

Infrared Spectra of Ferrites*

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The infrared spectra of 7 ferrites of the formula $M\text{Fe}_2\text{O}_4$, where M designates a divalent metal, are presented and analyzed. Electronic absorption was observed in the visible and near-infrared regions. Two absorption bands arising from interatomic vibrations were measured and force constants calculated for the stretching of bonds between octahedral or tetrahedral metal ions and oxide ions. These force constants are in agreement with the elastic and thermodynamic properties of these compounds and are sensitive to distribution of metal ions between the alternate sites. The integrated vibrational band intensities were measured: they are compatible with predominantly ionic bonding for these structures.

STUDIES of the relations between structure and the electromagnetic response of ferromagnetic semiconductors are useful in understanding their properties. Since the electric and magnetic properties of these materials are decisively dependent on the precise configuration of the atoms or ions in these structures, methods of nondestructive analysis are especially suited to such investigations. In particular, the vibrational, electronic, and magnetic dipole spectra can give information about the position and valence of the ions in the crystal lattices.

In the present work, the infrared spectra of seven ferrites with the general formula $M\text{Fe}_2\text{O}_4$, where M represents a divalent metal ion, were examined in the frequency range $280\text{--}4000\text{ cm}^{-1}$; in several cases the investigation was carried up to the visible range. No previous infrared studies of these materials were found in the literature with the exception of the reflection spectrum of magnetite in the near infrared measured by Coblenz.¹

EXPERIMENTAL

The spectra were recorded on a Beckman IR-3 spectrophotometer equipped with CaF_2 , KBr, and KRS-5 prisms. Calibration was made by recording H_2O , NH_3 , CO_2 , CH_4 , HCl , and HBr lines previously measured with considerable accuracy on grating instruments.²

The samples were made according to the technique of Stimson³ and Schiedt⁴; 2.5 mg of the ferrite was mixed with 0.8 g of powdered KBr, and placed in a cylindrical die of 20 mm diam. The die was evacuated (0.1 mm Hg) for about 30 min to insure dryness and the sample then pressed for about 10 min at 30 tons/inch². Clear disks of approximately 1 mm thickness were obtained with usable transmission to 280 cm^{-1} . The ferrites them-

selves were prepared by precipitation and thermal decomposition of the corresponding oxalates as described by Wickham.⁵

Measurements were made at room temperature and at liquid nitrogen temperatures in a Dewar cell with AgCl windows. The cell construction was essentially the same as described by Wagner and Hornig.⁶

DATA

Spectra of $M\text{Fe}_2\text{O}_4$ in the range $280\text{--}2500\text{ cm}^{-1}$ are shown in Fig. 1; M designates Co, Fe, Mg, Mn, Ni, or Zn. The spectrum of the mixed ferrite $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$, the low-temperature spectrum of Fe_3O_4 , and the reflection spectrum of NiFe_2O_4 are presented in Fig. 2. Low-temperature spectra of the other simple ferrites were examined above 430 cm^{-1} , but differed only in minor detail from the room temperature spectra.

ANALYSIS

A cursory inspection of the spectra shows two absorption bands below 1000 cm^{-1} as a common feature of all the ferrites. Absorption in this region is not restricted to this class of compounds but occurs in the spectra of most metallic oxides.⁷ The bands arise from lattice vibrations of the oxide ions against the cations. At higher frequencies, gradually increasing absorption caused by electronic transitions is observed.

Electronic Spectra

The high-frequency absorption possesses a low-frequency cutoff which cannot be defined without ambiguity. For cases where the absorption reaches a maximum or approaches a limiting value, the frequency of $\frac{1}{2}$ maximum optical density may be taken as a reference point. Alternatively, the inflection point in the graph of optical density *vs* frequency, if present, may be chosen as the reference frequency. This latter

* Sponsored by the Office of Naval Research, the Army Signal Corps, and the Air Force.

¹ W. W. Coblenz, *Additional Investigations of Infrared Spectra* (Carnegie Institution, Washington, D. C., 1908).

² Downie, Magoon, Purcell, and Crawford, *J. Opt. Soc. Am.* **43**, 941 (1953).

³ M. M. Stimson and M. J. O'Donnell, *J. Am. Chem. Soc.* **74**, 1805 (1952).

⁴ U. Schiedt and H. Reinwein, *Z. Naturforsch.* **7b**, 270 (1952); *Appl. Spect.* **7**, 75 (1953).

⁵ D. G. Wickham (personal communication).

⁶ E. L. Wagner and D. F. Hornig, *J. Chem. Phys.* **18**, 296 (1950).

⁷ Bands in this region have been observed in Al_2O_3 , MgO , Fe_2O_3 , TiO_2 , BaTiO_3 , etc. See, for example, L. Harris, *J. Opt. Soc. Am.* **45**, 27 (1955); F. Matossi, *J. Chem. Phys.* **19**, 1543 (1951).

