

### The possibility of $d$ -electron coupling in olivine at high pressures

CLARKE (1959) has discussed various types of transitions, including electronic transitions, which may occur in materials subjected to very high pressures and RINGWOOD (1958) has presented convincing evidence that  $(\text{Mg,Fe})_2\text{SiO}_4$  may change from an olivine to a spinel structure within the mantle of the earth. There is in addition, a type of electronic transition not mentioned by CLARKE which could occur with  $\text{Fe}_2\text{SiO}_4$  and which appears a most probable process with pressures available in the mantle. It is the purpose of this note to suggest that contraction may occur due to coupling of  $d$ -electrons in the ferrous ion.

It is well known that in a field-free transition-metal ion such as  $\text{Fe}^{2+}$  the  $d$ -electrons are fully degenerate (i.e. the energy of the five  $d$ -orbitals are identical). The electronic arrangement of the six  $d$ -electrons of the ferrous ion would be as indicated in (a) Fig. 1. When the ion is placed in a negative octahedral field such as that produced by six oxygens surrounding the ion, the degeneracy of the  $d$ -levels is destroyed and the orbitals become grouped into two sets of unequal energy. In the terminology of ligand-field theory (GRIFFITH and ORGEL, 1957) these sets comprise three orbitals of low energy ( $t_{2g}$ ) and two orbitals of higher energy ( $e_g$ ). These are related to the different spatial configurations of the  $d$ -orbitals in relation to the octahedral field (see GILLESPIE and NYHOLM, 1957). In many cases this splitting of the  $d$ -levels gives rise to the absorption observed in the visible regions of the spectrum. The difference in energy of the levels may thus be estimated from the position of these absorption bands (ORGEL, 1955).

If the splitting of the levels becomes sufficiently large, the electrons may obtain from coupling sufficient energy to overcome a repulsion barrier (also deduced from spectra) and may pair-off, giving a new electronic configuration in which Hund's rule does not apply. Thus for the ferrous ion we may have the three configurations illustrated in Fig. 1.

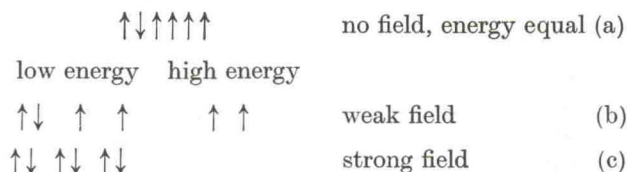


Fig. 1. Possible electron configurations in  $\text{Fe}^{2+}$

Normally, when coupling such as (c) occurs, there are changes in the magnetic properties (in the case of  $\text{Fe}^{2+}$  a change from paramagnetism to diamagnetism) and at the same time there is a considerable change in the size of the ion. It is difficult to obtain examples of such changes in simple binary compounds for in most of these the field is too weak to cause coupling; the most familiar examples involve complex ions. With these there may be added complexities (e.g. in  $\text{Fe}(\text{CN})_6^{-4}$ ) such as multiple bonding in the coupled species due to better hybrid bonds. In general, a coupled ion will form stronger covalent bonds for the same reason. In the hydrated ferrous ion  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ , which is paramagnetic, the  $d^2sp^3$ -octahedral hybrid which is formed from  $4d$ -,  $4s$ -,  $4p$ -orbitals of the iron, will allow weaker covalent bonding than in a coupled, diamagnetic species where  $3d$ -,  $4s$ -,  $4p$ -orbitals would form the hybrid. Conversely, as bonds become more covalent there is an increased possibility of coupling.

