

ORDERING OF TRANSITION METAL IONS IN OLIVINE

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There appears in the literature a discrepancy between crystal-field predictions and the experimental occupancies of the two cation sites $M(1)$ and $M(2)$ by $3d$ metal ions in the olivine structure. In particular, the extensive amount of Ni-Mg ordering has been thought to be surprising in view of the slight ordering observed in some Fe-Mg olivines (Rajamani, Brown & Prewitt 1975). The purpose of this note is to show in a general way that the differences in the degree of ordering for Ni^{2+} , Co^{2+} and Fe^{2+} olivines are in line with simple crystal-field theory.

The predicted crystal-field stabilization energy, E_{st} , for Ni^{2+} , Co^{2+} and Fe^{2+} in regular octahedral coordination is shown (Table 1, column

2) in terms of the parameter $Dq = \frac{Ze^2 \langle r^4 \rangle}{L_o^5}$

(column 1), where e is the electronic charge, Ze is the effective charge of one of the six ligand ions considered as a point charge, and $\langle r^4 \rangle$ is defined as follows: $\langle r^4 \rangle = \int_0^\infty f(r^2) r^{n+2} dr$,

where $f(r)$ is the radial wave function for the $3d$ ion (Walsh, Donnay & Donnay 1974); L_o is the $M-O$ bond length of the regular octahedron. Column 1 shows the experimentally determined Dq values for hydrated crystals (Tanabe & Sugano 1954). Column 2 also shows the E_{st} values in cm^{-1} derived from the data of column 1. The magnitudes of Dq (column 1) and consequently those of E_{st} (column 2) should, of course, be slightly different in the olivine structure; however, their relative values will be closely similar. In addition, the 3-fold orbital degeneracy of the ground states of Co^{2+} and Fe^{2+} will be removed at $M(1)$ and $M(2)$, and this will result in additional stabilization energy. As has been shown for Fe^{2+} in the olivine structure (Walsh *et al.* 1974), the adjustments are sufficiently small so that their effect on the ordering can be ignored as a first approximation. The reason is that the additional stabilization energies at $M(1)$ and $M(2)$ are nearly equal. Since the volume ratio of $M(1)$ to $M(2)$ octahedra is almost identical for Ni^{2+} , Co^{2+} and Fe^{2+} olivines (Rajamani *et al.* 1975; Walsh *et al.* 1974; Ghose & Wan 1974), $\Delta E_{st} = E_{st}(1) -$

TABLE 1. CRYSTAL-FIELD AND ORDERING DATA FOR Ni , Co , AND Fe IN OCTAHEDRAL COORDINATION

	1 Dq (exper.) ^a	2 E_{st}	3 ΔE_{st}	4 K_d	5 K_d (predicted) (exper.) ^f
Ni^{2+}	820 cm^{-1}	12 $Dq=9840cm^{-1}$	680 ^b	--	2.92 ^c
Co^{2+}	840	6 $Dq=5040$	348	1.5	1.97 ^d
Fe^{2+}	1030	4 $Dq=4120$	284	1.22	1.06 ^e

^aTanabe & sugano (1954), ^bWalsh *et al.* (1974), ^cRajamani *et al.* (1975), ^dGhose & Wan (1974), ^eValue 1.06 is the average for ten olivines listed in Walsh *et al.* (1974, Table IIA), where Sample 0L2 has been omitted since it is the only Fe^{2+} olivine showing slight ordering in $M(2)$. ^f $K_d = M(1)/M(2)$ occupancy ratio.

$E_{st}(2)$, the difference in stabilization energy between $M(1)$ and $M(2)$ for Ni^{2+} , Co^{2+} and Fe^{2+} , is proportional to the corresponding E_{st} in cm^{-1} (Table 1, column 2).

ΔE_{st} has been calculated (Walsh *et al.* 1974) for Ni^{2+} in olivine to be 680 cm^{-1} . Using this value and that of E_{st} in cm^{-1} (column 2), ΔE_{st} is estimated (column 3) for Co^{2+} and Fe^{2+} . We define the $3d$ -ion distribution coefficient K_d to be the ratio of the $3d$ -ion occupancy at $M(1)$ to that at $M(2)$. Using the experimental data for Ni olivine (Rajamani *et al.* 1975), K_d is found to be 2.92. Employing this value and column 3, K_d for Co^{2+} and Fe^{2+} are estimated in column 4. Column 5 lists the K_d values obtained from X-ray data for the three corresponding olivines, and the agreement with the predictions for Co^{2+} and Fe^{2+} in column 4 is reasonable. The agreement for Co^{2+} is the poorer of the two, which suggests that a more detailed calculation of the kind previously published (Walsh *et al.* 1974) should and will be carried out by us.

In summary, contrary to statements in the literature (Rajamani *et al.* 1975; Ghose & Wan 1974), Ni^{2+} is expected to be strongly ordered in $M(1)$, Fe^{2+} slightly ordered in $M(1)$, and Co^{2+} ordered in $M(1)$, the degree of ordering pre-

dicted for Co^{2+} being less than the experimental results.

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*The prediction of Burns (1970) that Fe^{2+} has a slight preference for the $M(2)$ site is due to an error in his Fig. 5.3(a) and on p. 83, where for a total T_2 splitting of 1860 cm^{-1} the additional stabilization energy at $M(1)$ due to the deviation from cubic symmetry is incorrectly stated to be 620 cm^{-1} instead of 1240 cm^{-1} .

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