each with a half-full, spherically symmetric d shell, form bonds which are partially covalent. Although these ions form ionic bonds in Fe_2O_3 and MnO , the wurtzite structure of one phase of MnS indicates that the possibility of covalent-bond formation is by no means negligible. In the tetrahedral sites of the spinel lattice, where the steric constraints favor the formation of tetrahedral covalent bonds, these ions undoubtedly form bonds with a partially covalent character. Evidence for this lies not only in the fact that the ferrosinels are frequently inverse, with a definite tendency for Fe^{III} ions to go into the tetrahedral sites, but also in the observation that inverse ferrosinels have a lattice parameter which is roughly 0.06 Å smaller than would be expected if the lattice were normal.⁷ This reduction in lattice parameter could be due to a shorter cation-anion bond for Fe^{III} in the tetrahedral sites than Fe^{3+} in the octahedral sites, the difference in bond length indicating the degree of covalence in the tetrahedral bonds.

2. Octahedral Orbitals

The octahedral, hybrid (d^2sp^3) orbitals occur in the transition elements which have partially filled d shells. In this case six bonds are directed toward the centers of six faces of a cube. These bonds are not easily identified since they are accommodated, without distortion, in an octahedral site just as are ions which form predominantly ionic bonds. These bonds would form most readily

about cations with an outer configuration d^3 or d^8 . If an ion with electron configuration d^6 forms an ionic bond in an octahedral site, it contributes 4.90 Bohr magnetons to the magnetic susceptibility whereas it contributes no paramagnetic moment if it is bound covalently.¹⁷ The bond cannot be partially ionic and partially covalent since this would require mixing two states of different electron spin. In complex ions like $[Fe(CN)_6]^{4-}$ the Fe^{II} forms covalent bonds, but in the oxides the large electronegativity of the oxygen ions causes Fe^{2+} to form ionic bonds. In d^3 ions like Cr^{III} and V^{II} , however, there is no spin change involved in changing from ionic to covalent bonding so that partially covalent bonds can be formed which cannot be distinguished from ionic bonds by magnetic measurements. It is probable that these ions are stabilized in the octahedral sites by partial covalent-bond formation.

3. Square Orbitals

Finally there are the square, coplanar (dsp^2) orbitals which point toward the four corners of a square. These occur in the transition elements that have one d orbital available for hybridization, such as cations with outer electron configuration d^4 , d^8 , or d^9 . Cations which form square, covalent bonds can be accommodated in an octahedral site.

The cation Cu^{II} is known to form square bonds in complex ions,¹⁸ cupric oxide,¹⁹ and cupric salts.¹⁹ Although the Cu^{II} cation may, theoretically, form either four tetrahedral (sp^3) orbitals or four square (dsp^2) orbitals, the square-bond formation in CuO clearly indicates that the latter bond type is the more stable bond for Cu^{II} in an oxide lattice. Therefore the Cu^{II} cation is more stable in the octahedral sites of the spinel lattice where the steric constraints favor the formation of square bonds.

Since cations with the outer electron configuration d^8 can accommodate at most only ten additional electrons in a hybrid dsp shell, their maximum coordination number is five. Therefore they cannot form octahedral (d^2sp^3) bonds since this would require exciting two electrons to some higher energy level. Since there are two vacancies in the d shell, square (dsp^2) orbitals can be formed. In order to hybridize such orbitals, however, the cation must reverse one electron spin to reduce its paramagnetic moment to zero. There are many nickel, palladium, and platinum complexes,^{17,19} such as $[Ni(CN)_4]^{2-}$, which are both coplanar and diamagnetic. It is significant that in their cyanide complexes Ni^{II} has coordination number four whereas Fe^{II} and Fe^{III} have coordination number six. Because an electron spin is reversed when d^8 cations form covalent bonds, the bonds these cations form are either covalent or ionic, but never a mixture of the two. Since NiO has the rock-salt

¹⁸ D. P. Mellor and D. P. Craig, Proc. Roy. Soc. (N. S. Wales) 75, 27 (1941).

¹⁹ A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, London, 1950), second edition.

structure with the Ni^{2+} electrovalently bonded, it may be assumed that Ni^{2+} forms electrovalent bonds in the oxides with the spinel structure. The large difference in electronegativities between nickel and oxygen is the decisive factor favoring ionic-bond formation. Palladium, however, is less electropositive than nickel and does form square bonds in PdO . If Pd^{II} were in a spinel, it should form square bonds in the octahedral sites.

Cations with the outer electron configuration d^4 , such as Mn^{3+} , can hybridize empty (dsp^2) orbitals for coordinate covalence without altering their paramagnetic moment. Since it would require energy to reverse an electron spin to form (d^2sp^3) orbitals, the square bond is the most stable covalent-bond configuration. These ions can be accommodated in octahedral sites with the formation of partially or completely covalent bonds.

D. Summary

In Table II there is a summary of the covalent-bond strengths and the cation distributions favored by the covalent forces. The strength estimates depend, of course, upon the relative sizes of the cations and the interstices. They also depend upon the electronegativity difference between the anions and the cations. Finally, they depend upon the strength of the covalent bond in the opposite set of lattice sites. If a bond cannot be partially covalent, covalent effects have no influence unless the bond is completely covalent. If such a bond is marked "weak" in Table II it means it has a small chance of being completely covalent. If such a covalent bond is formed, however, its influence is strong.

As a rule of thumb, it is suggested that the covalent forces be considered first in any prediction of the cation distribution in a spinel lattice. If these are weak, the energy term E_e may be neglected and the Madelung energy and geometrical considerations of Verwey and his co-workers may be used. If the covalent forces are moderate or strong, these are usually the predominant ordering influence. With such a simple, qualitative rule, all of the observed structures given in Table I, except $\text{Co}(\text{CoSn})\text{O}_4$, can be predicted. Since the Madelung energy strongly favors the observed structure in $\text{Co}(\text{CoSn})\text{O}_4$, it is concluded that the covalent forces, which are weaker in this instance than when associated with any of the other Group IV cations, are not sufficiently strong to reverse the order.

Mg_2GeO_4 and MgSiO_4 have the olivine structure. The olivine structure may be described either as an assembly of $[\text{GeO}_4]^{4-}$ or $[\text{SiO}_4]^{4-}$ groups with the Mg^{2+} ions between them, or as an infinite array of approximately close-packed oxygen ions with Ge^{IV} or Si^{IV} in tetrahedral and Mg^{2+} in octahedral interstices. This structure is analogous to the spinel. It differs, however, in that the tetrahedral bonding is so much stronger than the octahedral bonds that the cubic close packing of the oxygen ions is distorted.

The phenacite structure, which is formed by Zn_2SiO_4 , has a tetrahedral coordination about both the Zn^{II} and the Si^{IV} cations. The $\text{Si}-\text{O}$ and $\text{Zn}-\text{O}$ covalent bonds are apparently sufficiently strong to force all the cations into tetrahedral sites and distort the oxygen lattice from close packing.

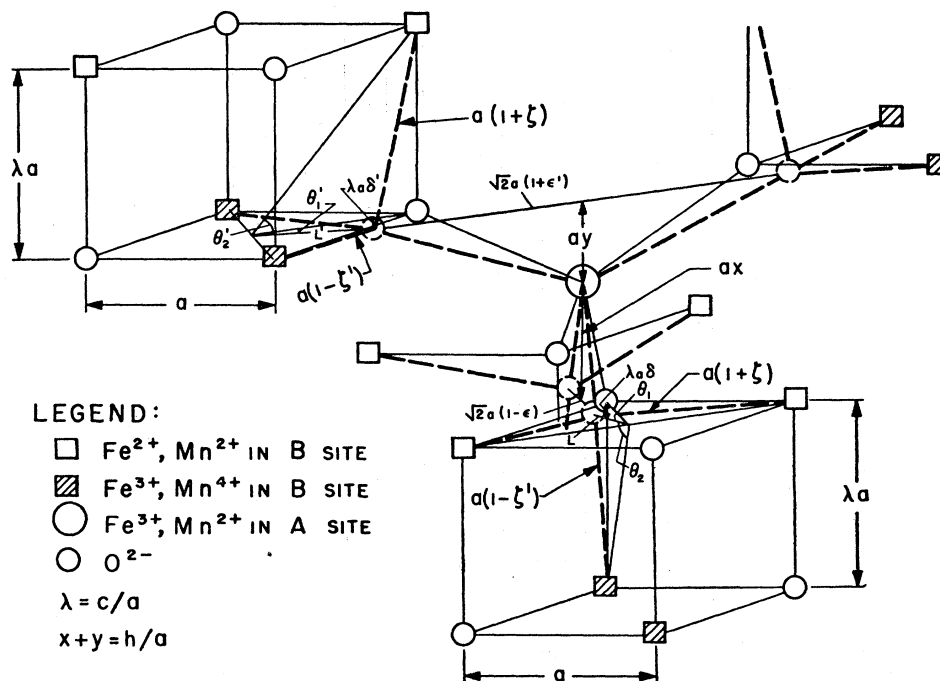


FIG. 1. Ionic model of distortion to tetragonal symmetry due to ordering of B-site ions.

TABLE II. Estimated strengths for possible covalent forces in spinel lattices and predicted magnetic moments in Bohr magnetons for cations bonded in various ways.