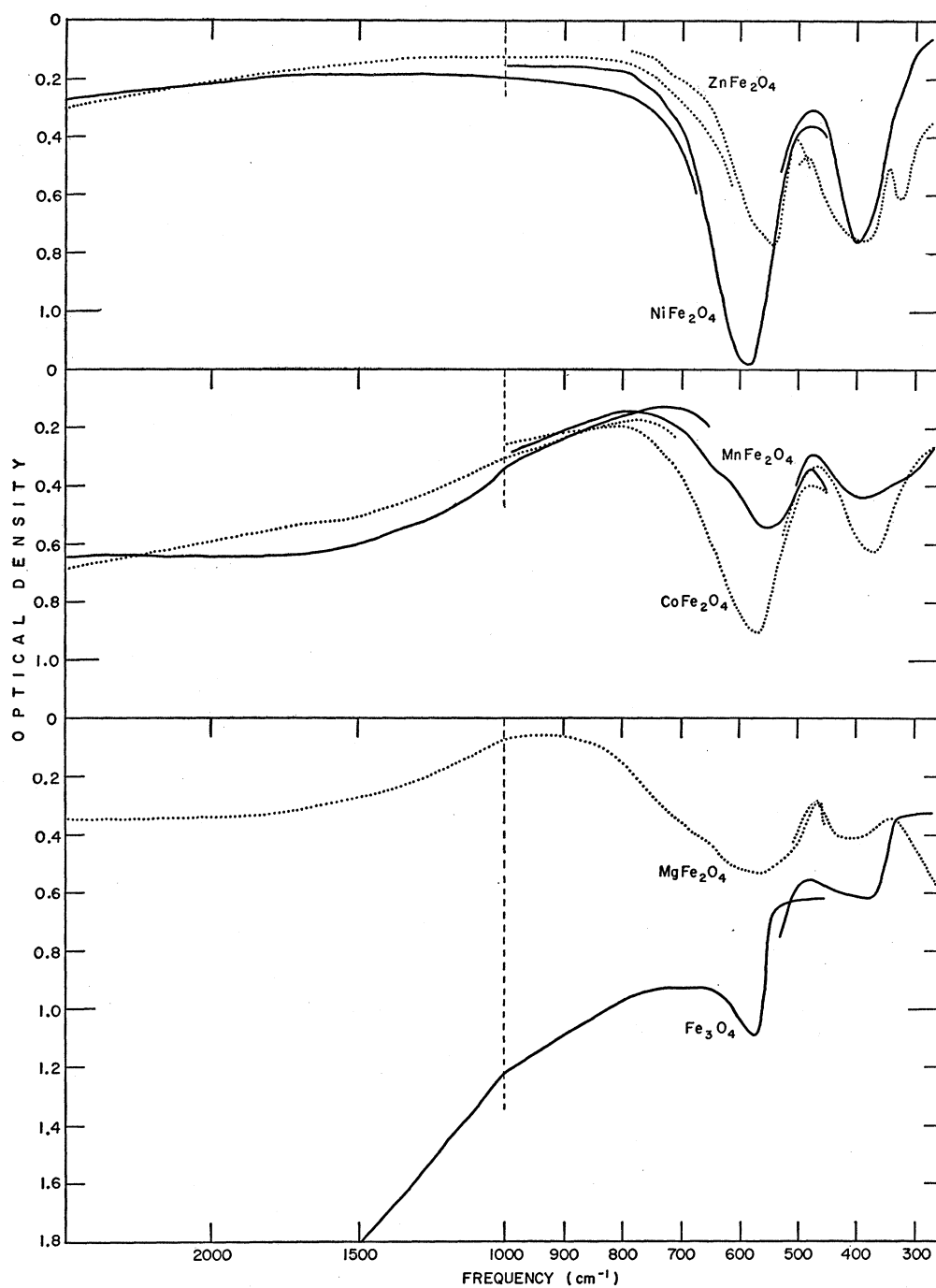


FIG. 1. Infrared absorption spectra of simple ferrites. Optical density measured relative to standard KBr disk. Sample weight: 2.50 mg (Fe 5.00 mg); sample area: 3.14 cm². Multiple lines indicate alternate runs or prism changes.

criterion will be used except where noted. Table I shows these threshold values for the electronic transition. These data are subject to considerable uncertainty because that portion of the scattering caused by the ferrite particles cannot be distinguished from absorption losses.

If these absorptions represent transitions to a conduction band of the crystal, the tabulated values can be expressed as activation energies. Some of the electronic bands give an indication of structure at higher frequencies; the scattering losses of our samples preclude their positive identification.

