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Cation Distribution in Spinels: Lattice Energy *versus* Crystal Field Stabilisation Energy

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Ever since the discussions by McClure[1] and by Dunitz and Orgel,[2] the observed distributions of metal cations between the octahedral and tetrahedral sites in spinels AB_2O_4 have been regarded as a classic exemplar of the chemical significance of crystal field stabilisation energy (CFSE).

Although it is to be expected that the normal spinels will have lattice energies different from the corresponding inverse spinels, neither of these papers[1,2] makes any quantitative assessment of the change in lattice energy on inversion, and indeed McClure effectively dismisses this as unimportant, largely on the grounds that, of the examples he cites, the structure of the majority for which the CFSE is non-zero are correctly predicted by the CFSE alone, even though *no* CFSE prediction can be made for about one-third of his examples: of these, some are normal and some inverse. Navrotsky and Kleppa[3] also dismissed the change in lattice energy as essentially unimportant.

Calculations have since been made[4–6] of the Madelung constants of cubic spinels in terms of the lattice parameter a, the degree of inversion λ ($\lambda = 0$ for normal, 0.5 for inverse), and the anion displacement parameter δ: in an ideal spinel having close packed anions, the fractional coordinate x of the anions at positions 32,e in space group *Fd3m* is 0.375, and in non-ideal spinels $\delta = x_{obs} - 0.375$. Observed values of δ range from -0.003 in $MgIn_2O_4$[7] to $+0.017$ in $MgGa_2O_4$[8] and in $HgCr_2S_4$[9] amongst the 2–3 spinels, and from zero in $SnCo_2O_4$[10] and $MoFe_2O_4$[11] to $+0.015$ in $TiFe_2O_4$,[7] $TiMg_2O_4$[7] and $SnZn_2O_4$[10] amongst the 4–2 species (Mössbauer spectra indicate[12] that tin spinels contain Sn(IV) rather than Sn(II)). These extreme values of δ correspond to changes in Madelung energy on inversion, M(normal) – M(inverse) of $+525.8$ kJ mol^{-1} in $MgIn_2O_4$ and -1071.6 kJ mol^{-1} in $MgGa_2O_4$ as the extreme 2–3 examples, and of -1400.3 kJ mol^{-1} in $MoFe_2O_4$ and $+270.5$ mol^{-1} in $TiMg_2O_4$ as the extremes amongst 4–2 species.

In view of the availability of Madelung constants for spinels, it seems worthwhile to reconsider the distribution of cations in those species AB_2X_4 (X = O, S, Se, Te) for which δ is known, in terms of the changes on inversion in both CFSE and Madelung energy.

In the Table are listed values of ΔU = U(normal) – U(inverse), Δ(CFSE) = CFSE(normal) – CFSE (inverse), and the total stabilisation energy of the normal form with respect to the inverse. ΔU values were calculated,[4–6] using n = 9 as the exponent of the Born repulsion term, from the observed values of a and δ, structural data, except where otherwise noted, being taken from Wyckoff:[13] CFSE values were calculated,[14] assuming for the Racah parameters that C = 4B, using f, g, and B data given by Jorgensen,[15,16] and estimated g factors as follows: Cr(II), 10.0; Mn(III), 21.0; Cu(II), 9.5; Mo(IV), 30.0: f for S^{-2} was taken as 0.89,[15] and similar values were adopted for Se^{-2} and Te^{-2}.

Of the twenty-two 2–3 oxides listed in the Table, the predicted structure is observed for fifteen: of those incorrectly predicted, the calculated total energy change on inversion is small for $CuFe_2O_4$ (-20.9 kJ mol^{-1}) and for $NiFe_2O_4$ (-50.6 kJ mol^{-1}), so these discrepancies are probably not significant. The remaining five are all predicted to be normal but observed to be inverse: similarly, amongst the 4–2 oxides $SnCo_2O_4$ and $TiZn_2O_4$ are found to be inverse, although predicted to be normal (the structure of $NiMn_2O_4$ is probably[17] $Mn_t^{II}(Ni^{III},Mn^{III})_oO_4$, rather than $Mn_t^{III}(Ni^{II},Mn^{III})_oO_4$, and so is normal, with M(II) in the tetrahedral site).