A. Transition cations.

Config.	Cations	Orbitals	Electron-spin config. ^a								Estimated strength ^b	Magnetic moment	
			d				s	p					
d ⁰	Ti ^{IV} V ^V Cr ^{VI}	Tet. (sp ³)						↑↑	↑↑	↑↑	↑↑	Moderate	0
	Zr ^{IV} Nb ^V Mo ^{VI}	Oct. (d ² sp ³)	↑↑	↑↑				↑↑	↑↑	↑↑	↑↑	Very weak	0
	Hf ^{IV} Ta ^V W ^{VI}	Sq. (dsp ²)	↑↑					↑↑	↑↑	↑↑		Very weak	0
d ¹	V ^{IV}	Tet. (sp ³)	→					↑↑	↑↑	↑↑	↑↑	Weak	1.73
	Nb ^{IV} Mo ^V	Oct. (d ² sp ³)	→	↑↑	↑↑			↑↑	↑↑	↑↑	↑↑	Very weak	1.73
	W ^V	Sq. (dsp ²)	→	↑↑				↑↑	↑↑	↑↑		Very weak	1.73
d ²	V ^{III} Cr ^{IV}	Tet. (sp ³)	→	→				↑↑	↑↑	↑↑	↑↑	Very weak	2.83
	Mo ^{IV} Ru ^{VI}	Oct. (d ² sp ³)	→	→	↑↑	↑↑		↑↑	↑↑	↑↑	↑↑	Weak	2.83
	W ^{IV} Os ^{VI}	Sq. (dsp ²)	→	→	↑↑			↑↑	↑↑	↑↑		Very weak	2.83
d ³	V ^{II} Cr ^{III} Mn ^{IV}	Tet. (sp ³)	→	→	→			↑↑	↑↑	↑↑	↑↑	Very weak	3.88
	Mo ^{III}	Oct. (d ² sp ³)	→	→	→	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	Moderate	3.88
		Sq. (dsp ²)	→	→	→	↑↑		↑↑	↑↑	↑↑		Weak	3.88
d ⁴	Cr ^{II} Mn ^{III} Fe ^{IV}	Tet. (sp ³)	→	→	→	→		↑↑	↑↑	↑↑	↑↑	Weak	4.90
	Mo ^{II} Ru ^{IV}	Oct. (d ² sp ³)	→	→	→	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	Very weak	2.83
	Os ^{IV}	Sq. (dsp ²)	→	→	→	↑↑		↑↑	↑↑	↑↑		Strong	4.90
d ⁵	Mn ^{II} Fe ^{III} Co ^{IV}	Tet. (sp ³)	→	→	→	→	→	↑↑	↑↑	↑↑	↑↑	Moderate	5.91
	Ru ^{III}	Oct. (d ² sp ³)	→	→	→	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	Very weak	1.73
	Os ^{III} Ir ^{IV}	Sq. (dsp ²)	→	→	→	↑↑		↑↑	↑↑	↑↑		Very weak	3.88
d ⁶	Fe ^{II} Co ^{III}	Tet. (sp ³)	↑↑	→	→	→	→	↑↑	↑↑	↑↑	↑↑	Weak	4.90
	Ru ^{II} Rh ^{III} Pd ^{IV}	Oct. (d ² sp ³)	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	Weak	0
	Ir ^{III} Pt ^{IV}	Sq. (dsp ²)	↑↑	↑↑	→	→		↑↑	↑↑	↑↑		Very weak	2.83
d ⁷	Co ^{II} Ni ^{III}	Tet. (sp ³)	↑↑	↑↑	→	→	→	↑↑	↑↑	↑↑	↑↑	Weak	3.88
	Rh ^{II}	Sq. (dsp ²)	↑↑	↑↑	↑↑	→		↑↑	↑↑	↑↑		Weak	1.73
d ⁸	Ni ^{II}	Tet. (sp ³)	↑↑	↑↑	↑↑	→	→	↑↑	↑↑	↑↑	↑↑	Weak	2.83
	Rh ^I Pd ^{II} Ag ^{III}	Sq. (dsp ²)	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑		Moderate	0
	Pt ^{II} Au ^{III}												
d ⁹	Cu ^{II}	Tet. (sp ³)	↑↑	↑↑	↑↑	↑↑	→	↑↑	↑↑	↑↑	↑↑	Moderate	1.73
		Sq. (dsp ²)	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	→	Strong	1.73

^a Solid arrows refer to cation-electron spins; dashed arrows to spins of anion electrons entering into coordinate covalence.^b Strength estimates are modified by (1) relative size of interstice and cation (i.e., amount of orbital overlap), (2) difference in electronegativities of cation and anion, (3) type of bonding in other interstices, and (4) the atomic weight of the cation.

TABLE II (continued).

B. Other cations

Cation	Estimated strength ^a	Cation	Estimated strength ^a
Li ⁺	Electrovalent	Ga ³⁺	Mod. strong tet. (<i>sp</i> ³)
Mg ²⁺	Electrovalent	In ³⁺	Mod. tet. (<i>sp</i> ³) and sq. (<i>dsp</i> ²)
Al ³⁺	Electrovalent	(C ⁴⁺)	Extremely strong tet. (<i>sp</i> ³)
Zn ²⁺	Strong tet. (<i>sp</i> ³)	Si ⁴⁺	Very strong tet. (<i>sp</i> ³)
Cd ²⁺	Strong tet. (<i>sp</i> ³)	Ge ⁴⁺	Strong tet. (<i>sp</i> ³)
Hg ²⁺	Mod tet. (<i>sp</i> ³)	Sn ⁴⁺	Mod tet. (<i>sp</i> ³)

^a Strength estimates are modified by (1) relative size of interstice and cation (i.e., amount of orbital overlap), (2) difference in electronegativities of cation and anion, (3) type of bonding in other interstices, and (4) the atomic weight of the cation.

IV. LATTICE DISTORTION

It is proposed that in spinels the lattice distortions to tetragonal symmetry are due to covalent-bond formation whereas those to orthorhombic symmetry are due to cation ordering in the octahedral sites. In Sec. A, below, there is a discussion of the distortions due to ionic ordering. In Sec. B there is a theoretical discussion of tetragonal distortion due to coplanar covalent-bond formation and an application of the theory to CuFe₂O₄. In Sec. C both models are applied to spinels containing manganese. Experimental observations are shown to be consistent with the covalent model. In Sec. D it is proposed that the indates and metallic indium are also distorted by covalent-bond formation.

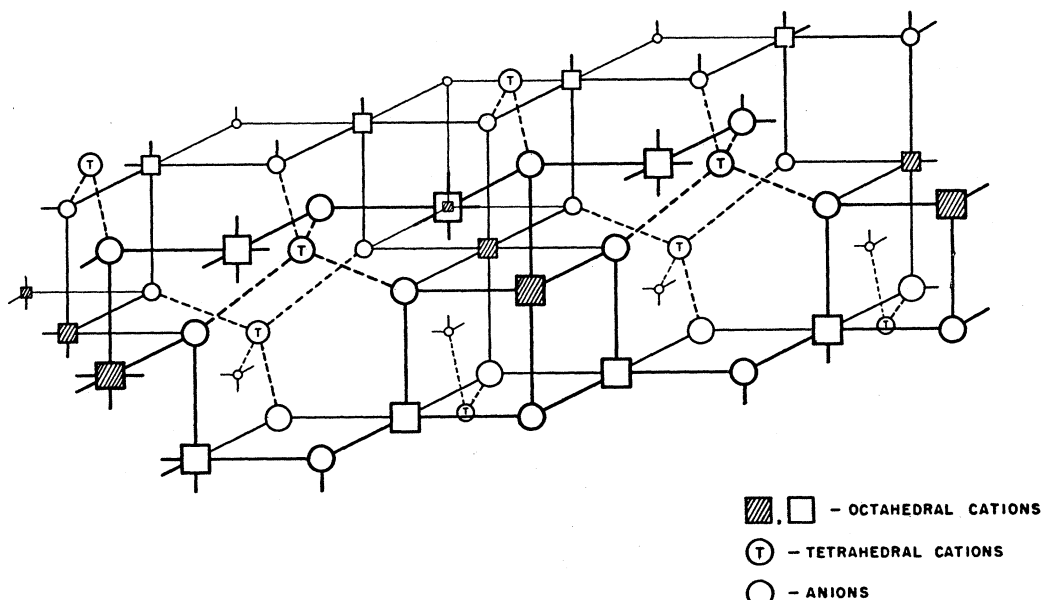
A. Lattice Distortion and Ionic Ordering

Since 1929^{20,21} it has been known that magnetite (Fe₃O₄) undergoes a phase transition as the temperature

is raised through 119°K. This phase transition produces a ninety-fold increase in the electrical conductivity over the temperature range $118.9^{\circ}\text{K} \leq T \leq 119.9^{\circ}\text{K}$.^{8,22} After Verwey and de Boer⁴ had determined that Fe₃O₄ is inverse, Verwey²³ suggested that below the transition temperature the Fe²⁺ and Fe³⁺ ions in the octahedral sites are ordered in alternating planes perpendicular to the *c* axis. Above the transition temperature disorder is produced by the movement of electrons between Fe²⁺ and Fe³⁺ ions. The transition temperature is low because the transition is electronic, rather than ionic.

If the lattice distortion below 120°K is due to cation ordering in an ionic lattice, it should be possible to calculate the ordered-phase lattice parameters from a knowledge of the ionic radii. Verwey predicted that a tetragonal distortion would result if there was an ordering of Fe²⁺ and Fe³⁺ cations into alternate planes of octahedral, or *B*, interstices. Such a distortion would be possible only in a purely ionic lattice in which the tetrahedral, or *A*, site is distorted as shown in Fig. 1. The generality of this distortion for all tetrahedral sites is apparent from the representation of the spinel structure in Fig. 2. Although, as was first suggested by Bickford,²⁴ orthorhombic symmetry will result if the tetrahedral site is not distorted as shown, there is no obvious reason why, if a purely ionic model is correct, a distortion to tetragonal symmetry should not occur provided the oxygen-oxygen separation is $\sqrt{2}a(1-\epsilon) > 2.64$ Å.

The cation-oxygen distance depends upon the size of the cation. If the Fe²⁺-O²⁻ distance is $a(1+\zeta)$ and the Fe³⁺-O²⁻ distance is $a(1-\zeta')$, then the distortion

FIG. 2. The spinel lattice with ordering in the *B* sites.

²⁰ P. Weiss and R. Forrer, Ann. phys. (10) 12, 279 (1929).

²¹ R. W. Millar, J. Am. Chem. Soc. 51, 215 (1929).

²² B. A. Calhoun, Phys. Rev. 94, 1577 (1954).

²³ E. J. W. Verwey, Nature 144, 327 (1939); E. J. Verwey and P. W. Haayman, Physica 8, 979 (1941).

