The identification of Fe^{2+} in the M4 site of calcic amphiboles: discussion

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Abstract

Using the extended Huckel method, the 3d electronic energies of Fe^{2+} in gillespite, olivine (M1 and M2 sites) and garnets are calculated using the positions of the oxygen ions in the coordination polyhedra. These calculated energies are linearly related to the observed electronic energies, and an empirical relationship is defined so that the extended Huckel method can be used to calculate electronic energies of Fe^{2+} in other silicates. This method is tested by computing the energy levels of Fe^{2+} in the M1 and M2 sites of the pyroxene, ortho-ferrosilite. There is rather good agreement between the calculated values and the previously reported observed values.

Electronic energies of Fe^{2+} in grunerite in the M1, M2, M3 and M4 sites are calculated, and we confirm that the band at 4000 cm^{-1} is due to Fe^{2+} in M4. On the basis of other evidence we suggest that the band at 10,000 cm^{-1} is due to Fe^{2+} in M4 *and* M2.

Introduction

The polarized electronic spectra of complex ferous silicates have been interpreted in the last ten years with the aid of crystal field theory (Burns 1965, 1970b). In the comparatively simple case of square planar Fe^{2+} in gillespite (BaFeSi$_4$O$_{10}$) the interpretation was relatively straight forward (Burns *et al.*, 1966). However for orthopyroxenes (White and Keester 1966, Bancroft and Burns, 1967, Runicman *et al.*, 1973a, Goldman and Rossman 1976, 1977a), olivines (Burns 1970a, Runciman *et al.*, 1973b, Burns 1974), and garnets (White and Moore, 1972, Runciman and Sengupta, 1974, Huggins 1975), there have been considerable difficulties in interpreting the spectra, and each paper corrects mistakes or oversights in previous papers. It now appears, however, that the above mineral spectra are reasonably well understood.

The amphibole polarized spectra (Burns 1965, 1970b, Goldman and Rossman, 1977b) present an even greater interpretive challenge. Ferrous ion can, and does, enter four cation sites (labelled M1, M2, M3 and M4), each with a distinct shape and size (Burns 1970b and Papike *et al.*, 1969). For example, the M4 site is a large and very distorted 6 or 8 coordinate site, whereas the M1 and M3 sites are much smaller and more regular 6 coordinate sites. While Burns (1970b) attributed peaks in cummintonite-grunerites and actinolite in the 9000-11000 cm^{-1} region to Fe^{2+} in all of the four sites, Goldman and Rossman (1977b) have reinterpreted many of the amphibole spectra claiming that only iron in the M4 site causes the band at ca 10000 cm^{-1}, and a newly discovered band at ca 4000 cm^{-1}.

In this paper, we use extended Huckel molecular orbital theory to calculate the energy levels of ferrous ions in gillespite, olivine, pyroxene, garnet and grunerite. The assumptions in the extended Huckel calculations are inherently nonrigorous—especially in the case of polar molecules or ions (Dewar, 1969). However, by using a set of consistent parameters, the calculations should give correct trends in electronic energies for a series of silicates. We show that this is indeed the case for the better understood spectra of gillespite, olivines, garnets and pyroxenes. Our calculations on amphiboles, combined with polarized electronic spectra, indicate strongly that more than just the M4 ferrous ions contribute to the spectra.

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Results and discussion

The extended Huckel calculations on characterized spectra

All calculations were performed using a locally modified version of QCPE program No 256 (Dibout, 1974). The program had been modified to accept the double zeta type orbitals (a linear combination of two Slater type functions to approximate one atomic orbital), and the off diagonal matrix elements were calculated using an approximation suggested by Cusachs (1965) (see McGlynn *et al.*, 1972 for details of this calculation):

$$H_{ij} = S_{ij}(2 - |S_{ij}|)(H_{ii} + H_{jj})/2$$

where:

S_{ij} = the overlap integral between the ith and jth atomic orbitals,

H_{ii} = the valence state ionization energy (VSIE) of orbital i,

$|S_{ij}|$ = the overlap integral evaluated in the local (diatomic) coordinate system defined by orbitals i and j.