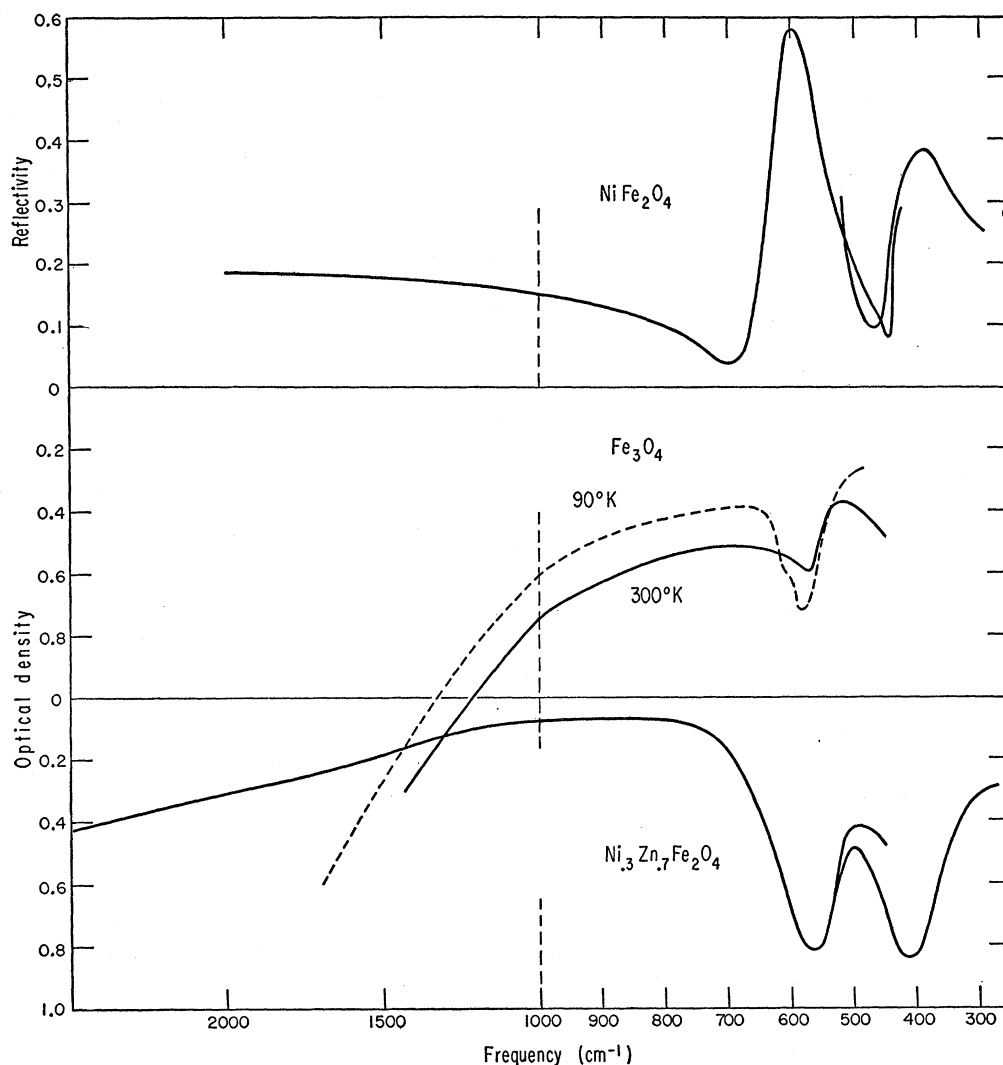


FIG. 2. Special infrared spectra of ferrites. Top: reflection spectrum of single crystal of NiFe_2O_4 (normal incidence $[110]$ face). Center: low-temperature absorption spectrum of Fe_3O_4 (2.50 mg). See legend of Fig. 1. Bottom: absorption spectrum of mixed ferrite $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$. See legend of Fig. 1.

Vibrational Spectra

The bands in the 300 to 700 cm^{-1} region are assigned to the fundamental vibrations of the ions of the crystal lattice. For the analysis of such spectra, it is necessary to consider the vibrational spectrum of periodic structures. The vibrational problem is most conveniently treated by classification of crystals according to the continuity of bonding as (1) continuously bonded; (2) discontinuously bonded; and (3) intermediate. In continuously bonded crystals, the atoms are bonded to all nearest neighbors by equivalent forces (ionic, covalent, or van der Waals) and the frequency distribution of vibrations given by a Debye or Born-von Karman treatment of the classical mechanical problem. In this class, we include simple ionic crystals such as the alkali halides; diamond and its homologues;

metals; and rare-gas crystals. In the discontinuously bonded or molecular crystal, sets of atoms are tightly bound by (intramolecular) chemical valence forces and separated from adjacent sets by weak (intermolecular) van der Waals forces. In a first approximation, the spectrum resembles that of a gas molecule with the vibrational lines slightly broadened due to weak inter-

TABLE I. Threshold frequency of the electronic absorption band.

Compound	cm^{-1}	ev
CoFe_2O_4	900 ± 50	0.11
FeFe_2O_4	1200 ± 200	0.15
MgFe_2O_4	1060 ± 50	0.13
MnFe_2O_4	930 ± 50	0.12
$\text{NiFe}_2\text{O}_4^a$	2700 ± 600	0.33
ZnFe_2O_4	2300 ± 200	0.29

^a Inflection point ill-defined due to nearly constant slope.

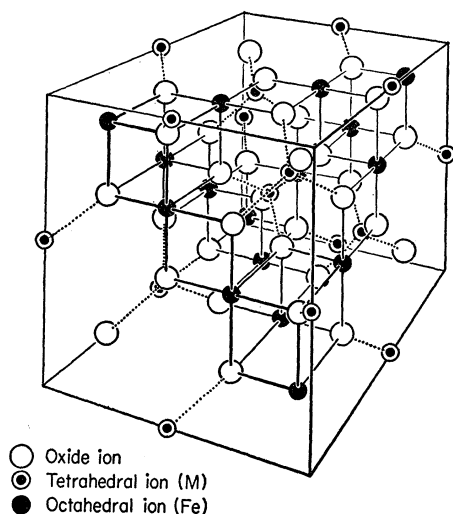


FIG. 3. Crystal structure of normal spinel (cubic unit cell).

molecular coupling; in addition, there is a low-frequency branch similar to the spectrum of a heavier rare-gas crystal. To this class belong the solid phases of polyatomic gases, most organic compounds, sulfur, and nonmetallic compounds.

In the third class, the intermolecular forces are somewhat greater than in the molecular case and the branches may overlap; the vibrational problem may occasionally be treated as a perturbation of the class 2 case. Examples of this group include ionic crystals containing polyatomic ions, hydrogen-bonded crystals, and strongly dipolar crystals.

X-ray diffraction studies of the ferrites⁸ lead to a structure equivalent to the mineral, spinel (Fig. 3). The metal ions are situated in two different types of positions, designated octahedral (*o*) and tetrahedral (*t*) sites according to the geometrical configuration of the oxygen nearest neighbors. Some doubt exists, however, concerning the distribution of the different metal ions between the alternate sites. No isolated molecular groupings occur in the structure, so we assign the ferrites to the class 1 or the continuous case.

The complete frequency distribution consists of $42N$ vibrational modes, where N is the number of primitive unit cells (PUC) in the crystallite (3 degrees of freedom for each ion; 14 ions per PUC). The selection rules require that only modes of proper symmetry absorb infrared radiation. The space group symmetry for a normal spin is $O_h^7(F 4_1/d \bar{3} 2/m)$, with 14 atoms per primitive unit cell ($M_2Fe_4O_4$). (The term normal or inverse spinel designates a structure in which M ions are situated on the tetrahedral or octahedral sites, respectively.)

The complete vibrational spectrum can be classified in terms of the vibrations of a single unit cell. Each

normal mode of the unit cell corresponds to N normal modes of the crystal which differ principally in the phase shift between adjacent cells. It is expedient to subdivide the ions of the PUC into two MO_4 groups and one Fe_4 group of tetrahedral symmetry (Fig. 4). This permits the classification of the vibrations into species of the point group T_d by referring to the well-known results for gas molecules of equivalent symmetry⁹ shown in Table II. Continuity requires that the same symmetry classification holds for the vibrations of the whole crystal since, if we imagine that the coupling between MO_4 and Fe_4 groups decreases, we approach the case of $3N$ gas molecules in the limit of zero interaction.