²⁴ L. R. Bickford, Jr., Phys. Rev. 78, 449 (1950).

of the tetrahedral interstice can be calculated from the geometrically derived relations:

$$\begin{aligned} (1+\epsilon) &= [2(1+\zeta)^2-1]^{\frac{1}{2}} \cos\theta_1, \\ \lambda\delta &= [(1+\zeta)^2-\frac{1}{2}]^{\frac{1}{2}} \sin\theta_1, \\ (1-\epsilon') &= [2(1-\zeta')^2-1]^{\frac{1}{2}} \cos\theta_1', \\ \lambda\delta' &= [(1-\zeta')^2-\frac{1}{2}]^{\frac{1}{2}} \sin\theta_1', \end{aligned} \quad (\text{IV.1})$$

where $\lambda\delta$ and $\lambda\delta'$ give the displacement of the oxygen ion from the planes of Fe^{2+} and Fe^{3+} ions, respectively; $\sqrt{2}a(1-\epsilon)$ and $\sqrt{2}a(1+\epsilon')$ give the separations of the tetrahedral oxygens near the Fe^{2+} and the Fe^{3+} planes, respectively; and θ_1, θ_1' are the declination angles shown in Fig. 1. The height $h = (x+y)a$ of the distorted tetrahedron can then be calculated from the geometric relation,

$$(h/a) = x+y = [d^2 - \frac{1}{2}(1-\epsilon)^2]^{\frac{1}{2}} + [d^2 - \frac{1}{2}(1+\epsilon')^2]^{\frac{1}{2}}. \quad (\text{IV.2})$$

Since an ionic model is used, the tetrahedral-site $\text{Fe}^{3+}-\text{O}^{2-}$ separation, (ad), is assumed identical for each of the four oxygen ions. If the interionic distances are known, a self-consistent calculation for λ can be carried out provided use is made of the requirement,

$$(h/a) = \lambda(1+\delta-\delta'). \quad (\text{IV.3})$$

If the values $a(1+\zeta) = 2.15$ Å, $a(1-\zeta') = 2.09$ Å, $a = 2.10$ Å, and $d = \sqrt{3}/2$ are chosen, then the predicted axial ratio for the tetragonal lattice is $c/a = \lambda = 1.022$.²⁵

Although tetragonal symmetry can be predicted by a purely ionic model in which a close packing of hard spheres is envisaged, orthorhombic symmetry must result if covalent forces play a significant role in the tetrahedral-site bonds. Since the covalent-bond contributions which are formed by overlap of $\text{Fe}^{3+}(sp^3)$ hybrid orbitals and the oxygen p wave functions have their maximum strength for tetrahedral coordination, they resist any distortion of the tetrahedral bond angles. The cation-anion bond angles in the distorted tetrahedral interstice of Fig. 1 would be more nearly tetrahedral if x were reduced and y were increased, i.e., if the cation were located closer to the neighboring B -site plane perpendicular to the c axis which contains Fe^{2+} cations than that which contains Fe^{3+} cations. Thus the resistance to distortion of the tetrahedral covalent-bond angles forces apart the B -site- Fe^{2+} cations and forces together the B -site- Fe^{3+} cations. Since the ordered, B -site- Fe^{2+} cations are arranged in parallel rows which are perpendicular to the similar set of parallel Fe^{3+} ions in alternate planes (see Fig. 2), a separation of the Fe^{2+} cations and an approach of the Fe^{3+} cations produces a shear strain so that an orthorhombic distortion results. The reported distortion is of this type. Abrahams and Calhoun²⁶ have measured with x-rays the dimensions of the unit cell at 78°K. They reported the orthorhombic axes to be $a = 5.912$, $b = 5.945$, $c = 8.388$ Å.

²⁵ See Appendix II.

²⁶ S. C. Abrahams and B. A. Calhoun, *Acta Cryst.* **6**, 105 (1953).

This discussion leads to the generalization that if two kinds of cation occupy octahedral interstices and if they order in alternate planes perpendicular to some c axis, then the lattice will suffer a distortion to tetragonal or orthorhombic symmetry. The magnitude of the distortion will depend upon the difference in cation size, and the degree of orthorhombicity will increase with the strength of the covalent bonds in the tetrahedral interstices.

B. Lattice Distortion and Square-Bond Formation

1. Theory

If a cation hybridizes (dsp^2) orbitals to form four square, covalent bonds in an octahedral interstice of the spinel lattice, the steric constraints will permit covalent bonds to be formed in any one of the three biaxial planes of the site. At high temperatures the covalent bonds will resonate between the three possible biaxial planes. All six octahedrally directed bonds are partially ionic, partially covalent, and, since they are equivalent, the cubic symmetry of the interstice is preserved. Below some ordering temperature, however, the covalent bonds are frozen into one of the three biaxial planes, and the octahedral-site cation is bound to the six near-neighbor anions by four coplanar covalent bonds and two linear electrovalent bonds. Because of orbital overlap, the four coplanar covalent bonds are shorter than the two electrovalent bonds, and the elementary octahedron becomes distorted from cubic to tetragonal symmetry with an axial ratio $c/a > 1$. If the elementary octahedra have tetragonal symmetry, the elastic energy of the crystal is minimized when their tetragonal axes are aligned parallel to one another. This produces a distortion of the bulk lattice from cubic to tetragonal symmetry with an axial ratio $c/a > 1$.

If λ is the fraction of square-bond-forming cations in octahedral sites, there exists a value $\lambda = \lambda_0$ below which no distortion of the crystal occurs. For $\lambda < \lambda_0$ there is no alignment of tetragonally distorted octahedra to produce a bulk distortion of the lattice. For a tetragonal distortion of the crystal it is necessary to have a continuously linked system of square bonds. For such a long-range order to occur, each octahedral ion that does not form square bonds must, on the average, have at least two of its six octahedral near neighbors that do. Therefore, for tetragonal distortion of the crystal lattice to occur, at least 25 percent of the octahedral cations must form square bonds. This means that the minimum λ_0 equals 0.25.

If the band model is applied to the crystal, the highest occupied electron-energy band is the (dsp^2) covalent band. Because orbital overlap decreases with decreasing distortion, the energy of the (dsp^2) covalent band is raised with decreasing axial ratio so that it becomes easier to remove electrons from it. At high temperatures some of the electrons are thermally excited from the covalent band. However, when an electron is excited,

a hole is left in the covalent band so that the coplanar covalent bonds in some octahedral site become partially ionic. This ionic character resonates among three mutually perpendicular planes and reduces the difference between the character of the bonds parallel, and that of the bonds perpendicular, to the c axis so that the tetragonal distortion is reduced. This, in turn, facilitates the removal of an electron from the covalent band. Thus the loosening of the square bonds from the planes perpendicular to the c axis is a cooperative phenomenon, and the transition from the tetragonal to the cubic phase occurs over a small temperature interval when the sample is heated.

Conversely, if the sample is cooled from above the transition temperature, there is a temperature at which the covalent band is sufficiently full for some of the covalent bonds to become frozen into place. This "freezing in" of covalent bonds increases c/a and therefore the orbital overlap. An increase in the orbital overlap reduces the number of electrons which can be thermally excited from the covalent bond so that more covalent bonds are frozen in. Again there is a fairly sharp transition temperature, but, because of the difference in axial ratios, this temperature is lower than that observed when the sample is heated. This temperature difference shows up as a thermal hysteresis which varies in temperature change with the magnitude of the axial ratio of the tetragonal phase.

In an ordered-bond model there is a correlation between the lattice distortion and the excitation energy as measured by the temperature dependence of the conductivity. A conductivity discontinuity and thermal hysteresis at the transition temperature are correlated with the discontinuity and hysteresis in the axial ratio. Further, the excitation energy decreases slowly with increasing temperature so that a plot of the logarithm of the conductivity *vs* the reciprocal of the temperature does not give an ideally straight line.

According to the square-bond model the axial ratio c/a depends upon the ratio of the ionic-bond length to the covalent-bond length. In Sec. IIIB, above, it was shown that the amount of covalence in the octahedral site, and therefore the bond length, depends on the type of bond in the tetrahedral interstices. If strong tetrahedral, covalent bonds are formed in the tetrahedral sites, the octahedral bond becomes more ionic and its length is increased so that the c/a ratio is decreased. The magnitude of this decrease is estimated in Appendix I.

The transition temperature at which the phase change from tetragonal to cubic symmetry occurs varies with the magnitude of the electronic-excitation energy. Since the excitation energy varies with the magnitude of the axial ratio c/a , the square-bond model leads to the prediction that the transition temperature varies monotonically as the c/a of the tetragonal phase provided all other factors are constant.

In summary, the square-bond model leads to the

following predictions. (a) If cations (such as Cu^{II} , Mn^{III} , Pd^{II}) which form stable (dsp^2) bonds occupy octahedral sites in an oxide with the spinel structure, then the lattice is distorted to tetragonal symmetry with $c/a > 1$. (b) At least 25 percent of the octahedral cations must form square covalent bonds if lattice distortion due to a long-range order of bond orientation is to occur. (c) The magnitude of the axial ratio c/a increases with the number of cations in octahedral sites which form square bonds. However, strong covalence in tetrahedral sites reduces the covalence in octahedral sites and hence the axial ratio. (d) There is a narrow temperature interval through which c/a decreases rapidly to 1 to give cubic symmetry. (e) Through the transition temperature interval there is a marked increase in electric conductivity σ and a marked decrease in the excitation energy. (f) The transition temperature depends upon the magnitude of c/a at absolute zero. (g) The transition shows a thermal hysteresis. (h) The excitation energy decreases with increasing temperature.

2. Application of Theory to CuFe_2O_4

Bertaut²⁷ has measured the lattice parameter and the cation-ordering parameter λ in CuFe_2O_4 as a function of temperature. The parameter λ is the fraction of octahedral interstices occupied by M^{2+} ions; the ferromagnetic formula is therefore written as $\text{M}_{1-2\lambda}\text{Fe}_{2\lambda}(\text{Fe}_{2-2\lambda}\text{M}_{2\lambda})\text{O}_4$. The values $\lambda=0, \frac{1}{3}, \frac{1}{2}$ correspond, respectively, to a normal, statistically disordered, and inverse spinel. Bertaut observed that CuFe_2O_4 is tetragonal below 760°C . The axial ratio c/a and the parameter λ both decreased monotonically from room temperature to 700°C . Above 760°C the Cu^{2+} cations are randomly distributed in the anion interstices, and the lattice is cubic. It is especially interesting that Bertaut, who was convinced that the distortion to tetragonal symmetry was due to cation ordering, was unable to find any x-ray superstructure lines. The only ordering through the transition is a concentration of Cu^{2+} ions in the octahedral sites; among the octahedral sites, however, these ions are randomly distributed. Since the distortion is not accompanied by ion ordering among octahedral sites, it appears that the distortion is due to square-bond formation. Since the copper ions in CuO are Cu^{II} and form square, coplanar bonds, they undoubtedly form similar bonds in the spinel lattice. Because of the steric constraints, these bonds can only be formed if the Cu^{II} is in an octahedral site. If square covalent bonds are formed in an octahedral site, the elementary octahedron is distorted from cubic to tetragonal symmetry, and the alignment of these octahedra produces the macroscopic tetragonal symmetry of the crystal. This hypothesis is consistent with the observation of van Santen and van Wieringen¹⁵ that in CuFe_2O_4 the oxygen octahedron surrounding the Cu^{2+} ion is tetragonally distorted.