The Roothaan equation was transformed,

$$H\,C = S\,C\,E$$

and followed by Lowdin orthogonalization, new matrixes were generated:

$$H' = S^{-1/2}H\,S \text{ and } C' = S^{1/2}\,C$$

A Mulliken population analysis (McGlynn *et al.*, 1972) was carried out to obtain gross atomic charges. The diagonal matrix elements were modified through

$$H_{ii}^* = H_{ii}(1 - \lambda) + \lambda\,(Aq_i^2 + Bq_i + C)$$

where

λ = a damping factor typically 0.01,
q_i = the charge on atom i
A,B,C   are parameters taken from Basch *et al.* (1965).

These procedures are repeated until successive values of charge differ by less than 0.05.

Values of VSIE and the orbital exponents were taken from Summerville and Hoffman (1977). A double zeta basis set was used only for the iron 3d orbital.

We consider that only the directly bonding oxygen atoms modify the Fe 3d electronic energies. The choice of charge on those oxygen atoms is

somewhat arbitrary, although for non-bonding silicate oxygens, the formal oxygen charge is considered to be -1. Our calculations are not expected to give good absolute energies anyway so we have performed calculations using mono-negative (case 1) and di-negative (case 2) oxygens for comparative purposes. Thus, for gillespite we have done calculations for both FeO_4^{2-} and FeO_4^{6-} clusters, and similar calculations have been performed for six-coordinate Fe^{2+} in olivine M1 and M2 sites and eight-coordinate Fe^{2+} in garnet (Table 1). The positions of the iron and oxygen atoms were taken from the literature [Hazen and Burnham 1974, Birle *et al.*, 1968, and Prandl (1971)]. The electronic transition energy is taken as the orbital energy difference between the initially occupied and the virtually unoccupied molecular orbital.

For minerals, such as olivine, that form solid solutions in which iron is replaced by other cations, the atomic positions are taken from the iron rich mineral.

The results of the calculations are compared with the observed energies, in Table 1, while the case 1 calculated values are plotted against the observed values in Figure 1. It was found that the ordering of the Fe d orbitals in gillespite and garnet are the same as those given by Burns, Clark and Stone (1966) and Routcliffe (1977) respectively. The calcu-

Table 1. A comparison between calculated and observed electronic energies (cm^{-1}) for Fe^{2+} in gillespite, olivine and garnet

| Mineral | Species | | Transition Energies from Ground States* | | |
| | | | Calculated** | | Observed*** |
	1	2	1	2	
Gillespite	$FeO_4^=$	FeO_4^{6-}	28700	17000	19000
			5200	3100	7500
			2830	1800	2800
			2830	1800	2800
Olivine M1	FeO_6^{4-}	FeO_6^{10-}	16800	12000	10930
			12800	9300	8060
			1400	800	1750
			720	160	550
Olivine M2	FeO_6^{4-}	FeO_6^{10-}	13900	8300	9290
			11300	6700	
			1500	720	1750
			400	240	750
Almandine Garnet	FeO_8^{6-}	FeO_8^{14-}	11600	11800	7640
			9300	9400	5820
			8000	7800	4420
			3000	2800	1200

* All energies are measured relative to the lowest electronic energy which is taken to be zero.
** The calculated energies 1) and 2) are for species 1) and 2) respectively.
***References to these observed values are: Gillespite, Burns et al (1966); Clark and Burns (1967); Olivine Burns (1970a,1974); and Routcliffe (1976); and for Garnet, Huggins (1975) and references therein.
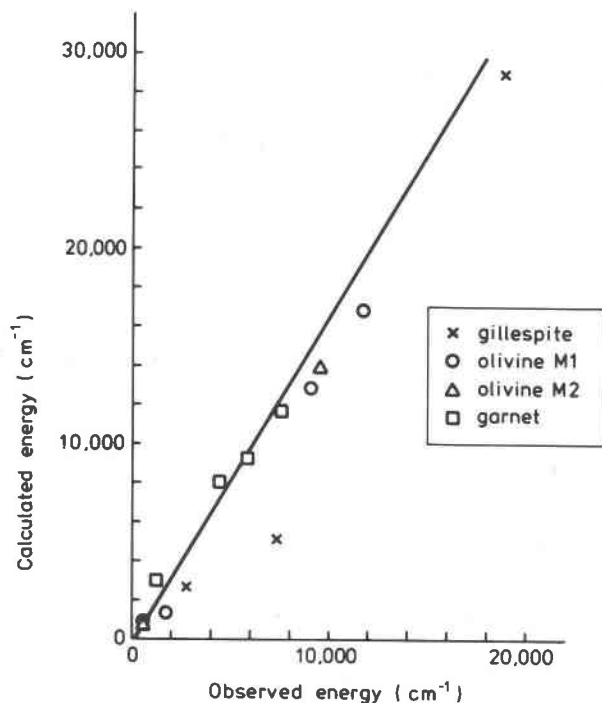
Fig. 1. Plot of observed energy against calculated energy and the least square line (equation 1)

lated trends are obviously in good agreement with the observed trends. The case 2 results give coincidentally better quantitative agreement than the case 1 results, but the plot of case 1 against observed results gives a good straight line with a correlation coefficient of 0.98.