Only species F_2 has the symmetry of a vector set and

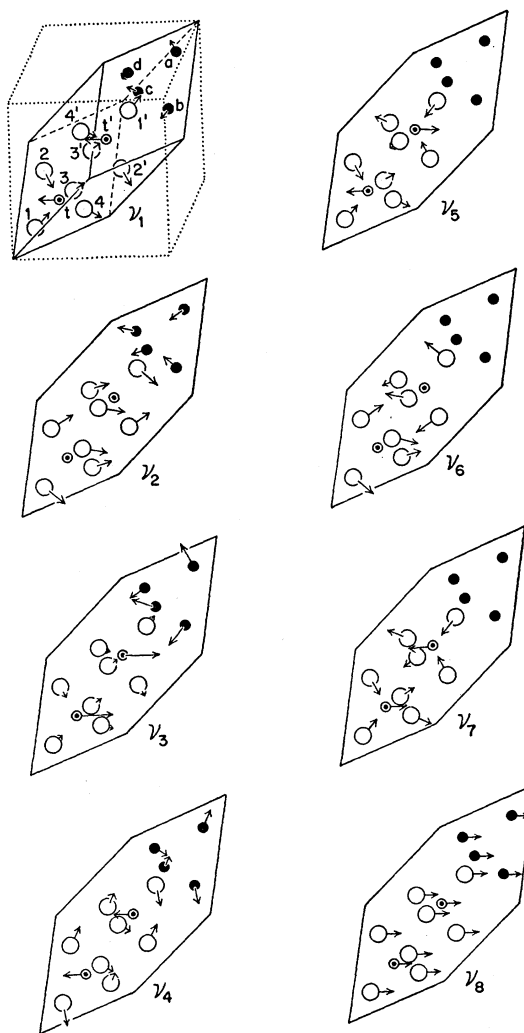


FIG. 4. Species F_2 normal vibrations of a spinel (schematic). Cubic unit cell (dotted line) (see Fig. 3). Rhombohedral primitive unit cell PUC (solid line). Tetrahedral groups $MO_4(t, 1, 2, 3, 4)$, $MO_4'(t', 1', 2', 3', 4')$, $Fe_4(a, b, c, d)$.

⁸ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. II, Chap. 8.

⁹ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), pp. 99 ff.

TABLE II. Symmetry classification of vibrations.

<i>T_d</i> species	Degeneracy	Degrees of freedom		
		<i>MO</i> ₄	<i>Fe</i> ₄	2 <i>MO</i> ₄ + <i>Fe</i> ₄
<i>A</i> ₁	(1)	(1)×1	(1)×1	(1)×3
<i>E</i>	(2)	(2)×1	(2)×1	(2)×3
<i>F</i> ₁	(3)	(3)×1	(3)×1	(3)×3
<i>F</i> ₂	(3)	(3)×3	(3)×2	(3)×8
Total		15	12	42

hence is infrared active. The selection rules further require that the phase shift between successive cells match that of the electromagnetic wave of equal frequency. Since the ratio of sound to light velocity is so low, this phase shift is extremely small and the active mode effectively corresponds to a vibration invariant with respect to lattice translations. Of the 42*N* normal vibrations, 24*N* belong to species *F*₂, 24 are invariant with respect to translation, and only eight discrete infrared bands should occur. In an inverse spinel, the local symmetry is lowered by substitution of $\frac{1}{2}$ of the octahedral sites by *M* ions. This splits each triply degenerate vibration into three vibrations of different frequency. Disorder in the lattice would destroy the translational invariance of the vibrations leading to a distribution of infrared active frequencies. Isotopic substitution would also produce this effect.

The precise form of the normal vibrations depends upon the potential energy field except where the requirements of symmetry uniquely determine the mode. Of the eight possible frequencies, three are internally inactive and one is the zero frequency translation. (The internally inactive vibrations arise because of the equivalence of the *MO*₄ groups and the location of the *Fe* ions on centers of symmetry.) The normal coordinates of species *F*₂ are pictured schematically in Fig. 4. Each oxide ion is bonded to three octahedral ions and one tetrahedral ion. In the normal spinel, the three octahedral bonds lie along the coordinate axes and provide an isotropic force field which would permit the oxide ion to oscillate in any direction with a constant frequency if the tetrahedral bonds were absent. The tetrahedral bonds have the effect of substantially

increasing the frequency for vibrations along the *t*-O axis (*ν*₁), while vibrations at right angles (*ν*₂) would change frequency only slightly if small bending force constants are assumed. The two low-frequency active modes, *ν*₃ and *ν*₄, involve oscillations of the metal ions in the isotropic force fields of their octahedral or tetrahedral environments.

Since only two infrared bands were accessible in the spectral range covered, only two potential constants of the energy field can be calculated, and the identification of these constants with particular bonds requires certain simplifying assumptions. In the following treatment, we shall neglect bending force constants: this approximation is probably closer to reality in the ionic than the molecular case, where it is occasionally employed in the evaluation of stretching force constants. We shall use the following expression for the potential energy: $2V = k_t \sum r_i^2 + k_o \sum r_o^2$, where *k_t* and *k_o* designate the force constants associated with unit displacement of the *t*-O and *o*-O bonds, respectively, and *r_t* and *r_o* represent the corresponding components of displacement from equilibrium in the direction of the appropriate bonds.

The determination of the vibrational frequencies and normal coordinates can be carried out by the method of symmetry coordinates devised by Wilson¹⁰; but in our case, the modes can be determined directly by inspection. Table III gives the coordinates for the four active vibrations.

The zero frequency result for *ω*₄ is not unexpected in view of the potential field chosen: if the *MO*₄ groups were isolated, there would be no restoring force for the degenerate bending vibration. Introduction of a bending-force constant would lead to simultaneous equations for *ω*₂ and *ω*₄ similar to the equations for *ω*₁ and *ω*₃.

We assign the high-frequency line observed to *ν*₁ and the low-frequency line to *ν*₂ for the following reasons: *ν*₂ has a lower frequency than *ν*₁ as was discussed qualitatively; the frequencies are about those expected for roughly equivalent force constants (if *k_t*=*k_o*, *ν*₁/*ν*₂≈√2); and the intensities are nearly equal, as expected if the motions are predominantly those of the oxide ion. The

TABLE III. Normal coordinates of infrared active vibrations.