²⁷ E. F. Bertaut, J. phys. radium **12**, 252 (1951).

The correlation between the axial ratio and the concentration of copper in octahedral sites as functions of temperature can be explained on the basis of the square-bond model. At room temperature Bertaut found 88 percent of the copper in octahedral sites ($\lambda=0.44$) and an axial ratio $c/a=1.06$. At 700°C the concentration of copper in octahedral sites had decreased to 74 percent ($\lambda=0.37$) and the axial ratio to $c/a=1.035$. The fact that Cu^{II} migrates from octahedral to tetrahedral sites indicates that Cu^{II} can be readily accommodated in tetrahedral sites although, because of square-bond formation, it is more stable in octahedral sites. The increase in entropy due to this migration apparently offsets the corresponding decrease in internal energy. That the decrease in the number of square bonds in octahedral sites due to the Cu^{II} migration is accompanied by a decrease in the distortion is consistent with the covalent model.

Quantitative correlation between Bertaut's observed axial ratios and λ produces the relation,

$$(\lambda-0.26)=3(c-a)/a \text{ for } \lambda \geq 0.26. \quad (\text{IV.4})$$

The factor $(\lambda-0.26)$ is a measure of the stress induced by square-bond formation. The strain is given by $(c-a)/a$. Equation (IV.4) expresses a linear stress-strain relationship (Hooke's law). It also states that in CuFe_2O_4 it is necessary to have 26 percent of the octahedral sites occupied by Cu^{II} before tetragonal distortion sets in. This corresponds closely to the estimate that at least 25 percent of the octahedral cations must form square bonds. Equation (IV.4) can be used to extrapolate to the case of a completely inverse CuFe_2O_4 , for which $\lambda=0.5$. In this case half the octahedral sites contain Cu^{II} , and Eq. (IV.4) gives $c/a=1.08$. In a hypothetical spinel in which all octahedral sites are occupied by Cu^{II} ions and in which no covalent bonding exists in tetrahedral sites, there are twice as many square bonds in the octahedral sites so that $c/a=1.16$. This latter value is significant for comparison with the axial ratios of other tetragonal spinels which are thought to have square-bond formation in all the octahedral interstices.²⁸

C. Tetragonal Spinel Containing Manganese

Hetaerolite (ZnMn_2O_4) and hausmannite (Mn_3O_4) each form a spinel lattice with tetragonal symmetry. Their axial ratios are reported as $c/a=9.23 \text{ \AA}/8.08 \text{ \AA}=1.14$,²⁹ and $c/a=9.42 \text{ \AA}/8.14 \text{ \AA}=1.16$,^{29,30} respectively. Mason²⁹ and Romeijn¹⁴ have determined that the Zn^{II} cations of hetaerolite are in the tetrahedral interstices. This cation arrangement corresponds to the optimum configuration for covalent bonding (see Table II) as well

as for Madelung energies. Since the Mn^{II} cations may also form partially covalent bonds in tetrahedral interstices, it may be analogously assumed that in the hausmannite lattice Mn^{II} cations occupy tetrahedral interstices. This means that there are only two possible cation arrangements for these tetragonal spinels, *viz.*, $\text{Zn}^{2+}(\text{Mn}^{2+}\text{Mn}^{4+})\text{O}_4$ or $\text{Zn}^{2+}(\text{Mn}_2^{\text{III}})\text{O}_4$ for hetaerolite and $\text{Mn}^{2+}(\text{Mn}^{2+}\text{Mn}^{4+})\text{O}_4$ or $\text{Mn}^{2+}(\text{Mn}_2^{\text{III}})\text{O}_4$ for hausmannite. If the former arrangement is correct, then the distortion to tetragonality might be due to an ordering of Mn^{2+} , Mn^{4+} cations in alternating planes perpendicular to the c axis. Such a model was first proposed for hausmannite by Verwey.¹³ If the latter arrangement is correct, then some mechanism other than ionic ordering, such as square-bond formation, must be responsible for distorting the lattice to tetragonal symmetry. Since it is impossible to distinguish between Mn^{2+} , Mn^{3+} , and Mn^{4+} by x-rays, it is necessary to use other measurements to distinguish between the two alternatives. Before the predictions on the basis of the two models are compared with various measurements, however, it should again be pointed out that Mn^{3+} has the electron configuration d^4 which, according to Sec. III, is particularly suited for the hybridization of empty (dsp^2) orbitals for coordinate-covalent square-bond formation. The square-bond model is, therefore, particularly satisfactory for spinels which contain Mn^{3+} , or rather Mn^{III} . Seven physical properties are discussed below.

1. Tetragonal Symmetry

The distortions to tetragonal symmetry in both hetaerolite and hausmannite must be caused by the same mechanism. Since Zn^{II} , which is well known to form tetrahedral covalent bonds, is tetrahedrally coordinated in hetaerolite, the tetrahedral-site bonds are certainly largely covalent. Therefore if the lattice distortion from cubic symmetry were due to an ordering of Mn^{2+} and Mn^{4+} ions in the octahedral interstices, the lattice would have orthorhombic symmetry as in Fe_3O_4 . However, the lattice has tetragonal symmetry.

If the square-bond model is correct, then hetaerolite, which has strong covalent bonding in both the tetrahedral and octahedral interstices, should have a smaller axial ratio than hausmannite which has strong covalent bonds only in the octahedral sites. The calculation of Appendix I shows that a reduction from $c/a=1.16$ to $c/a=1.14$ is the order of axial-ratio reduction to be expected.

Further, an axial ratio $c/a=1.16$ for hausmannite, which forms square bonds in each occupied octahedral site and no covalent bonds in the tetrahedral sites, is exactly the ratio which is predicted from the extrapolation of the CuFe_2O_4 data.

2. Transition Temperatures

The transition of Mn_3O_4 from tetragonal to cubic symmetry was first observed at 1170°C by McMurdie

²⁸ McGuire *et al.*, *Ceram. Age* **60**, 22 (1952), report that CuCr_2O_4 is also an inverse, tetragonal spinel with $c/a=1.1$. Its axial ratio varies with temperature in an analogous manner to that of CuFe_2O_4 .

²⁹ B. Mason, *Am. Mineralogist* **32**, 426 (1947).

³⁰ G. Aminoff, *Z. Krist.* **64**, 475 (1926).

and Golovato³¹ who used a high-temperature x-ray technique. Romeijn¹⁴ has measured the dc conductivity of Mn_3O_4 and ZnMn_2O_4 and found a conductivity discontinuity in the temperature intervals $1075^\circ\text{C} \leq T \leq 1150^\circ\text{C}$ and $950^\circ\text{C} \leq T \leq 1025^\circ\text{C}$ for the respective materials.

Although the Madelung bonding energy of the completely ordered state of Fe_3O_4 is 39.6 kcal/mole¹⁰ greater than that of the disordered state, whereas the thermal energy corresponding to a transition temperature of $T=120^\circ\text{K}$ is 0.23 kcal/mole, the retention of considerable short-range order above 120°K can account for this discrepancy. If the phase transition to cubic symmetry were due to the same mechanism in Mn_3O_4 as in Fe_3O_4 , then the transition temperature should be approximately four times higher in the 2-4 spinels since the Madelung-energy change due to octahedral-site ordering is four times as great. There is no reason to assume that the retention of short-range order above the transition temperature should be strikingly different in Mn_3O_4 than in Fe_3O_4 . The analogous transition temperature for Mn_3O_4 would be 480°K , a value which is only a third of the observed transition temperature of 1443°K .

Since the covalent model offers an entirely different mechanism for lattice distortion, no correlation between the transition temperature of Fe_3O_4 and Mn_3O_4 is to be expected. There should, however, be a correlation of transition temperatures among the tetragonal spinels. On the basis of the square-bond model, the transition temperature varies with the magnitude of the axial ratio. This prediction is consistent with observations on CuFe_2O_4 , ZnMn_2O_4 , and Mn_3O_4 whose transition temperatures are 760°C , 1025°C , and 1170°C , corresponding to axial ratios 1.06, 1.14, and 1.16, respectively.

3. Conductivity Discontinuity

Romeijn¹⁴ has measured the conductivity of Mn_3O_4 and ZnMn_2O_4 as a function of temperature and found that there is a conductivity and excitation-energy discontinuity associated with the phase change from tetragonal to cubic symmetry. Although there is a similar effect in Fe_3O_4 , the discontinuity in magnetite occurs over a 1°C interval and exhibits no thermal hysteresis, whereas the manganate discontinuities occur over a 75°C interval, are considerably less pronounced, and exhibit a marked thermal hysteresis.

This contrast again corroborates the hypothesis that the phase transition in magnetite is due to a different mechanism than that in the manganates. The observed thermal hysteresis and resistivity discontinuity are greater in Mn_3O_4 than in ZnMn_2O_4 . Also, the excitation-energy discontinuity is greater in Mn_3O_4 . Such a correlation was predicted in Sec. B by means of the covalent model.

³¹ H. F. McMurdie and E. Golovato, J. Research Natl. Bur. Standards **41**, 589 (1948).

4. Resistivity at Room Temperature

Verwey and de Boer⁴ investigated the electrical resistivity of hausmannite at room temperature and found that it was 10^8 to 10^9 that of Fe_3O_4 . Romeijn reported $\rho(\text{Mn}_3\text{O}_4)/\rho(\text{Fe}_3\text{O}_4) \approx 10^7$ ohm-cm/ 5×10^{-3} ohm-cm = 2×10^9 . The relatively high conductivity of $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$ is due to the transfer of electrons from octahedral Fe^{2+} to octahedral Fe^{3+} ions. In $\text{Mn}^{2+}(\text{Mn}^{2+}\text{Mn}^{3+})\text{O}_4$ there is no exchange of electrons possible, and the observed high resistivity follows.

