MAGNETIC MOMENT OF Fe²⁺ IN PARAMAGNETIC MINERALS

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ABSTRACT

The effective magnetic moment of Fe^{2+} in monoclinic pyroxenes, orthorhombic pyroxenes, cordierite, amphibole, biotite, wolframite and sphalerite calculated from susceptibility data is found to be a variable with values spanning the theoretical range from 4.90 to 6.70 Bohr magnetons. Interpretation of this variability in terms of site symmetry is explored and found incomplete.

INTRODUCTION

Correlation of paramagnetic susceptibility of minerals with the concentrations of magnetic ions contained is frequently attempted and found unsatisfactory. Some of the reasons for this are readily seen. Susceptibilities are frequently anisotropic and misleading measurements of average susceptibilities can result unless special care is taken to avoid preferred orientation of the sample. More often than not phase impurities are present in natural mineral samples. If the inclusion is minor and paramagnetic its presence can be ignored and its magnetic ion content considered part of the host. A better approximation would obviously result if the inclusion were identified, a modal analysis made, and its contribution to susceptibility subtracted. For this purpose the susceptibility of the included species is required.

The susceptibility of a ferromagnetic impurity, present even in very small amount, can completely mask the susceptibility of the host. Samples containing ferromagnetic inclusions in small quantity can be handled by making measurements at several high field strengths and extrapolating to infinite fields where the impurity will be saturated, hence behave as a minor paramagnetic impurity (Bates, 1961).

Ideally, paramagnetic susceptibilities are related to the concentrations and ionic magnetic moments of constituent ions by Langevin's formula

$$\chi_m = \frac{N\beta^2\mu^2}{3kT} \qquad (1)$$

where

χ_m = magnetic susceptibility per mole
N = Avogadro's number
μ = the magnetic moment of the ion
k = Boltzmann's constant
β = Bohr magneton
T = temperature °K.

Ideal paramagnetism is not commonly observed. Due to interaction among neighboring magnetic ions and crystal fields the susceptibility frequently obeys the Curie-Weiss law (Van Vleck 1959),

$$\chi_m = \frac{N\beta^2\mu^2}{3k\lfloor T - \theta\rfloor} \tag{2}$$

where θ is known as the Curie Temperature. The magnitude of θ may depend on composition and thermal history.

Thus, unless θ is identical for all minerals in a group for which susceptibility composition correlation is attempted, lack of precision must be expected.

Because the μ of Fe^{2+} is significantly different from that of Fe^{3+} and Mn^{2+}, precise correlation of χ with the combined $Fe + Mn$ content cannot be expected, although it is attempted and may be useful for some rough purposes.

There are several reasons to believe that the ionic moments themselves cannot be safely assumed constant. Since the magnetic moments of ions are of quantum mechanical origin, their detailed discussion without the explicit use of quantum mechanics is not complete. However, for the purpose of this communication it will suffice to say that the magnetic moment of an ion results from the unbalanced orbital motion of the electrons and their unpaired spins. Experimental moments for the transition metals often approach a "spin only" approximation, calculated on the assumption that orbital contributions are quenched. The effective moment of an ion may assume values different from the "spin only" moment; under conditions where the orbital contribution is not quenched, a higher moment is predicted. The upper and lower limits of the magnetic moment are easily established by quantum mechanics. Furthermore, it can be shown from group theory and quantum mechanics (Van Vleck, 1959, Tinkham, 1964) that generally the orbital contribution to the magnetic moment of an ion in a crystalline environment is determined in part by coordination symmetry. Although the upper and lower limits of the magnetic moments calculated from quantum mechanics are available in the literature and are reported in Table 1, with the empirical moments

TABLE 1. MAGNETIC MOMENTS OF FREE IONS

Ion	Spin only (theoretical)	Maximum (theoretical)	Stoner's (empirical)
Fe^{2+}	4.90	6.70	5.25–5.53
Mn^{2+}	5.92	5.92	5.88
Fe^{3+}	5.92	5.92	5.88

chosen by Stoner (1934), the theoretical calculations of exact magnetic moments in environments of intermediate symmetry are very complex and have been attempted for very simple systems only.