<i>ν</i> ₁ , <i>ν</i> ₂			<i>ν</i> ₂		<i>ν</i> ₄	
<i>a</i> = <i>u</i> (-1 1 1)	1=1	1 1	<i>a</i> = <i>U</i> (-2 -1 -1)	1=2	-1 -1	<i>a</i> , 2= <i>x</i> 1 1
<i>b</i> = <i>u</i> (-1 -1 -1)	2=1	-1 -1	<i>b</i> = <i>U</i> (-2 1 1)	2=2	1 1	<i>b</i> , 1= <i>x</i> -1 -1
<i>c</i> = <i>u</i> (-1 -1 1)	3=1	-1 1	<i>c</i> = <i>U</i> (-2 1 -1)	3=2	1 -1	<i>c</i> , 4= <i>x</i> -1 1
<i>d</i> = <i>u</i> (-1 1 -1)	4=1	1 -1	<i>d</i> = <i>U</i> (-2 -1 1)	4=2	-1 1	<i>d</i> , 3= <i>x</i> 1 -1
<i>t</i> = <i>v</i> (-1 0 0)			<i>t</i> ≡0			<i>t</i> =- <i>X</i> 0 0
<i>m_tv</i> +2 <i>m_ou</i> =4 <i>m_o</i> =64			<i>m_oU</i> =2 <i>m_o</i> =32			<i>m_tX</i> =(2 <i>m_o</i> +4 <i>m_o</i>) <i>x</i>
$\omega_1, \omega_2^2 = 4k_t \frac{m_t}{(1/v + \frac{1}{2})}$			$\omega_2^2 = 2k_o \frac{(1/U + 1)}{m_o}$			<i>X</i> =2- <i>x</i>
$= 2k_o \frac{m_t}{(1/u + 1)}$						<i>ω</i> ₄ ≡0

where 1=1', 2=2', etc., *t*=*t'*, *ω*=2*πν*.

¹⁰ J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. 2, 630 (1934).

TABLE IV. Infrared spectral frequencies of ferrites.

Compound	ν_1	ν_2	Other ν 's (cm^{-1})
CoFe_2O_4	575	374	shoulder <i>ca</i> 320
FeFe_2O_4	570 ^a (579 ^a , 610 ^a)	370-80	
MgFe_2O_4	565	406	{380 430-40} shoulder <i>ca</i> 735
MnFe_2O_4	550	392	shoulder <i>ca</i> 645, 320
NiFe_2O_4	587	396	
ZnFe_2O_4	555 ^a (540, 575)	393	shoulder <i>ca</i> 325
$\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$	563	409	

^a Liquid N₂.

last fact rules out overtones or combinations of lower frequency vibrations as the source of one of the absorption bands. The presence of weaker bands and line broadening in this region may be due to splitting of degeneracies, overtone or combination bands and precise assignment is not possible.

Table IV gives the measured frequencies of the vibrational bands of the ferrites. The customary narrowing of bands was not observed at liquid N₂ temperature, which may indicate splitting of degeneracies or disorder, but no significant trend from normal to inverse spinels was apparent.

The force constants were computed as follows: ν_2 was used to determine k_o : three values were obtained corresponding to $m_o = \text{Fe}$, M , and $(\text{Fe} + M)/2$, respectively. Next, ν_1 and each of the values of k_o were used to determine u and v ; the corresponding values of m_t were M , Fe , and Fe , respectively. Finally, substitution in the alternate frequency equation gave k_t . Table V summarizes the results.

The first column of each section corresponds to a normal spinel, while the next two columns represent inverse structures. The mixed ferrite was calculated with the masses indicated. For MgFe_2O_4 , the disparity in masses becomes serious, and calculations based on subdividing the low-frequency band into several com-

ponents is necessary. The accompanying spectrum is considerably broadened with evidence of multiplet structure. The assigned values are considered to represent the actual constants for reasons discussed below.

DISCUSSION

Of the three ferrites believed to be predominantly inverse, i.e., Co, Fe, and Ni,¹¹ with tetrahedral sites occupied by Fe, the constants k_t are very nearly equal (*ca* 1.66×10^5 dynes/cm). For ZnFe_2O_4 , which is a normal spinel, as well as Mg and Mn in which some doubt exists as to the configuration,¹¹ the values of k_t are substantially lower. This phenomenon, if generally true, might assist in the elucidation of the structure of complex ferrites.

One would predict a lowering of the force constant for either site if the mean ionic charge for such a site were lowered. The lowered electrostatic energy would lead to a slight increase of the $t\text{--O}$ bond length and a reduction in the repulsive forces between the ions leading to a lower force constant. In the case of Mg, it is likely that some divalent Mg ions are situated on tetrahedral sites which would be consistent with the hypothesis advanced above, and would explain the broad high-frequency shoulder occurring in the infrared spectrum. For MnFe_2O_4 , one would expect that either Mn^{++} ions occupy some tetrahedral sites, or that Fe^{++} occurs in some tetrahedral sites, and an equivalent amount of Mn^{+++} or Mn^{++++} is present in the lattice. The former case would represent a tendency to a normal spinel structure, while the latter would be atomically inverse but electrically normal. Either situation would not affect the saturation magnetic moment of the crystal.¹¹

The valence bond-force constants may be used to calculate the elastic constants of the crystal, and they in turn are useful in the evaluation of the compressibility and heat capacity. For this calculation, it is convenient to compute the energy required to compress

TABLE V. Force constants of the ferrites.