5. Paramagnetism of Mn_3O_4

If Mn_3O_4 consists of $\text{Mn}^{2+}(\text{Mn}^{2+}\text{Mn}^{4+})\text{O}_4$, there should be an antiferromagnetic coupling between the octahedral and tetrahedral Mn^{2+} cations which is comparable in strength to that between the Fe^{3+} cations in Fe_3O_4 . However, Mn_3O_4 is paramagnetic at room temperature, and Millar³² has measured the specific heat from 72°K to room temperature and found no λ -point in this range.

It will be shown in Sec. V, below, that paramagnetism in Mn_3O_4 follows from the covalent model.

6. γ - Mn_2O_3

The oxide γ - Mn_2O_3 is a spinel with 8/3 cation vacancies per unit cell. It has tetragonal symmetry with an axial ratio $c/a=1.16$.⁴ This is the same axial ratio as that found in Mn_3O_4 ; the mechanism which produces the distortion to tetragonal symmetry is apparently the same in each case.

If the distortion mechanism consists of an ordering of Mn^{2+} and Mn^{4+} ions in the octahedral interstices, then γ - Mn_2O_3 must have a unit cell with eight Mn^{4+} ions in octahedral sites and (8/3) Mn^{2+} ions in tetrahedral sites. The (32/3) Mn^{2+} would be distributed over the remaining interstices of each type. Such a configuration, however, would minimize neither the Madelung energy, which favors all the Mn^{4+} ions in octahedral sites, nor any covalent-energy contribution due to tetrahedral-bond formation, which favors Mn^{2+} ions in the tetrahedral interstices. It is difficult to see, therefore, how such a cation distribution could possibly represent the minimum-energy configuration.

In the covalent model, on the other hand, all the cations are Mn^{3+} , or Mn^{III} , and the distortion is due to square-bond formation in the octahedral sites. If the Mn^{III} form square, quadricovalent bonds in the octahedral sites, the manganese ions are more stable in these lattice positions, and the correct formula for γ - Mn_2O_3 is $\text{Mn}_{2/3}(\text{Mn}_2)\text{O}_4$. All the vacancies are in the tetrahedral sites, and the axial ratio should, as it does, equal the value 1.16 which was calculated in Sec. IV B. Finally, the observed high electric resistivity⁴ must follow as the covalent bond is full, and there is only one type of cation present.

³² R. W. Millar, J. Am. Chem. Soc. **50**, 1875 (1928).

7. Lattice Parameters

If the distortion to tetragonal symmetry in Mn_3O_4 is due to the formation of square, covalent bonds about Mn^{3+} ions in the octahedral interstices, then the a -axis is a measure of the covalent-bond length and the c -axis is a measure of the ionic-bond length. If the cubic symmetry above the transition temperature is due to a resonance of the coplanar bonds among the three biaxial planes of the octahedral interstices, then the lattice parameter above the transition temperature is the measure of a bond length which is $\frac{2}{3}$ covalent and $\frac{1}{3}$ ionic. At room temperature $c=9.42$ Å and $a=8.14$ Å, so that the equivalent cubic lattice parameter is $a_0=\frac{2}{3}a+\frac{1}{3}c=8.56$ Å. The coefficient of thermal expansion is estimated as

$$\Delta a_0/a_0\Delta T \approx 10^{-5} \text{ per degree.}$$

Since $a_0=8.56$ Å, this gives $\Delta a_0 \approx 0.09$ Å for $\Delta T=1100^\circ\text{C}$. At the transition temperature, 1170°C , the lattice becomes cubic with a measured lattice parameter $a'=8.64$ Å. The lattice parameter which is calculated from the assumptions of square-bond formation in $\text{Mn}^{2+}(\text{Mn}_2^{\text{III}})\text{O}_4$ is $a_0+\Delta a_0=8.65$ Å. The agreement is satisfactory.

C. The Indates and Metallic Indium

Passerini³³ has measured the lattice parameters of CaIn_2O_4 and CdIn_2O_4 . Each of these crystals was found to be tetragonal; their respective axial ratios are 1.12 and 1.14. The cation distribution in these indates has not yet been determined. MgIn_2O_4 , on the other hand, was found by Barth and Posnjak³⁴ to be cubic and inverse.

It is known that Cd^{II} tends to occupy tetrahedral interstices where (sp^3) -covalent-bond formation is possible. It may therefore be assumed that CdIn_2O_4 is normal. Ca^{2+} , like Mg^{2+} , forms ionic bonds so that it might be expected to occupy octahedral sites as do the Mg^{2+} ions in MgIn_2O_4 .

If the lattice distortions to tetragonal symmetry are due to cation ordering in the octahedral sites, then MgIn_2O_4 , which is inverse and has the larger difference in ionic radii (ionic radii of Mg^{2+} , In^{3+} , Cd^{2+} , Ca^{2+} are 0.78 Å, 0.92 Å, 1.03 Å, 0.99 Å, respectively), should give a larger distortion than CdIn_2O_4 and CaIn_2O_4 . On the contrary MgIn_2O_4 is cubic, and CdIn_2O_4 and CaIn_2O_4 are tetragonal.

On the other hand, since the axial ratio of CdIn_2O_4 is identical with that of ZnMn_2O_4 , which probably has (sp^3) covalent bonding in the tetrahedral sites and (dsp^2) covalent bonding in the octahedral sites, it is pertinent to inquire whether CdIn_2O_4 can form the same type of bonds. Although gaseous In^{3+} has a full $3d$ shell so that square-bond formation appears improbable, a study of metallic indium suggests the opposite.

³³ L. Passerini, Gazz. chim. ital. **60**, 754 (1930).

³⁴ T. F. W. Barth and E. Posnjak, Z. Krist. **82**, 325 (1932).

Metallic indium is face-centered tetragonal with an axial ratio $c/a=1.076$.³⁵ Since the lattice is distorted from cubic symmetry, it is not possible to explain the distortion by the interaction of the conduction electrons with the lattice, i.e., by the interaction of the Fermi surface with the Brillouin-zone energy-discontinuity surfaces.³⁶ In γ -Mn, which is also face-centered tetragonal but with $c/a=0.937$,³⁷ it is possible to explain the distortion as due to magnetic-exchange interactions,³⁸ but such interactions are not present in indium. Also, the indium distortion is in an opposite sense from that in γ -Mn.

In the usual discussion of energy bands in metals the d , s , and p bands are considered separately. However, if the d , s , and p bands overlap, a hybrid band would be more stable. In metallic indium there is doubtless an overlap of d , s , and p bands. It is suggested, therefore, that there is a hybrid, covalent, (dsp^2) band in indium. This band is full with one electron per indium atom left over for metallic bonding (see Fig. 3). If there is a (dsp^2) band, it will be reflected in square covalent bonds about each indium atom. The four nearest neighbors of each indium atom are indeed located at the corners of a coplanar square. It is suggested, therefore, that just as in the case of tetragonal spinels, the distortion to tetragonal symmetry in metallic indium is due to the formation of square covalent bonds. Further evidence for this suggestion is given in Appendix III.

The study of metallic indium indicates that when indium is in a lattice, the $3d$ electrons can be active in bond formation. It is probably just as correct, therefore, to consider the outer-electron configuration of In^{3+} to be d^9s as to consider it d^{10} . When the steric constraints favor (dsp^2) -bond formation, the configuration d^9s makes one d wave function available for hybridization which can enter into coordinate covalence with four coplanar oxygens as illustrated in Fig. 4. If In^{III} does indeed form square bonds, then the square-bond model is applicable to the indates. In^{III} in an octahedral site tends to cause tetragonal distortion through covalent square-bond formation. Normal indates have, therefore, tetragonal symmetry due to covalent square-bond formation in the octahedral sites. On the other hand, In^{III} in a tetrahedral site tends to prevent tetragonal distortion because its strong (sp^3) bonds weaken the covalent bonds in octahedral sites. This was shown in Sec. IIIB, where it was stated that the oxygen p orbitals are directed toward that near-neighbor cation which forms

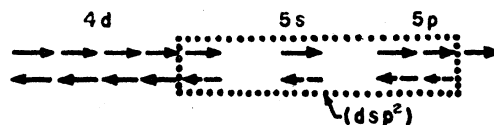


FIG. 3. Metallic indium with a full covalent (dsp^2) band.

³⁵ W. Betteridge, Proc. Phys. Soc. (London) **A50**, 519 (1938).

³⁶ J. B. Goodenough, Phys. Rev. **89**, 282 (1953).

³⁷ A. Westgren and G. Phragmen, Z. Physik **33**, 777 (1925).

³⁸ C. Zener, Phys. Rev. **81**, 440 (1951).

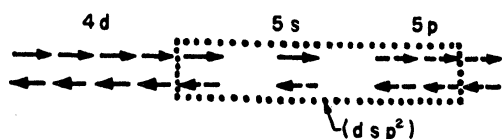


FIG. 4. Electron-spin configuration for In^{III} forming four coplanar covalent bonds.

the strongest covalent bond with oxygen. In inverse indates, tetragonal distortion is possible only if enough octahedral cations form sufficiently strong covalent square bonds.

Since $\text{In}(\text{MgIn})\text{O}_4$ is cubic, there appears to be insufficient covalent bonding in octahedral sites for tetragonal distortion. There has to be a certain minimum number of covalently bound ions in octahedral sites for tetragonal distortion. This number depends on the strength of these covalent bonds. In CuFe_2O_4 the minimum number was shown [Eq. (IV.4)] to be 26 percent of the octahedral cations. Since in $\text{In}(\text{MgIn})\text{O}_4$ the octahedral covalent bonds are weaker than in CuFe_2O_4 , the minimum fraction of covalently bound ions in octahedral sites should here be greater than 26 percent. In $\text{In}(\text{MgIn})\text{O}_4$ each oxygen is surrounded by one tetrahedral indium and three randomly distributed octahedral indium and magnesium ions. Magnesium is bound electrovalently. One oxygen can be bound covalently to one tetrahedral and two octahedral indium ions through the admixture of oxygen (sp^3) orbitals (Sec. IIIB, and Appendix I). Since only 50 percent of the oxygen ions have two octahedral indium near-neighbors, only 50 percent of the octahedral indium ions form significantly strong square bonds. This means that only 25 percent of the octahedral cations can form square bonds; as shown above this is insufficient to cause tetragonal distortion.