$$E_{calc} = 1.52 \ E_{obs} - 537 \ (cm^{-1}) \qquad (1)$$

Considering the approximations used in the extended Huckel method, and the fact that this method has seldom been used successfully in calculating the energies of highly ionic compounds, the correlation is excellent. The calculation can predict correctly trends for silicate minerals.

As a final check, the Fe^{2+} electronic energies in the pyroxene ortho-ferrosilite were calculated. Burnham (1966) has determined the crystal structure of this mineral. The calculated energies are compared in Table 2 to the energies determined by Mao and Bell (1971) and once again a satisfactory agreement is observed.

The amphibole spectra

Goldman and Rossman (1977b) have argued that bands at 9700 cm^{-1} (in β) and 4050 cm^{-1} (in α) in calcic amphiboles (and by implication in other am-

phiboles) are caused by Fe^{2+} in the M4 site. They have based their assignment on four main pieces of evidence: (1) the similarity of the amphibole spectra to those of other large distorted sites such as the pyroxene M2 position, (2) the intensities of the 9700 cm^{-1} and 4050 cm^{-1} bands correlate, (3) the barycentre energy of the two bands is close to that predicted by Faye (1972) and (4) the intensity of the 9700 cm^{-1} band is such that it must be caused by Fe^{2+} in a very distorted site.

Our calculated results in Table 3 support the important assignment (Goldman and Rossman, 1977b) of the ~4000 cm^{-1} band to Fe^{2+} in the M4 site. However the origin of the band at ca 9700 cm^{-1} is debateable. Our calculations indicate that Fe^{2+} in the M1, M2 and M3 sites could all give rise to a band in the 10,000 cm^{-1} region as suggested by Burns (1970b). The evidence given below suggests that Fe^{2+} in the M2 will give an observable intensity in amphibole spectra. Goldman and Rossman's (1977b) data are then critically evaluated.

Burns (1970b) and Bancroft and Burns (1969) have published a polarized electronic spectrum of glaucophane which shows barely discernible peaks in the region of 10,000 cm^{-1} in the β polarized spectrum despite the presence of Fe^{2+} in sites M1 and M3. The chemistry, Mössbauer and infrared spectra of this sample suggest little or no Fe^{2+} in M2 or M4. This spectrum strongly suggests that the Fe^{2+} in the slightly distorted, M1 and M3 sites in amphiboles will not give appreciable intensity at 10,000 cm^{-1}. However, Fe^{2+} in M2 may still give significant intensity at $\simeq$10,000 because the M2 site is more distorted than M1 and M3. To indicate this difference, we calculate in Table 4 the distortion parameters of sites M1 to M4 of grunerite using the

Table 2. Calculated and observed electronic energies (cm^{-1}) for Fe^{2+} in orthoferrosilite

| Position | Calculated* | | Observed** |
	Extended Huckel	From Eqn. 1	
M1	16100	10900	10549
	13900	9500	8333
	400	620	
	160	460	
M2	16500	11200	10627
	8200	5800	4878
	1200	1100	2350
	560	700	

* All energies are measured relative to the lowest electronic energy which is taken to be zero.
** Mao and Bell (1971) and Goldman and Rossman (1977).

two distortion parameters recommended by Fleet (1976), and also the distance of the site from the center of symmetry. The position of the center of symmetry is calculated by summing the coordinates of the oxygen atoms on the coordination polyhedra. (This is analogous to finding the position of the moment of inertia of a solid object.) The greater the distortion of the octahedra, the greater the expected intensity of the band; moreover, the further the Fe^{2+} is from the center of symmetry, the greater the intensity of the band. Thus the noncentro-symmetric nature of the olivine M2 site leads to a much more intense band than the Fe^{2+} in olivine M1. Using the ϵ values for olivine and amphiboles given by Goldman and Rossman (1977b), it is immediately apparent that these distortion parameters can only be considered in a qualitative way. However, they do indicate that the ϵ value for M2 Fe^{2+} is probably greater than the olivine M1 value of 2.4.