In summary, there are two types of sources of imprecision in calculation of susceptibility of minerals or correlation of susceptibility with composition. The first can be avoided by proper, if tedious, execution of susceptibility measurements. The second consists in failure to recognize that ionic moments are not constants and that the rule by which they are related to susceptibility may include a factor characteristic of the sample, i.e. the Curie Point.

We have examined some of the susceptibility data available in the literature with the objective of determining the extent to which the effective moment of Fe^{2+} is variable and if possible detecting any relationship between moment and site symmetry.

Selection of Data

The first criterion for the selection of data was the absence of ferromagnetic impurities. Therefore we selected data which had been corrected for ferromagnetic impurities by the original authors or for which sufficient information was available to make such a correction possible as a part of our analysis using the method described by Bates (1961). Data obtained by indirect methods or methods which could lead to preferred orientation of cleavable minerals were not used. Data on seven mineral or mineral series including 54 separate samples survived the selection process. Each series is represented by at least 3 individual samples each of different origin and composition. Most details of origin and composition which are recorded in the original references are of secondary importance in this context, hence are omitted from the brief descriptions given in Table 2. Each set of analytical data was further examined for purity and analytical accuracy by calculating the mole balances. The phase purity of several wolframite samples was considered doubtful, e.g., one contains 6% Cu, perhaps as $CuFeS_2$. One cordierite sample (#4) contains 2.05% TiO_2. One sphalerite sample (designated "Gilman") has excess sulfur and another (designated "Chester") contains 2% Cu perhaps as $CuFeS_2$. Such samples were excluded from our analysis.

The effect of temperature on susceptibility was observed in only a few papers, and then not for all samples. The largest Curie temperature observed was about 70° K which is significant. However, owing to the lack of more extensive information we were forced to use the simple form of the Langevin formula, equation (1), and to emphasize the approximate nature of moments so calculated by labeling the μ "effective", μ_{eff}.

<div align="center">Table 2. Selected Data</div>

Mineral series	Data from	No. of samples	Magnetic ion and concentration range wt %	Method of χ-measurement
Amphiboles	Syono (1959–60)	6	$Fe^{2+}(3.03–20.20)$ $Fe^{3+}(0.13–6.99)$ $Mn^{2+}(0.16–1.13)$	Faraday
Biotites	Syono (1959–60)	5	$Fe^{2+}(12.45–16.35)$ $Fe^{3+}(0.52–14.16)$ $Mn^{2+}(0.36–1.8)$	Faraday
Monoclinic Pyroxenes	Chevallier and Mathieu (1958)	12	$Fe^{2+}(6.90–22.6)$ $Fe^{3+}(0.87–1.54)$ $Mn^{2+}(0.14–0.54)$	Faraday
Orthorhombic Pyroxenes	Akimoto, Horai and Boku (1958–59)	8	$Fe^{2+}(2.49–37.8)$ $Fe^{3+}(0.00–2.75)$ $Mn^{2+}(0.01–0.94)$	Faraday
Cordierites	Syono (1959–60)	4	$Fe^{2+}(2.01–8.96)$ $Fe^{3+}(0.05–1.90)$ $Mn^{2+}(0.04–1.44)$	Faraday
Wolframites	Spokes and Mitchell (1958)	14	$Fe^{2+}(0.34–17.70)$ $Mn^{2+}(0.40–17.25)$	Guoy
Sphalerites	Spokes and Mitchell (1958)	5	$Fe^{2+}(0.27–16.4)$	Guoy

Calculations of Magnetic Moment

Equation (1) can be used with total chemical analyses and susceptibility measurements on several samples to calculate the effective moments of all magnetic ions contributing to the susceptibility. For samples containing more than one species of magnetic ions equation (1) can be written as

$$\chi_g = \frac{N\beta^2}{3kT} \sum_i \frac{\mu_i^2 P_i}{W_i} \tag{3}$$

where χ_g is susceptibility per gram and μ_i, P_i, W_i are the magnetic moment, weight percent and atomic weight of the ith species of the magnetic ions.

All of the minerals contained Fe^{2+} and at least minor amounts of Fe^{3+} and Mn^{2+}. In view of the commonly reported precision of chemical analyses at low concentration and of susceptibility measurements, the calculation of effective moments for minor constituents was deemed unjustified. Neglect of the susceptibility contribution of an ion present in a concentration less than a few percent could result in significant error in calculating μ_{eff} for major components. Minor element contributions are relatively small however, and, the error introduced by using Stoner's moments to calculate corrections is also small. Measured susceptibilities corrected by subtracting the calculated contributions of minor constituents, symbolized χ_c, were used in evaluation of μ_{eff} for the major components.