It is concluded that all normal indates are tetragonal, and that the inverse indates are cubic if the bivalent cation is electrovalent. If the bivalent cation can form covalent square bonds, the indate should be tetragonal

even when inverse. Therefore it is predicted that if CuIn_2O_4 or PdIn_2O_4 form spinels, they will be found to be tetragonal, whether normal or inverse.

If the square-bond model is accepted for indates, the axial ratio of CdIn_2O_4 must equal that of ZnMn_2O_4 , as has been observed. In each case the spinel is normal, and covalent bonds are formed in both tetrahedral and octahedral sites, so that the axial ratio $c/a=1.14$ is less than that of Mn_3O_4 (as explained in Appendix I).

Finally, the axial ratio of CaIn_2O_4 , $c/a=1.12$, is greater than the extrapolated value for completely inverse CuFe_2O_4 , $c/a=1.08$. Therefore this spinel cannot be inverse. This conclusion finds further support in the fact that if it were inverse, it would not be distorted because Ca^{2+} forms electrovalent bonds. The axial ratio $c/a<1.16$ is due to incomplete covalent bonding in the octahedral sites. If this indate were completely normal, this weakening could not be due to covalent bonding in tetrahedral sites. It is concluded, therefore, that CaIn_2O_4 is partially inverse; the concentration of covalently bound cations in octahedral sites is then less than that in the spinels with axial ratios 1.16 and 1.14, and the presence of In in both octahedral and tetrahedral sites causes a further reduction in axial ratio.

It is significant that gallates are cubic and that metallic gallium does not have the close-packed, tetragonally distorted structure. Apparently gallium, like mercury, tends to form pairs of atoms, presumably through $(1/3)s + (1/\sqrt{3})p_z + (\sqrt{5}/3)d_z$ hybrid orbitals.

H. Summary

In Table III there is a summary of the properties of those spinels which become orthorhombic or tetragonal. The orthorhombic- Fe_3O_4 transition is seen to be quite separate in character from the tetragonal transitions. The orthorhombic distortion has been definitely established as due to ordering of the octahedral Fe^{2+} and Fe^{3+} cations. The distortions due to ionic ordering are believed to be orthorhombic rather than tetragonal.

TABLE III. A comparison of some physical properties of spinels which distort from cubic symmetry below a transition temperature T_i . σ_a/σ_b and $(\epsilon_a - \epsilon_b)$ are the ratio of conductivity and the difference in electron activation energy above and below T_i .

Composition	Spinel distortion	Axial ratio	T_i	σ_a/σ_b	$\epsilon_a - \epsilon_b$ in ev	Thermal hysteresis
Fe_3O_4	Orthorhombic	$a:b:c=5.912:5.945:8.388^a$	-153°C^b	90^b	-0.05^b	None ^b
Mn_3O_4	Tetragonal	$c/a=1.16^{a,d}$	1170°C^e	5^e	-0.55^e	$\sim 45^\circ\text{C}^e$
CuFe_2O_4	Tetragonal	$c/a=1.16^{f,g}$	760°C^g	...	...	...
CuCr_2O_4	Tetragonal	$c/a=1.1^h$	...	...	...	...
$\gamma\text{-Mn}_2\text{O}_3$	Tetragonal	$c/a=1.16^i$	...	...	...	...
ZnMn_2O_4	Tetragonal	$c/a=1.14^d$	1025°C^e	2^e	-0.4^e	$\sim 40^\circ\text{C}^e$
CdIn_2O_4	Tetragonal	$c/a=1.14^j$	...	...	...	...
CaIn_2O_4	Tetragonal	$c/a=1.12^j$	...	...	...	...

^a S. C. Abrahams and B. A. Calhoun, *Acta Cryst.* **6**, 105 (1953).

^b B. A. Calhoun, *Phys. Rev.* **94**, 1577 (1954).

^c McMurdie, Sullivan, and Maurer, *J. Research Natl. Bur. Standards* **45**, 35 (1950).

^d B. Mason, *Am. Mineralogist* **32**, 426 (1947).

^e F. C. Romeijn, *Philips Research Repts.* **8**, 304 (1953).

^f Extrapolated value for every octahedral site occupied by a Cu^{2+} cation. Measured values are $c/a=1.06$ and 1.035 at 20°C and 700°C , respectively.

^g E. F. Bertaut, *J. phys. radium* **12**, 252 (1951).

^h McGuire, Howard, and Smart, *Ceram. Age* **60**, 22 (1952).

ⁱ E. J. W. Verwey and J. H. de Boer, *Rec. trav. chim.* **55**, 531 (1936).

^j L. Passerini, *Gazz. chim. ital.* **60**, 754 (1930).

This necessarily follows if there is covalent bonding in the tetrahedral sites which resists a distortion of its coordination angles.

The tetragonal symmetry in Mn_3O_4 , $\gamma\text{-Mn}_2\text{O}_3$, ZnMn_2O_4 , CuFe_2O_4 , CuCr_2O_4 , CdIn_2O_4 , and CaIn_2O_4 is believed due to the formation of an ordered system of four coplanar, covalent bonds and two linear, ionic bonds in the octahedral sites which are occupied by Mn^{III} , Cu^{II} , or In^{III} cations. If the indiate is inverse, the indium ions which are in the tetrahedral sites bond covalently; those in the octahedral sites form an ordered array of square bonds only if the bivalent ions also form covalent bonds. The lattice is therefore cubic if the bivalent cation is electrovalent. The tetragonal symmetry of metallic indium is also believed due to the formation of a (dsp^2) covalent bond.

Finally it is believed that there are no Mn^{4+} cations in Mn_3O_4 , $\gamma\text{-Mn}_2\text{O}_3$, and ZnMn_2O_4 .

V. MAGNETIC EXCHANGE

A. Exchange Mechanisms

Three mechanisms, known as direct exchange, double exchange, and superexchange, have been used to explain the interaction between electron spins. These interactions are based on the Pauli exclusion principle. Direct exchange tends to align the net spin on neighboring lattice elements antiparallel to each other. In spinels cations are separated by anions without net spin so that direct exchange is negligible.

Double exchange, as proposed by Zener,³⁹ requires the transfer of electrons between two kinds of ions, particularly two of the same element but with different charges, and hence is inhibited if these cations are ordered. Double exchange tends to align spins parallel to each other; also it produces a relatively high conductivity.

Kramers⁴⁰ suggested the third mechanism, called superexchange. Superexchange is due to the admixture of excited states with the ground state of a system containing two like cations separated by an anion. The excited states are the result of removing an electron from the oxygen ion O^{2-} and placing it in an empty or half-filled cation orbital. If the cation orbital is empty, the transferred electron aligns its spin parallel to the net spin already on the cation in accordance with Hund's rule. If the orbital is already half filled, the transferred electron aligns its spin antiparallel to that of the electron already there, and hence to the existing net spin on the cation. The O^{1-} ion from which the electron is transferred has a net spin which is antiparallel to that of the removed electron. The net spin on the oxygen ion is therefore antiparallel to the spin of the reduced cation if the cation d shell was originally less than half filled; parallel, if the cation d shell was originally at least half filled. These alignments are shown in Fig. 5.

³⁹ C. Zener, Phys. Rev. 82, 403 (1951).

⁴⁰ H. A. Kramers, Physica I, 182 (1934).

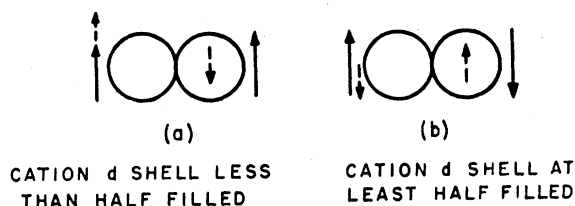


FIG. 5. Spin alignment in superexchange.

According to the superexchange model the net spin on the O^{1-} ion interacts directly with that of a neighboring cation on the other side. It was predicted, therefore, that the two cations orient their spin parallel if their d shells are less than half filled, antiparallel if the d shells are more than half filled.

Kramers' model is inconsistent in two ways with the concepts of covalence in spinels which are proposed in this paper. In the first place it was assumed that when the cation d shell is at least half filled, any additional electron will occupy a half-filled d orbital and align its spin antiparallel to that existing on the cation. The Pauli principle would indeed appear to predict such an alignment. It should be recalled, however, that this prediction is based on the supposition that there are no unfilled orbitals available that are degenerate with the $3d$ orbitals. When a new electron is added to a cation, it can either occupy an empty orbital or a half-filled one. In the former case energy may be required to raise the electron to the energy of the empty orbital, but this energy may be offset when the new electron aligns its spin parallel to the existing spin on the cation. In the latter case no energy is required to raise the electron to a higher level, but no exchange energy is gained, because the electron now must align its spin antiparallel to the existing spin. Therefore the spin alignment in superexchange depends on whether the exchange energy is larger or smaller than the difference in energy between d orbitals and the next level. It has been shown that, because of covalent overlap, there are indeed hybrid orbitals whose energy is about the same as that of the filled, or partially filled, d orbitals. Therefore superexchange would always produce parallel alignment when hybrid cation orbitals are occupied because, in effect, the d shell is extended by s and p orbitals of the same energy and is therefore less than half filled.

In the second place Kramers assumed the transfer of an electron from an oxygen ion to a cation. Somehow this transferred electron must retain its identity as an oxygen p electron since it is assumed that the spin on the resultant O^{1-} ion remains antiparallel to that of the transferred electron. Without covalence it is not at all clear why an electron should be simultaneously identified with both a cation and an anion. On the other hand, if the excited state of the system is covalent, this would indeed be the case.