Compound	$m_o = \text{Fe}$	M	k_o	$\frac{1}{2}\text{Fe} + M$	Assigned	$m_t = M$	Fe	k_t	Fe	Assigned
CoFe_2O_4	0.838	0.854	0.846	0.85	1.705	1.677	1.645	1.66		
FeFe_2O_4	{0.820 ^a 0.865 ^a			0.84		{1.66 ^a 1.632 ^a		1.65		
MgFe_2O_4	0.988 ^b 0.865 ^c	{0.752 ^d 0.788 ^d	0.864 ^b	0.86	1.178 ^b 1.253 ^c	{1.521 ^d 1.469 ^d	1.522 ^b	1.52		
MnFe_2O_4	0.920	0.915	0.917	0.92	1.394	1.402	1.402	1.40		
NiFe_2O_4	0.939	0.957	0.948	0.95	1.715	1.69	1.66	1.67		
ZnFe_2O_4	0.925			0.925	{1.422 ^e 1.542 ^e			1.477		
$\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$	$m_o = (0.85 \text{ Fe} + 0.15 \text{ Ni})$ $m_t = (0.3 \text{ Fe} + 0.7 \text{ Zn})$			1.005				1.455		

^a Calculations based on: $\nu_2 = 370\text{--}380 \text{ cm}^{-1}$.^b Calculations based on: $\nu_2 = 406 \text{ cm}^{-1}$.^c Calculations based on: $\nu_2 = 380 \text{ cm}^{-1}$.^d Calculations based on: $\nu_2 = 430\text{--}440 \text{ cm}^{-1}$.^e Calculations based on: $\nu_1 = 540\text{--}575 \text{ cm}^{-1}$.¹¹ E. J. W. Verwey and E. L. Heilmann, J. Chem. Phys. 15, 174 (1947).

TABLE VI. Elastic constants of the ferrites.

Ferrite	r_0	C_2	$x_0 = r_0/3$	$C_1 = C_2/9$	$c_{11} = c_{12} = 1/\beta$
CoFe ₂ O ₄	0.3305	7.932	0.1102	0.8813	1.794×10^{12} dynes/cm ²
FeFe ₂ O ₄	0.3305	7.932	0.1102	0.8813	1.772×10^{12} dynes/cm ²
NiFe ₂ O ₄	0.3188	7.656	0.1063	0.8506	1.944×10^{12} dynes/cm ²

the unit cell a standard distance: A , in three dimensions; and B , along one axis. The unit-cell edge a_0 is determined by two o -O bonds parallel to a_0 and two t -O bonds at $\cos^{-1}(1/\sqrt{3})$ with a_0 .

For case A , unit displacement requires that $2r_t/\sqrt{3} + 2r_o = 1$. Since the unit cell contains 32 t -O bonds and 96 o -O bonds, we may write:

$$V_3 = (32/2)k_t r_t^2 + (96/2)k_o r_o^2$$

as the potential energy per unit cell for 3-dimensional compression. If we set $k_t = \gamma k_o$ and substitute to eliminate r_t , we obtain:

$$V_3 = 12k_o[\gamma - 4\gamma r_o + 4(1+\gamma)r_o^2] = C_3(\gamma)k_o$$

for unit displacement.

To determine the individual displacements yielding the lowest energy, we set:

$$\partial V_3 / \partial r_o = 0, \quad A[-4\gamma + 8(1+\gamma)r_o] = 0, \quad r_o = \gamma/2(1+\gamma).$$

For an arbitrary displacement,

$$V_3 = C_3 k_o (a - a_0)^2 = C_3 k_o a_0^2 \alpha^2,$$

where $\alpha = (a - a_0)/a_0$. Dividing by the unit-cell volume a_0^3 , we finally obtain the expression for the potential energy per unit volume:

$$\bar{V}_3 = C_3 k_o \alpha^2 / a_0.$$

Elasticity theory gives the following expression for the energy density:

$$\bar{V} = \frac{1}{2} \sum_{i,j=1}^6 c_{ij} \alpha_i \alpha_j. \quad (12)$$

In the special case of uniform compression of a cubic crystal, we have $\bar{V}_3 = \frac{3}{2}(c_{11} + 2c_{12})\alpha^2$. It follows that $c_{11} + 2c_{12} = 2C_3 k_o / 3a_0$.

For case B , we resolve r_t into components x_t , y_t , and z_t , and subdivide the displacements of the 96 o -O bonds into 32 x_o , 32 y_o , and 32 z_o . By symmetry, $y_t = z_t$, $r_t = (x_t + 2y_t)/\sqrt{3}$, and for unit displacement along the x axis and zero displacements along the y and z axes, we have:

$$\begin{aligned} 2x_t + 2x_o &= 1, \\ 2y_t + 2y_o &= 0, \end{aligned} \quad V_1 = 16k_t \left(\frac{x_t + 2y_t}{\sqrt{3}} \right)^2 + 16k_o (x_o^2 + 2y_o^2).$$

Substituting to eliminate x_t , y_t , and k_t yields:

$$V_1 = (4k_o/3)(\gamma - 4\gamma x_o - 8\gamma y_o + 4\gamma x_o^2 + 16\gamma x_o y_o + 16\gamma y_o^2 + 12x_o^2 + 24y_o^2) = C_1(\gamma)k_o$$

for unit displacement. To minimize the energy, we set:

$$\begin{aligned} \partial V_1 / \partial x_o &= 0, \quad A(-4\gamma + 8\gamma x_o + 16\gamma y_o + 24x_o) = 0, \\ \partial V_1 / \partial y_o &= 0, \quad A(-8\gamma + 16\gamma x_o + 32\gamma y_o + 48y_o) = 0. \end{aligned}$$

Solving for x_o and y_o gives:

$$x_o = \frac{\begin{vmatrix} \gamma & 4\gamma \\ \gamma & 6+4\gamma \end{vmatrix}}{\begin{vmatrix} 6+2\gamma & 4\gamma \\ 2\gamma & 6+4\gamma \end{vmatrix}}, \quad y_o = \frac{\begin{vmatrix} 6+2\gamma & \gamma \\ 2\gamma & \gamma \end{vmatrix}}{\begin{vmatrix} 6+2\gamma & 4\gamma \\ 2\gamma & 6+4\gamma \end{vmatrix}},$$

or $x_o = y_o = \gamma/6(1+\gamma)$. For arbitrary displacements, $V_1 = C_1 k_o a_0^2 \alpha^2$ and $\bar{V}_1 = C_1 k_o \alpha^2 / a_0$.