The corrected susceptibility data can be divided into two groups according to the number of ions for which moments are to be calculated. In the first group, namely the pyroxenes, cordierite and sphalerite, there is
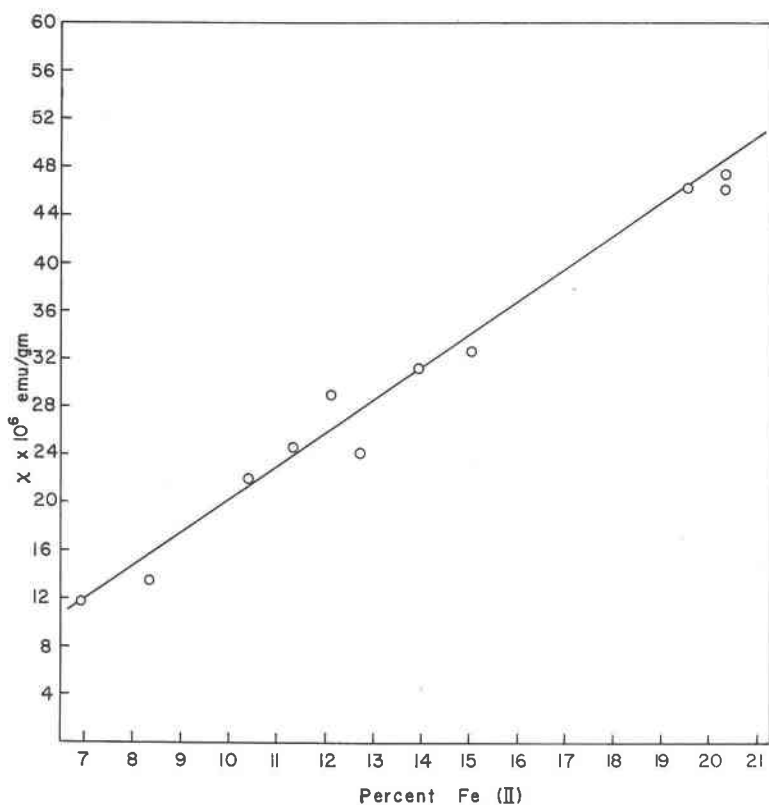

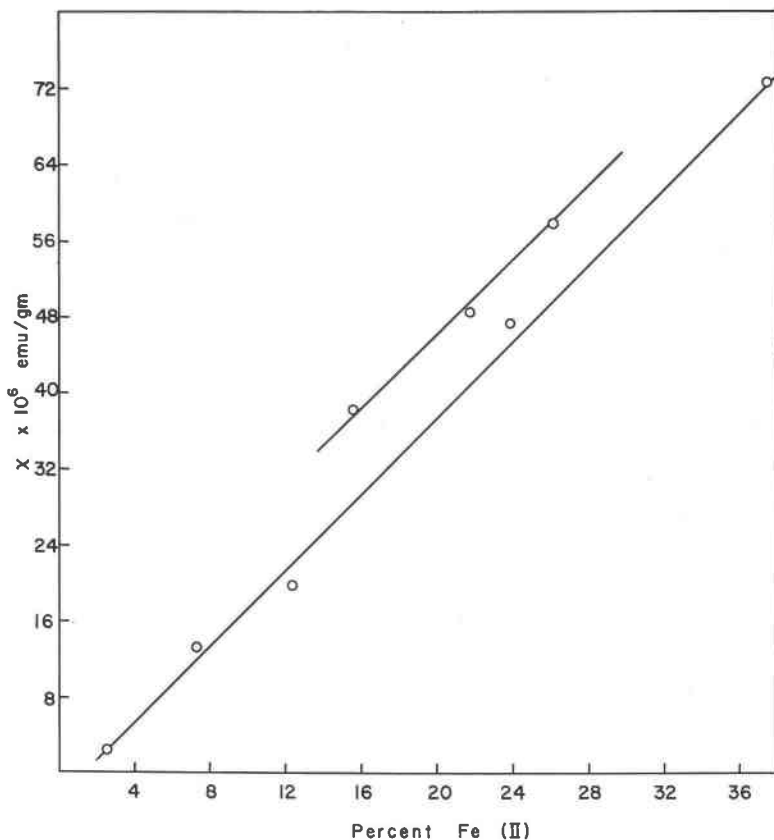FIG. 1. Corrected susceptibility vs. percent Fe^{2+} for monoclinic pyroxenes.