In crystals both sides of an O^{2-} p orbital may overlap with an empty cation orbital. For coordinate covalence

the overlapping O^{2-} orbital and empty cation orbital should be nearly degenerate. In ionic crystals this is not the case for the ground state of the ion. However, if the cation in an electrovalent crystal has a net spin, exchange energy is gained if one of the two electrons in the oxygen p orbitals is excited to become part of the cation. Since only one electron participates in this bond, the bond is called "semicovalent." "Semicovalence" is thus defined as a bond due to the coupling of a single anion electron to the net spin of a cation. Fe^{3+} and Mn^{2+} , which have been observed to favor tetrahedral sites in the spinel lattice, are thought to be stabilized in these sites through semicovalence. In Sec. IIIC, 1, the term "partially covalent" was used to explain this stabilization.

Obviously the electron that participates in semicovalence has a spin parallel to that of the cation. The other anion electron therefore has a spin antiparallel to the spin of that cation. This other electron may participate in semicovalence with a cation on the other side of the anion. In that case the spins of the two cations would be coupled antiparallel to each other. This model provides a mechanism for antiferromagnetic coupling between two cations separated by an anion. This mechanism is called "semicovalent exchange." Its strength depends on the overlap between the O^{2-} p orbitals and the cation orbitals, and therefore on the cation-oxygen-cation angle. If semicovalence occurs with one cation only, the interaction between the anion and other cations is confined to direct exchange, and weak ferromagnetic coupling may result.

In summary, since the superexchange model has only been tested in the case of ferromagnetism and antiferromagnetism (ferromagnetic coupling can be explained by other mechanisms, such as double exchange), it is suggested that semicovalent exchange is a more consistent model for the antiferromagnetic-exchange interactions which have previously been attributed to superexchange. There are three conditions which favor semicovalent exchange: the formation of predominantly electrovalent bonds, cations with empty hybrid orbitals which overlap with a full anion p orbital, and a location of interacting cations on opposite sides of an anion.

B. Magnetic Properties of Some Oxides

There are two exchange mechanisms which are important in predominantly electrovalent metallic oxides, double exchange and semicovalent exchange. Double exchange, which causes ferromagnetic alignment and increased conductivity, occurs between cations of like atoms, but different ionization, if they are randomly distributed on equivalent lattice sites. In a spinel lattice there is negligible double-exchange interaction between tetrahedral- and octahedral-site cations.

Semicovalent exchange couples cation moments antiferromagnetically. This coupling is strongest when the cation-anion-cation bond is 180° . In the spinel lattice

neighboring octahedral cations make a 90° angle with their common anion, and the semicovalent exchange between them is small compared to that between the tetrahedral and octahedral cations. These mechanisms are applied below to several metal oxides, and in each the semicovalent-exchange mechanism is compared with superexchange.

It should be noted that cations which form coordinate-covalent bonds do not participate in either semicovalent exchange or double exchange. Such ions are therefore paramagnetic.

1. Some Antiferromagnetic Crystals

In oxides which have cations in one valence state only, double exchange cannot occur. If the metal is a transition element, semicovalent exchange is possible. Many such lattices are known to be antiferromagnetic. A typical example is MnO which has the rock-salt structure. Whereas superexchange would require the formation of $Mn^{1+}O^{1-}$ in an excited state, semicovalent exchange couples the system antiferromagnetically through electron pairs whose orbitals contain an admixture of excited $Mn^{II}O^{II}$ states.

It is interesting that the Curie points of manganous compounds with the same rock-salt structure increase with the substitution of anions of lower electronegativity, *viz.*, MnO ($122^\circ K$), MnS ($165^\circ K$), $MnSe$ ($247^\circ K$), $MnTe$ ($307^\circ K$).⁴¹ Such a relation is consistent with a model which predicts that the strength of the antiferromagnetic coupling is increased as the admixed excited states become more nearly degenerate with the electrovalent ground state. It is consistent, therefore, with both superexchange and semicovalent exchange.

If one compares the Curie points of the oxides of Mn , Fe , Co , and Ni , all of which have the rock-salt structure, a similar progression of Curie temperatures is noted, *viz.*, MnO ($122^\circ K$), FeO ($198^\circ K$), CoO ($291^\circ K$), NiO ($523^\circ K$). On the basis of a superexchange model this progression can be attributed to the progressive increase in the ionization potential of the bivalent ion. On the basis of a semicovalent model it may be attributed to a progressive decrease in the energy of the hybrid (d^2sp^3) orbitals. The high Curie point of NiO indicates that semicovalence has a significant stabilizing effect on Ni^{2+} in octahedral sites of O^{2-} ions. Although there is no normal covalence in the $Ni^{2+}-O^{2-}$ bond, semicovalence is possible. The apparent preference of Ni^{2+} for octahedral sites in the spinel lattice¹⁴ may indeed be due to this stabilization. Further, this stabilization may well explain the normal spinel structure of $Ge(Ni_2)O_4$ and $Ge(Co_2)O_4$ as contrasted with the olivine structure of $Ge(Mg_2)O_4$. Since Mg^{2+} , Co^{2+} , and Ni^{2+} have comparable ionic radii, this difference in crystal structure cannot be understood from any previous model.

⁴¹ H. Bizette, J. phys. *radium* **12**, 161 (1951).

2. Fe_3O_4

Fe_3O_4 is an inverse spinel, $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$. The interaction between the tetrahedral Fe^{3+} ions and the octahedral ions can be fully explained by semicovalent exchange but only partially by superexchange. According to both models the tetrahedral Fe^{3+} ions would couple antiferromagnetically with the octahedral Fe^{3+} ions. However, superexchange does not provide for the $\text{Fe}^{3+}-\text{Fe}^{2+}$ interaction since it applies only to interactions between identical ions. Semicovalent exchange corresponds to antiferromagnetic coupling in this case also. Between the low-temperature transition and the Curie point the spins on the octahedral sites are also aligned parallel to each other through double exchange. Therefore all the spins of the octahedral-site cations are aligned parallel to one another and antiparallel to those of the tetrahedral-site cations. In this temperature interval both the superexchange and semicovalent-exchange mechanisms provide for the ferromagnetism of Fe_3O_4 . Below 119°K, however, the Fe^{3+} and Fe^{2+} cations are ordered so that double exchange cannot occur. At these low temperatures the superexchange model provides no mechanism for a parallel alignment of all the octahedral-site spins. Since Fe_3O_4 is ferromagnetic below 119°K, the antiparallel alignment of all octahedral-site spins with respect to the tetrahedral-site spins, and the consequent parallel alignment of the octahedral-site spins must be due to semicovalent exchange. Semicovalent exchange provides the more adequate model.

3. Mn_3O_4

It is proposed in this paper that the structure of Mn_3O_4 is $\text{Mn}^{2+}(\text{Mn}_2^{\text{III}})\text{O}_4$. Elsewhere the structure $\text{Mn}^{2+}(\text{Mn}^{2+}\text{Mn}^{4+})\text{O}_4$ has been proposed. Mn^{2+} in tetrahedral sites is partially covalent. Mn^{III} forms square covalent bonds. Octahedral Mn^{2+} and Mn^{4+} would be ionically bound. In the $\text{Mn}^{2+}(\text{Mn}^{2+}\text{Mn}^{4+})\text{O}_4$ model Mn^{2+} octahedral-tetrahedral interactions would be antiferromagnetic according to both superexchange and semicovalent exchange. The $(\text{Mn}^{2+} \text{ tetrahedral})-(\text{Mn}^{4+} \text{ octahedral})$ interaction cannot be treated with superexchange, but semicovalent exchange predicts antiferromagnetic exchange. Thus the structure $\text{Mn}^{2+}(\text{Mn}^{2+}\text{Mn}^{4+})\text{O}_4$ would be ferromagnetic just like $\text{Fe}^{2+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$. Yet down to 72°K Mn_3O_4 has been found to be paramagnetic.

In the structure $\text{Mn}^{2+}(\text{Mn}_2^{\text{III}})\text{O}_4$ there would be no octahedral-tetrahedral semicovalent exchange because all octahedral-site cations are covalently bound. There would be no double exchange because Mn^{2+} and Mn^{III} are ordered in different types of sites. Thus the model $\text{Mn}^{2+}(\text{Mn}_2^{\text{III}})\text{O}_4$ is paramagnetic. Since Mn_3O_4 has been found to be paramagnetic as low as 72K°, this observation supports the $\text{Mn}^{2+}(\text{Mn}_2^{\text{III}})\text{O}_4$ model in preference to the $\text{Mn}^{2+}(\text{Mn}^{2+}\text{Mn}^{4+})\text{O}_4$ model.

4. CuFe_2O_4

This spinel is partially inverse with the formula $\text{Fe}_2\text{Cu}_{1-2\lambda}(\text{Cu}_{2\lambda}\text{Fe}_{2-2\lambda})\text{O}_4$ as discussed in Sec. IV B, 2. If Cu^{II} forms square covalent bonds in the octahedral sites, as is suggested in this paper to explain the tetragonal structure of CuFe_2O_4 , then the octahedral copper does not contribute to the magnetism.

Since the exchange between the octahedral- and tetrahedral-site cations is the only spin interaction of significance in CuFe_2O_4 , it is expected that the octahedral-site spins, if they contribute at all to the magnetic moment, are parallel to one another and antiparallel to the tetrahedral-site spins. If $M_{a\mu\beta}$ and $M_{b\mu\beta}$ are the atomic moments of tetrahedral-site and octahedral-site copper respectively, where $\mu\beta$ is a Bohr magneton, then the magnetic moment per molecule of CuFe_2O_4 is $|(2-2\lambda)5+2\lambda M_b-(2\lambda)5-(1-2\lambda)M_a|\mu\beta = |(1-2\lambda)10-M_a+2\lambda(M_b+M_a)|\mu\beta$. Pauthenet and Bochirol⁴² report $2.19\mu\beta$ for the magnetic moment of a CuFe_2O_4 sample which had been quenched from a 700°C anneal. Bertaut²⁷ found that a similarly treated CuFe_2O_4 sample had an ordering parameter $\lambda=0.37$. Although a direct comparison between data from two different, though similarly treated, samples is not strictly justified, it is interesting that for $\lambda=0.37$ the predicted magnetic moment of CuFe_2O_4 is $(2.6+0.74M_b-0.26M_a)\mu\beta$ which, for $M_a=1$ and $M_b=0$, is $2.3\mu\beta(>2.19\mu\beta)$. It is reasonable to assume, therefore, that the octahedral-site copper ions do not contribute to the magnetic moment.