There are several plausible explanations for the discrepancies. Firstly, the Madelung energy and its change on inversion are very sensitive to the anion displacement parameter δ and hence to x. Most spinels have values of δ around $+0.010$ (*i.e.* x = 0.385): for such a spinel of cell length a = 8.5 Å, a change of $\pm$ 0.001 in x represents a change in ΔU on inversion of *ca.* 92.5 kJ mol^{-1} for 2–3 species and of *ca.* 97.0 kJ mol^{-1} for 4–2 species. Consequently an experimental uncertainty of $\pm$ 0.001 in x will lead to an uncertainty in ΔU which is greater than Δ(CFSE) for all species except those containing Cr(III) or Mo(IV), and in many examples it is probable that the experimental uncertainty in x is of this magnitude.

Secondly there is the question of oxidation states: the example of $NiMn_2O_4$ has already been mentioned. In the case of $CuMn_2O_4$, it has been suggested[18] that this compound is not a simple Mn(III) species but should be formulated as $(Cu_p^{II}Mn_{1-p}^{II})_t(Cu_{1-p}^{II}Mn_{1-p}^{IV}Mn_{2p}^{III})_oO_4$ (with $0 < p < 0.33$), whose lattice energy cannot easily be calculated. In $MnFe_2O_4$, the manganese ions suffer oxidation on transference to the octahedral sites[19] and the constitution is more properly described as $(Mn_p^{II}Fe_{1-p}^{III})_t(Fe_{1-p}^{II}Mn_{1-p}^{III}Fe_{2p}^{III})_oO_4$, having p = 0.81: other examples of this type of behaviour are[17] $CoMn_2O_4$ and $FeMn_2O_4$. A different phenomenon occurs in $FeFe_2O_4$; below

TABLE. Changes in Lattice Energy and in CFSE on Inversion.