FIG. 2. Corrected susceptibility vs. percent Fe^{2+} for orthorhombic pyroxenes.

only one magnetic ion, Fe^{2+} (the contribution of other ions having been subtracted) and therefore μ_i^2 can be evaluated graphically from equation (1). The plots of χ_c versus P_i are shown in Figures 1, 2, 3, 4.

In orthorhombic pyroxenes three samples, the upper line in Figure 2, contain larger amounts of Mn^{2+} than the remaining samples. Since within these samples the amount of Mn^{2+} is comparable, a separate correlation line is drawn. It is conceivable that interaction of Fe^{3+} and Mn^{2+} can result is a larger contribution to the susceptibility than was subtracted in our correction procedure based on equation 3.

Extrapolation to zero Fe^{2+} (Figure 4) gives -0.5×10^{-6} as the diamagnetic susceptibility of ZnS in fair agreement with -0.8×10^{-6} obtained by Voigt and Kinoshita (1907).

In the second group, namely the amphiboles, biotites and wolframite, $i = 2$, so equation (3) can be written as
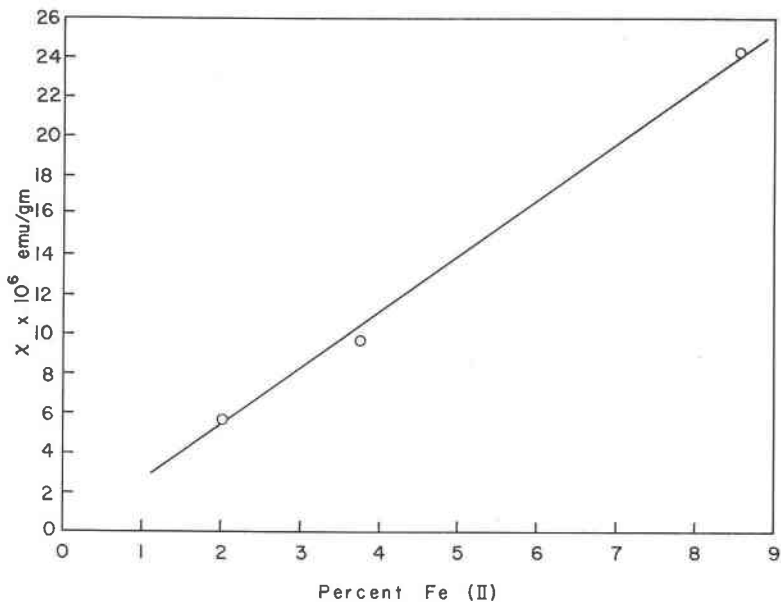
FIG. 3. Corrected susceptibility vs. percent Fe^{2+} for cordierites.

$$\frac{\chi_c}{P_1} = \frac{N\beta^2\mu_1{}^2}{3kTW_1} + \frac{N\beta^2\mu_2{}^2}{3kTW_2}\frac{P_2}{P_1} \tag{4}$$

which is the equation of a straight line in χ_c/P_1 and P_2/P_1. The magnetic moments μ_1 and μ_2 were calculated from least square fit of the data to equation (4).

The calculated magnetic moments of Fe^{2+} are given in Table 3.
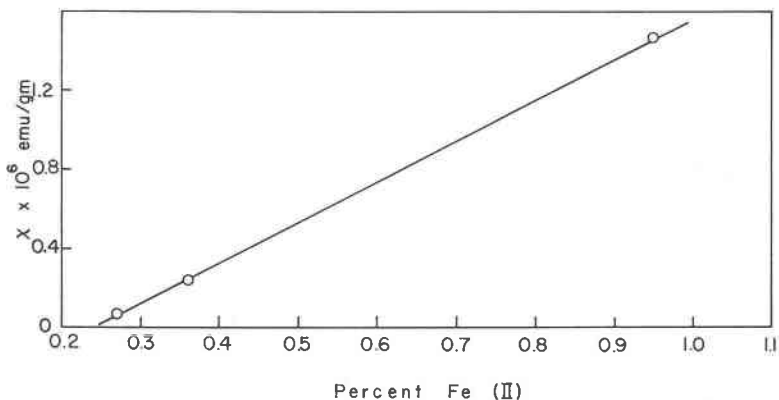

FIG. 4. Corrected susceptibility vs. percent Fe^{2+} for sphalerite.