VI. SUMMARY

The covalent bond in spinels has been shown to influence cation ordering, lattice distortions, and magnetic-exchange interactions. Covalent bonding modifies the Madelung-energy and geometrical calculations of previous workers. Octahedral and square covalent-bond formation are as significant as is tetrahedral-bond formation in determining cation ordering in spinels. From only qualitative considerations it was possible to predict nearly all the observed cation distributions.

While orthorhombic distortion, as observed in Fe_3O_4 , can be ascribed to cation ordering in octahedral sites, tetragonal distortion is shown to be due to ordering of the square bonds in octahedral sites. The two distortion mechanisms are vastly different, as is evident from the difference in transition temperature, thermal hysteresis, etc. A certain minimum concentration of square-bond-forming cations in octahedral sites must be exceeded for the lattice to distort. Covalent bonds in tetrahedral sites tend to hinder tetragonal distortion.

The structure of Mn_3O_4 was found to be $\text{Mn}^{2+}\times(\text{Mn}_2^{\text{III}})\text{O}_4$ rather than $\text{Mn}^{2+}(\text{Mn}^{2+}\text{Mn}^{4+})\text{O}_4$. The tetragonal structures of metallic indium and the indates are accounted for by the square-bond model.

⁴² R. Pauthenet and L. Bochirol, J. phys. radium **12**, 249 (1951).

Semicovalence is defined as covalent bonding due to the coupling of a single electron spin to the net spin on a cation. This coupling leads to semicovalent exchange, a mechanism producing antiferromagnetic coupling of cation spins. The paramagnetism of $\text{Mn}^{2+}(\text{Mn}_2^{\text{III}})\text{O}_4$ is explained on the basis of semicovalent exchange, as is the magnetization of Fe_3O_4 below 119°K .

APPENDIX I. THE INFLUENCE OF OXYGEN (sp^3) -ORBITAL HYBRIDIZATION ON THE AXIAL RATIO OF TETRAGONAL SPINELS

In Sec. IIIB, it has been pointed out that the oxygen p^3 orbitals in a spinel are instrumental in the formation of covalent bonds between oxygen and its near neighbors in octahedral sites. Where there are empty cation orbitals in tetrahedral sites the oxygen can be bound covalently to at least two octahedral and one tetrahedral cation through the admixture of oxygen (sp^3) orbitals with the p^3 orbitals. The p^3 orbitals overlap strongly with the empty orbitals in the octahedral sites but not with those in tetrahedral sites while the set of (sp^3) orbitals that overlap strongly with a tetrahedral site do not overlap as strongly with the octahedral sites as do the p^3 orbitals. Therefore the admixture of oxygen (sp^3) wave functions with the p^3 wave functions increases the amount of covalent bonding of oxygen with a tetrahedral near neighbor but decreases the amount of covalent bonding with the octahedral near neighbors.

It has been proposed that the tetragonal distortion of many spinels is due to square covalent bonds in octahedral sites. When covalent bonds are formed by one oxygen with both octahedral and tetrahedral sites through (sp^3) admixture, the bonds are less covalent in the octahedral sites than they would have been if no covalent bonds with the tetrahedral ions existed. Therefore the axial ratio of a tetragonal spinel is a maximum when only the octahedral cations are covalently bound, and decreases with increasing amount of covalence in tetrahedral sites.

This can be quantitatively shown as follows. The amount of covalence in the octahedral sites due to oxygen p^3 -orbital overlap and that in tetrahedral sites due to oxygen (sp^3) -orbital overlap is arbitrarily set at unity. The amount of covalence in the octahedral sites due to oxygen (sp^3) -orbital overlap is given by $\delta (<1)$, that in the tetrahedral sites due to p^3 overlap by the very small fraction ϵ . The wave function for the (sp^3) orbitals and the p^3 orbitals are admixed in the ratio $\alpha:\beta$, where $\alpha^2+\beta^2=1$. The normalized mixed wave function is then denoted by $\alpha(sp^3)+\beta(p^3)$. The amounts of co-

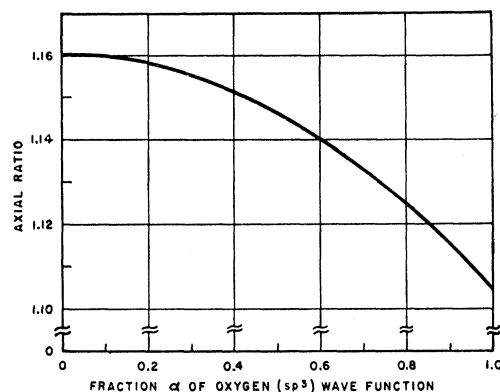


FIG. 6. The axial ratio as a function of the amount of admixture of oxygen (sp^3) orbitals.

valence due to each term in the wave function is shown in Table IV. [The physical properties are proportional to the square of the wave functions; cross products $\alpha\beta(sp^3)(p^3)$ are neglected here.] Therefore the amount of covalence in octahedral sites is $(\alpha^2\delta+\beta^2)$. The amount of electrovalence is $1-(\alpha^2\delta+\beta^2)$. If it is assumed that the bond length is a linear function of the amounts of covalence and electrovalence, the following bond length is then derived:

$$a' = (\alpha^2\delta+\beta^2)a + (1-\alpha^2\delta-\beta^2)c, \quad (\text{A.1})$$

where a is the covalent bond length in octahedral sites in the absence of (sp^3) admixture, and c is the electrovalent bond length in octahedral sites. The axial ratio is then given by

$$\frac{c}{a'} = \frac{c}{(\alpha^2\delta+\beta^2)a + (1-\alpha^2\delta-\beta^2)c}. \quad (\text{A.2})$$

In spinels in which there is no appreciable covalent bonding in tetrahedral sites, such as Mn_3O_4 , the axial ratio has been observed to be $c/a=1.16$. The amount of overlap of oxygen (sp^3) orbitals with octahedral cation orbitals is estimated to be about 70 percent of that of oxygen p^3 orbitals with octahedral cation orbitals. On the assumption that $\delta=0.8$, the axial ratio is plotted in Fig. 6 as a function of the admixture of oxygen (sp^3) orbitals.

For spinels like CdIn_2O_4 and ZnMn_2O_4 an axial ratio 1.14 has been observed; for Fig. 6 this is seen to correspond to $\alpha=0.6$, $\beta=0.8$. It is significant that such a large amount of admixture of (sp^3) orbitals, and hence considerable covalence in tetrahedral sites, only slightly reduces the axial ratio. In fact pure (sp^3) wave functions for oxygen ($a=1$, $\beta=0$) still allow enough covalence in the octahedral sites for distortion to an axial ratio $c/a=1.10$.

TABLE IV. Contributions of oxygen (sp^3) and p^3 orbitals to the covalence in tetrahedral and octahedral sites.

	Tetrahedral sites	Octahedral sites
$\alpha(sp^3)$	α^2	$\alpha^2\delta$
$\beta(p^3)$	$\beta^2\epsilon$	β^2

APPENDIX II. CALCULATION OF THE TETRAGONAL DISTORTION IN Fe_3O_4 FROM AN IONIC MODEL

To calculate θ_1 and θ_1' of Eq. (IV.1), it is first necessary to obtain θ_2 and θ_2' which, from the law of cosines,

TABLE V. Self-consistent calculation of λ for Fe_3O_4 .

λ	θ_1	θ_1'	ϵ	ϵ'	δ	δ'	Δ
1.020	1°57'	0°20'	0.0469	0.0095	0.0247	0.004	0.0013
1.024	2°10'	0°0'	0.0468	0.0095	0.0273	0	-0.0019

are given by

$$\cos\theta_2 = \frac{\lambda^2 + (1+\zeta)^2 - (1-\zeta')^2}{\{(2\lambda^2+1)[2(1+\zeta)^2-1]\}^{\frac{1}{2}}},$$

$$\cos\theta_2' = \frac{\lambda^2 + (1-\zeta')^2 - (1+\zeta)^2}{\{(2\lambda^2+1)[2(1-\zeta')^2-1]\}^{\frac{1}{2}}}.$$

The angles θ_1 and θ_1' then follow directly from the geometrical relation

$$\cos(\theta_1+\theta_2) = (2\lambda^2+1)^{-\frac{1}{2}} = \cos(\theta_2'-\theta_1').$$

If $(1+\zeta)^2=1.0486$, $(1-\zeta')^2=0.9905$, $d^2=0.75$, then the values listed in Table V follow where $\Delta=[d^2-\frac{1}{2}\times(1-\epsilon)^2]^{\frac{1}{2}}+[d^2-\frac{1}{2}(1+\epsilon')^2]^{\frac{1}{2}}-\lambda(1+\delta-\delta')$. The correct value of λ is that for which $\Delta=0$, or $\lambda=1.022$.

APPENDIX III. TETRAGONAL DISTORTION IN Cd-In ALLOYS

Betteridge³⁵ added small amounts of Cd to In and observed the change in lattice parameter. At 100°C,

14.5 atomic percent of Cd was soluble in In. The axial ratio decreased from $c/a=1.068$ for pure In to $c/a=1.0$ for 4.5 atomic percent Cd. At 20°C the solubility limit of Cd was 4.5 atomic percent. Between pure In and the solubility limit c/a decreased from 1.076 to 1.04.

Since the Cd atoms do not contribute to the square covalent bonds, the addition of Cd to In adds vacancies to the (dsp^2) band. The tetragonal distortion, and therefore the energy gap between the (dsp^2) band and the conduction band, is reduced. At 100°C and 4.5 atomic percent Cd enough covalent-band electrons have sufficient energy to go into the conduction band so that the covalent ordering is destroyed, and the lattice becomes cubic. At 20°C there are fewer covalent-band electrons which are excited into the conduction band, and the c/a ratio is higher, at all cadmium concentrations, than it is at 100°C. At 4.5 percent Cd and 20°C the covalent bonds are still strong enough to force the Cd out of solution. The tetragonal symmetry is therefore preserved.

If the phase transition from tetragonal to cubic symmetry occurs in 4.5 atomic percent Cd at 100°C, a similar transition might be expected a few degrees higher in pure In. The melting point of In is 156.4°C.⁴³ Apparently the low melting point of In occurs below the phase transition from tetragonal to cubic symmetry.

⁴³ Taylor Lyman, editor, *Metals Handbook, 1948 Edition* (American Society for Metals, Cleveland, 1948).