In the present discussion the most important aspect of the coupling process is related to the volume decrease associated with it and we may consider two examples to illustrate this effect. The first row transition metal ions are similar in size and show a gradual contraction with increasing atomic number. The ionic radii of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  given by

PAULING (1948) are 0.75 and 0.80 Å respectively. We would thus expect that Fe—X linkages would be only a little shorter than Mn—X linkages and this is certainly true in the majority of cases. But in the iso-structural disulphides, pyrite and hauerite, a serious departure occurs. With  $\text{MnS}_2$  the Mn—S distance of 2.59 Å is close to the radius sum of 2.64 Å while with  $\text{FeS}_2$  the Fe—S distance of 2.27 Å is much smaller than the radius sum of 2.59 Å. This contraction may be correlated with normal paramagnetism for  $\text{MnS}_2$  and coupling giving diamagnetism in  $\text{FeS}_2$  (NÉEL and BENIOT, 1953). In neither case should the degree of covalency be very different on the basis of simple electronegativity considerations. It is interesting to note that in the iodides  $\text{MnI}_2$  and  $\text{FeI}_2$  which should be equally covalent, the distances are similar and no coupling occurs. That  $\text{FeS}_2$  could be coupled while  $\text{MnS}_2$  is not, might be expected, for the coupling energy of the *d*-electrons in  $\text{Mn}^{2+}$  is much greater than in  $\text{Fe}^{2+}$ , a reflection of the general stability of half filled *d*- and *f*-shells (the coupling energy of  $\text{Mn}^{2+}$  is 146 kcal compared with 100 kcal for  $\text{Fe}^{2+}$ ).

A second example of this contraction may be taken from the complexes of cobalt. The normal ionic radii of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  are 0.72 and 0.63 Å, respectively. The Co—N distance in the spin-free complex  $\text{Co}(\text{NH}_3)_6^{2+}$  is 2.5 Å and by analogy a distance of 2.4 Å would be predicted in  $\text{Co}(\text{NH}_3)_6^{3+}$ . The measured distance in the latter diamagnetic complex is actually 1.9 Å illustrating the extreme value of the contraction in a case where there can be little multiple bonding (PARRY, 1950). ORGEL (1956) has also mentioned the expected contraction on coupling.

If it is considered reasonable that contraction occurs with electron coupling, it follows that coupling will be induced by pressure. It remains to examine the energies involved and the volume changes, to see if coupling is feasible in the mantle of the earth. Such transitions cannot occur in the metallic phase of the core as almost all the *d*-electrons are already involved in bonding in the metal.

Considering the specific case of olivine, to calculate the pressure of transition between paramagnetic and diamagnetic forms the following information is needed: the coupling energy of *d*-electrons in  $\text{Fe}^{2+}$ , the splitting of the *d*-levels in olivine, the effect of pressure and temperature on the splitting, the volume change associated with the transition. The coupling energy should be fairly independent of the environment, and GRIFFITH and ORGEL (1957) give a value of 50 kcal per electron. The splitting energy can be obtained from the absorption spectrum of olivine, and we may use a value of 27 kcal per electron from the data of CLARKE (1957). The selection of the band at  $9600\text{ cm}^{-1}$  is based on analogy with the value for the hydrated ferrous ion. McCLURE (1957) found that band shifts in oxygen co-ordinated cations are generally rather slight, a feature which will be discussed elsewhere. Thus at standard pressure and temperature the energy barrier is near 46 kcal/mole of ferrous ion. No data are available to allow estimates of the effect of pressure and temperature on the splitting in olivine. PARSONS and DRICKAMER (1958) have studied the effect of pressure on the spectrum of ions such as  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  and found a marked increase in splitting with pressure as would be expected from bond shortening with compression. Temperature will operate in the opposite direction, but if at depth the net effect is to decrease the molar volume, then one might anticipate increased splitting.

There are insufficient data on radius changes with coupling to allow any precise estimate of the expected volume change in fayalite. From the two examples listed above, a change of 0.1 Å does not appear excessive. With such a value the molar volume of diamagnetic fayalite would be similar to forsterite and the  $\Delta V$  of transition would be about  $3\text{ cm}^3\text{ mole}^{-1}$ . A transition would be expected at depths of the order of 1400 km. This estimate indicates pressures in excess of those found by RINGWOOD for the spinel transition so that coupling may be more likely to occur in the spinel modification. With the contraction used above, which may well be an underestimate, if the olivine in the mantle contains 10 mole