There are other spectroscopic arguments for Fe^{2+} in M2 giving appreciable intensity at $\simeq 10{,}000 \text{ cm}^{-1}$. For example, the cummingtonite–grunerite electronic spectra (Burns 1965, 1970b) suggest that more than one type of Fe species contributes to the peaks around $10{,}000 \text{ cm}^{-1}$. The cummingtonite β spectrum (Burns 1970, p. 96, Fe/(Fe+Mg) = 0.38) has only about 40% of the *area* of the grunerite β spectrum (Burns 1970, p. 97, Fe/(Fe+Mg) = 0.98); yet the Mössbauer spectra (Bancroft, Burns and Maddock, 1967) show that these two samples have

Table 3. Calculated electronic energies (cm^{-1}) for Fe^{2+} in grunerite

| Position | Calculated Energies | |
	Extended Huckel	From Eqn. 1
M1	17200	11700
	15000	10200
	480	
	320	
M2	16100	11000
	15700	10700
	460	
	370	
M3	16900	11500
	16100	11000
	560	
	400	
M4	16000	10900
	5700	4100
	890	
	400	

All energies are measured relative to the lowest electronic energy which is taken to be zero.

The structural parameters were taken from Finger (1969).

Table 4. Distortion parameters for grunerite and olivine positions

Mineral	Position	Bond length deviation Δ (Å)	Bond Angle deviation σ(degrees)	Distance from the centre of symmetry (Å)	ϵ Goldman and Rossman
Grunerite	M1	0.015	6.0	.003	
	M2	0.016	6.6	.036	
	M3	0.003	7.7	0.000	
	M4	0.145	20.5	1.527	20-80
Olivine	M1	0.023	11.2	0.000	2.4
	M2	0.045	11.1	1.745	8.6

$$\Delta^2 = \sum_{i=1}^{6} ((l_i - \bar{l})/\bar{l})^2/6$$

$$\sigma^2 = \sum_{i=1}^{12} (\theta - 90)^2/11$$

Where l_i is one of the 6 bond lengths and θ_i is one of the 12 angles in a distorted octahedra. (See Fleet (1976) and references therein).

similar amounts of Fe^{2+} in M4. The additional *area* in the grunerite spectrum must come from Fe^{2+} in sites other than M4 as Burns suggested. The glaucophane evidence above suggests that little intensity will come from Fe^{2+} in M1 and M3; so that most of the additional intensity must come from Fe^{2+} in M2 which increases from 0.11 per formula unit in cummingtonite to 1.92 per formula unit in grunerite. This evidence suggests that ϵ_{M2} could well approach 50% of ϵ_{M4}. Clearly more careful experimental measurements must be done on amphiboles to finalize the interpretation.

Burns (1970) has also published a spectrum of an actinolite (Berkeley 14785) and the spectrum has an intense band at 9666 cm^{-1}. From the chemical analysis of this actinolite (Burns and Greaves 1971), it can be inferred that all of the M4 position is occupied by Ca + Na + K + Mn. Thus the peak at 9660 cm^{-1} should be due mostly to Fe^{2+} in one of the other sites.

Finally, it seems important to comment on Goldman and Rossman's evidence that the $10{,}000 \text{ cm}^{-1}$ and $4{,}000 \text{ cm}^{-1}$ band are caused by the same type of Fe^{2+} site in M4 (Point 2 above). Their most important evidence centres around a heating experiment in which a tremolite was heated at 535°C for 8 hours, resulting in both bands decreasing by 50%. They themselves point out that this decrease cannot be made quantitative because of the vibrational overtones on the already weak peak at ca 4000 cm^{-1}.

In conclusion we have shown that very simple extended Huckel calculations can be used to predict Fe^{2+} electronic energies with reasonable accuracy. We have used the method to confirm Goldman and Rossman's assignment of the $4{,}000 \text{ cm}^{-1}$ band in

amphiboles to Fe^{2+} in M4 alone and we suggest that the 10,000 cm^{-1} band is due to Fe^{2+} in M2 as well as M4. Further experiments and intensity calculations are required to finalize the assignment of the 10,000 cm^{-1} band.

Acknowledgments

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