From elasticity theory: $\bar{V}_1 = \frac{1}{2} c_{11} \alpha^2$. Thus $c_{11} = 2C_1 k_o / a_0$, and using the results obtained for case A , we obtain $c_{12} = (C_3/3 - C_1)k_o / a_0$.

The compressibility is defined by the expression: $\beta = -\partial \bar{V} / \partial p$, where $\bar{V}$ denotes the volume of the crystal. It can be shown that $1/\beta = (c_{11} + 2c_{12})/3 = 2C_3 k_o / 9a_0$ for cubic crystals. Table VI gives the computed constants and compressibilities for Co, Fe, and NiFe₂O₄.

Experimental values reported for $1/\beta$ for magnetite range from 1.61 to 1.78×10^{12} dynes/cm², with measurements of $c_{11} = 2.70$ to 2.75×10^{12} dynes/cm² and $c_{12} = 1.04$ to 1.08×10^{12} dynes/cm² also quoted.¹³

The agreement with experiment is quite satisfactory for the compressibility. The discrepancy with the elastic constants can be traced to the neglect of the bending-force constants. In fact, in the approximation used for the potential field, there would be no resistance to one-dimensional compression if the lateral dimensions were free to expand (analogous to the zero frequency motion for ν_4). This leads to a value of c_{11} which is too low, and c_{12} is accordingly too high since it is derived by subtraction of a one-dimensional term from the three-dimensional term. The equality of c_{11} and c_{12} seems to be fortuitous.

The molar heat capacity at constant volume, C_v , may be calculated in the Debye theory approximation either by using the computed elastic constants or by using the limiting frequencies observed in the infrared spectrum.

In the former case, the elastic wave velocities are

¹² F. M. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 94 ff.

¹³ M. S. Doraiswami, Proc. Indian Acad. Sci. A25, 413 (1947).

TABLE VII. Molar heat capacity of magnetite (Fe₃O₄).

T°K	C _p ^a	C _v ^b	C _v (elas. const)	C _v (IR freq.) cal/mole
60.5	5.495	5.43	2.166	6.094
70.5	7.331	7.25	3.359	8.128
100.7	13.67	13.56	8.369	13.85
127.5	19.16	19.02	13.46	18.26
153.7	22.63	22.46	18.08	22.05
191.4	26.98	26.77	23.54	26.34
235.7	31.18	30.92	28.14	30.05
261.1	32.68	32.39	30.14	31.67
299.7	34.39	34.06	32.47	33.60

^a R. W. Millar, J. Am. Chem. Soc. **51**, 215 (1929).^b C_p - C_v = 0.0011T assumed.

given by: $v_l = (c_{11}/\rho)^{1/2}$, $v_t = [(c_{11} + c_{12})/2\rho]^{1/2}$, where v_l and v_t represent longitudinal and transverse wave velocities and ρ is density.

Using the x-ray computed density for FeFe₂O₄, 5.238, and the previously derived elastic constants, we arrive at the following values: $v_l = v_t = 5.816 \times 10^5$ cm/sec. From the relation $\bar{\nu}_{\max} = v\sigma_{\max}$, we may calculate the high-frequency cutoff of the elastic waves. We may assume that the shortest wave corresponds to $\frac{1}{2}$ wave per mean interatomic distance $\bar{d}$. Since $\bar{d} = \frac{1}{4}(3r_o + r_i) = 7.732 a_0/32$, we obtain $\sigma_{\max} = 2.07/a_0$ and $\bar{\nu}_{\max} = 1.438 \times 10^{13}$ sec⁻¹. This corresponds to a frequency of 480 cm⁻¹ which represents an approximate mean between the cut-off frequencies of the oxide and metal ion vibrations, ν_1 and ν_3 . The characteristic Debye temperature is defined by $\theta = hcv_{\max}/k = 1.438\nu_{\max} = 690^\circ$. This would give $C_v = 21Rf(T/690)$, where R is the gas constant and f is the Debye function.

In the second method, we may employ a two-parameter treatment by using the frequencies ν_1 and ν_3 as cut-off frequencies for oxide vibrations and metal ion vibrations, respectively. ν_1 was observed directly and ν_3 was calculated by solving the simultaneous equations for u and v in Table III. The results are: $\nu_1 = 570$ cm⁻¹, $u = 10.22$, $v = -19.28$, $\nu_3 = 237$ cm⁻¹, $\theta_1 = 820^\circ$, and $\theta_3 = 341^\circ$. Finally $C_v = R[12f(T/820) + 9f(T/341)]$.

The calculated molar heat capacity is compared in Table VII with the experimental values using a $C_p - C_v$ correction calculated from the experimental values of the thermal expansion coefficient and compressibility at room temperature and assuming the function to be linear in temperature.

The agreement is fairly good, especially with the IR frequency method. An improved fit could be obtained by empirically choosing a lower cut-off frequency in the elastic constant method.

INTENSITIES

The measurement of intensities of infrared bands can give useful information concerning the change of electric dipole moment with interatomic distance. For this purpose, the intensities of both ν_1 and ν_2 were measured.

We define the extinction coefficient k by the equation:

$$I_{\text{trans}}/I_{\text{incid}} = e^{-kx} = 10^{-Ax},$$

where I is the intensity (power) of the radiation, x is the path length, and A is the absorption coefficient. It can be shown that⁹

$$\bar{k} = (8\pi^2 N \nu / 3ch) ([M]^{n,m})^2$$

for gas molecules, where $\bar{k} = \int k(\nu) d\nu$, N is the number of molecules/cm³, ν is the frequency, c is the velocity of light, h is Planck's constant, and $[M]^{n,m} = \int \psi_n \mu \psi_m^* d\tau$ is the matrix element corresponding to the electric dipole transition moment between the states m and n . We may expand the transition moment in a power series in the normal coordinate q :

$$[M]^{n,m} = M_0 \int \psi_n \psi_m^* d\tau + \frac{dM}{dq} \int \psi_n q \psi_m^* d\tau + \frac{1}{2} \frac{d^2 M}{dq^2} \int \psi_n q^2 \psi_m^* d\tau + \dots$$

The first term vanishes by virtue of the orthogonality of the wave functions, while the third term is zero in the harmonic oscillator approximation for fundamental absorption bands. For harmonic oscillators, the integral

$$q^{0,1} = \int \psi_n q \psi_m^* d\tau = 1/(2\alpha)^{1/2},$$

where $\alpha = 4\pi^2 m c \nu / h$, where m is the reduced mass. Thus:

$$M_q^2 = \left(\frac{dM}{dq} \right)^2 = \frac{3\alpha c h}{4\pi^3 N} \bar{k} = \log_e \left(10 \frac{3mc^2}{\pi N x} \right) \cdot \bar{A} x = 1.975 \times 10^{21} \frac{m \bar{A} x}{N x}$$

TABLE VIII. Intensities and derived constants of ferrites.