TABLE 3. THE CALCULATED MAGNETIC MOMENT AND THE ENVIRONMENTAL SYMMETRY

Mineral	H_2O or OH	$\mu_{Fe^{2+}}$ calcu-lated	Symmetry structure	Site Wyckoff notation	Site symmetry	Source for structure
Theoretical Minimum		4,90				
Orthorhombic pyroxene (enstatite)	No	5.08	D_{2h}^{15}-$Pbca$	c	1	Wyckoff (1960)
Wolframite	No	5.10	C_{2h}^4-$P2/c$	f	2	Wyckoff (1960) Sasaki (1959)
Monoclinic pyroxene (diopside)	No	6.06	C_{2h}^6-$C2/c$	e	2	Wyckoff (1960)
Cordierite	Yes	6.15	D_{2h}^{20}-$Cccm$	g	2	Byström (1942)
Biotite	Yes	6.40	C_s^3-Cm	a b	m 1	Wyckoff (1960)
Amphibole (tremolite)	Yes	6.42	C_{2h}^3-$I2/m$	$\begin{cases} a \\ g \\ h \end{cases}$	2/m 2 2	Wyckoff (1960)
*Fayalite (synthetic)	No	6.03	D_{2h}^{16}-$Pnma$	a c	1 m	Wyckoff (1960)
Sphalerite	No	5.24	T_d^2	b	43m	Wyckoff (1931)
Theoretical Maximum		6.70				

* $\mu_{eff}Fe^{2+}$ reported by Santoro *et al.* (1966).

SYMMETRY OF Fe^{2+} ENVIRONMENT

The structural space groups and the possible Fe^{2+} sites are available in the literature and are reported in Table 3. The point group symmetry of Fe^{2+} sites is obtained from the International Tables for X-ray crystallography.

DISCUSSION

The data in Table 3 illustrate clearly that μ_{eff} for Fe^{2+} is a variable. It spans nearly the entire range between the theoretical minimum and maximum moments. It is tempting to correlate moments with some measure of site symmetry and apparent success is enjoyed when this is attempted. The success is probably illusory; comparison of the μ_{eff} in wolframite, diopside and cordierite remind us that the crystal field, hence

the moment, is not determined by symmetry alone but by interatomic distance or site dimensions as well, and that any tendency toward covalent or electron pair bonding must modify the effective number of unpaired electrons, hence the moment.

Nagata (1961) has observed that minerals containing H_2O or OH have higher than theoretical susceptibility, thus implying that H_2O or OH^- may be partially responsible for increased susceptibility. The data in Table 3 support this observation. However the association of H_2O or OH and high moment is not general, since the monoclinic pyroxenes contain no OH^- or H_2O yet the Fe^{2+} has a high μ_{eff}. The effect is probably due to crystal field effects, especially axial crystal fields are known to increase Lande's g-factor thus increasing the magnetic moments (Griffith 1961).

Also the interatomic distances between adjacent Fe^{2+} sites in minerals with large $\mu_{Fe^{2+}}$ are less than 3.5 Å. Thus if the adjacent sites are occupied with Fe^{2+}, exchange type interactions are possible, and may result in local pair formations or clusters and give large apparent $\mu_{Fe^{2+}}$.

Conclusions

The magnetic moment of Fe^{2+} in paramagnetic minerals is a variable.

Much of the observed scatter in the correlation of susceptibility with Fe^{2+} content in broad groups of minerals is significant and probably arises from variations in μ_{eff} in response to changes in site symmetry and dimensions.

After corrections have been made for ferromagnetic phase impurities and the paramagnetic contributions of minor constituents, good correlation of susceptibility with Fe^{2+} content can be expected. Different minerals will fall on lines of different slope unless the Fe^{2+} sites and bond types are identical.

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