Compound	Funda- mental	$\bar{A}x$	$\frac{Nx}{(\text{cm}^{-2})}$ $\times 10^{18}$	m (g) $\times 10^{-23}$	$\frac{Mq}{(\text{esu})}$ $\times 10^{-9}$	$Q(\epsilon)$
CoFe ₂ O ₄	ν_1	108	2.1	2.14	1.477	1.78
	ν_2	53.5		1.69	0.922	1.11
FeFe ₂ O ₄	ν_1	22	2.14	2.16	0.663	0.80
	ν_2	10.65		1.69	0.408	0.49
MgFe ₂ O ₄	ν_1	120.8	2.47	2.2	1.46	1.76
	ν_2	47.8		1.69	0.804	0.97
MnFe ₂ O ₄	ν_1	66	2.14	2.16	1.15	1.38
	ν_2	56.5		1.69	0.939	1.13
NiFe ₂ O ₄	ν_1	140.5	2.1	2.14	1.683	2.02
	ν_2	55.8		1.69	0.942	1.13
ZnFe ₂ O ₄	ν_1	88	2.05	2.2	1.37	1.65
	ν_2	91.6		1.69	1.22	1.47

Table VIII gives the measured values for the compounds studied. The last column is defined by the equation $Q = M_q/\sqrt{3}\epsilon$, where ϵ is the electronic charge. Thus Q represents the effective charge in electrons equivalent to the measured intensities. (Since the vibrations are triply degenerate, M_q represents the vector sum of the transition moments for the individual components and the factor $1/\sqrt{3}$ must be incorporated to yield the

correct value for a single axis. The effect of refractive index was neglected.)

It may be shown by a semiclassical calculation that the polarization per unit volume and hence the intensities of a set of weakly coupled harmonic oscillators are equal to those of an isolated, uncoupled set of equal density. The computed values are in the range of 2ϵ as expected for oxide ion vibrations.

Influence of Exchange and Correlation on Electron Transport in Metals*

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A result of the collective treatment of Bohm and Pines is that the dependence of electron energy ϵ on the wave vector k differs from that for noninteracting free electrons. It follows that the expressions for those properties, such as conductivity and thermoelectric power, which depend on the relationship between ϵ and k must be suitably modified. Electrical and thermal conductivity are altered in the same manner, suffering slight changes because of changes of the density of states at the Fermi energy and of the relaxation time. The Wiedemann-Franz ratio remains unaltered. For the alkali metals the calculated thermoelectric power is reduced slightly below the free-electron value. The changes in both conductivity and thermoelectricity are too small to permit quantitative comparison with experiment.

I. INTRODUCTION

IN a series of papers¹ Bohm and Pines have developed a new method for treating exchange and correlation effects in an electron gas. It was found that the influence of exchange and long-range correlation on the one-electron energies results in an energy *versus* wave vector relationship which is somewhat different from that given by the Hartree approximation. The collective description of electron interaction appears to be much superior to the Hartree-Fock approximation which neglects correlation of electrons with antiparallel spins and leads to incorrect results. In particular, near the Fermi energy the following relation holds²

$$\epsilon(k) = \frac{3.68k^2}{r_s^2} (m/m^*) - \frac{0.611}{r_s} \times \left[1 - 2\beta + \frac{\beta^2 + 3k^2 - 1}{2k} + \frac{1 - k^2}{k} \ln\left(\frac{1+k}{\beta}\right) \right], \quad (1)$$

where ϵ is in rydbergs, r_s is the average interelectronic distance in units of the Bohr radius, and k is the wave vector in units of k_F , k_F being the wave vector at the

Fermi energy. β is a parameter in the theory of Bohm and Pines which is a measure of the screening of the Coulomb interaction. Its value is given by $\beta = 0.353\sqrt{r_s}$.³ Equation (1) is to be compared with the free-electron expression

$$\epsilon_0(k) = \frac{3.68k^2}{r_s^2} \left(\frac{m}{m^*} \right). \quad (2)$$

The purpose of this note is to consider what changes appear in the expressions for the transport properties of an electron gas when Eq. (1) is used in place of the more common Eq. (2).

II. CONDUCTIVITY

The electrical and thermal conductivities of a metal are proportional to the density of states at the Fermi energy, $N(\epsilon_F)$, and to the relaxation time, τ .

The dependence of the relaxation time on the relationship between ϵ and k is a function of the type of scattering (lattice or impurity) and of the temperature. For lattice scattering in the high-temperature limit, an examination of the standard calculation of relaxation time⁴ shows that

$$\tau = Dk \left(\frac{d\epsilon}{dk} \right)^2 / \frac{d^2\epsilon}{dk^2}, \quad (3)$$

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¹ D. Bohm and D. Pines, Phys. Rev. **82**, 625 (1951); **85**, 836 (1952); **92**, 609 (1953); D. Pines, Phys. Rev. **92**, 626 (1953).

² The term involving $\beta^3/6$ which appears in D. Pines, Report to the Solvay Congress, Eq. (28), has been omitted in Eq. (1) because it is a higher-order term which is canceled by other higher-order corrections. The author would like to thank Dr. Pines for informing him of this result before publication.

³ D. Pines, private communication.

⁴ A. H. Wilson, *Theory of Metals* (Cambridge University Press, London, 1953), second edition, p. 263.