	a(Å)	δ	ΔU(kJ mol^{-1})	Δ(CFSE)(kJ mol^{-1})	Total (kJ mol^{-1})	Structure Observed
A. 2–3 Oxides						
$CdCr_2O_4$	8.596	+0.010	−449.9	−167.7	−617.6	N
$CdIn_2O_4$	9.115	+0.010	−424.3	0	−424.3	I
$CoAl_2O_4$	8.1068	+0.015	−914.2	+29.7	−884.5	N
$CoCo_2O_4$[a]	8.065	+0.013	−805.3	−74.2	−879.5	N
$CuFe_2O_4$	8.445	+0.005	−56.4	+35.5	−20.9	I
$CuMn_2O_4$[b]	8.33	+0.015	−872.8	−45.8	−918.6	N
$FeFe_2O_4$	8.3963	+0.004	+22.0	+16.6	+38.6	I
$MgAl_2O_4$	8.0800	+0.012	−651.7	0	−651.7	N
$MgCr_2O_4$	8.333	+0.010	−464.1	−167.7	−631.8	N
$MgFe_2O_4$	8.389	+0.007	−216.3	0	−216.3	I
$MgGa_2O_4$	8.280	+0.017	−1071.6	0	−1071.6	I
$MgIn_2O_4$	8.81	−0.003	+525.8	0	+525.8	I
$MnFe_2O_4$[b]	8.511	+0.0096	−421.7	0	−421.7	0.81 N
MnV_2O_4	8,52	+0.0133	−726.4	−81.0	−807.4	N
$NiAl_2O_4$	8.048	+0.015	−920.9	+85.9	−835.0	0.25 N
$NiCr_2O_4$	8.320	+0.010	−464.8	−81.8	−546.6	N
$NiFe_2O_4$	8.3522	+0.006	−136.5	+85.9	−50.6	I
$NiGa_2O_4$	8.262	+0.012	−637.3	+85.9	−551.4	I
$NiMn_2O_4$[b]	8.4028	+0.0085	−337.1	+38.3	−298.8	N
$ZnAl_2O_4$[c]	8.086	+0.012	−651.2	0	−651.2	N
$ZnCr_2O_4$	8.327	+0.015	−890.0	−167.7	−1057.7	N
$ZnFe_2O_4$	8.443	+0.014	−792.3	0	−792.3	N
B. 4–2 Oxides						
$MoFe_2O_4$	8.501	0.000	−1400.3	+141.8	−1257.5	0.50 N
$SnCo_2O_4$	8.644	0.000	−1377.2	−29.7	−1406.9	I
$SnZn_2O_4$	8.70	+0.015	+262.4	0	+262.4	I
$TiFe_2O_4$	8.50	+0.015	+268.5	−16.6	+241.9	I
$TiMg_2O_4$	8.44	+0.015	+270.5	0	+270.5	I
$TiZn_2O_4$	8.467	+0.005	−821.1	0	−821.1	I
C. Sulphides						
$CaIn_2S_4$[d]	10.795	+0.016	−753.9	0	−753.9	N
$CdCr_2S_4$	10.207	0.000	+270.6	−149.2	+121.4	N
$CdIn_2S_4$[d]	10.818	+0.011	−421.9	0	−421.9	N
$CrIn_2S_4$	10.59	+0.011	−431.0	+35.4	−395.6	I
$CoCr_2S_4$	9.923	+0.007	−182.8	−122.8	−305.6	N
$CoIn_2S_4$	10.580	+0.009	−300.2	+26.4	−273.8	I
$CuCr_2S_4$	9.629	+0.006	−118.5	−115.5	−234.0	N
$CuTi_2S_4$	9.880	+0.007	−183.6	−14.3	−197.9	N
CuV_2S_4	9.824	+0.009	−323.3	−37.3	−360.6	N
$FeCr_2S_4$	9.995	+0.010	−386.9	−134.4	−521.3	N
$FeIn_2S_4$	10.619	+0.009	−299.1	+14.8	−284.3	I
$HgCr_2S_4$	10.2006	+0.017	−869.8	−149.2	−1019.0	N
$HgIn_2S_4$[d]	10.833	+0.013	−599.5	0	−599.5	N
$MgIn_2S_4$	10.708	+0.009	−296.6	0	−296.6	I
$MnCr_2S_4$	10.110	+0.011	−451.4	−149.2	−600.6	N
$NiIn_2S_4$	10.485	+0.009	−302.9	+76.4	−226.5	I
$ZnCr_2S_4$[e]	9.986	+0.009	−318.6	−149.2	−467.8	N
D. Selenides and Tellurides						
$CdCr_2Se_4$	10.721	+0.008	−232.4	*ca.* −150	*ca.* −380	N
$CuCr_2Se_4$	10.357	+0.005	−46.0	*ca.* −115	*ca.* −160	N
$ZnCr_2Se_4$	10.440	+0.010	−370.4	*ca.* −150	*ca.* −520	N
$CuCr_2Te_4$	11.051	+0.004	+16.7	*ca.* −115	*ca.* −100	N

[a] W. L. Roth, *J. Phys. Chem. Solids, 25,* 1 (1964). [b] See text. [c] N. W. Grimes and R. Hilleard, *J. Phys. C, Solid State Phys., 3,* 866 (1970). [d] H. Hahn and W. Klingler, *Z. Anorg. Allgem. Chem., 263,* 177 (1950). [e] P. M. Raccah, R. J Bouch and A. Wold, *J. Appl. Phys., 37,* 1436 (1966).

110 K the substance is inverse $Fe_t^{III}(Fe^{II},Fe^{III})_oO_4$, but at higher temperatures Mössbauer spectroscopy shows that the identity of the Fe(II) and Fe(III) ions in the octahedral sites is lost because of fast electron hopping.[20]

Thirdly, some of the calculated lattice energies may be incorrect because certain spinels do not crystallise in *Fd3m*. It has been suggested[21,22] that at least some spinels crystallise in $F\bar{4}3m$, with their B cations displaced from the special positions 16,d in *Fd3m* to general positions 16,e of type *x,x,x, etc.* in $F\bar{4}3m$. In a neutron diffraction study of $MgCr_2O_4$,[23] refinements in both space groups gave atomic coordinates identical within experimental uncertainty: however the authors were unable to rule out positively displacements of the chromium ions of up to 0.02 Å. Such displacements would of course markedly alter the lattice energy. Finally, it has been assumed throughout that the spinels all exhibit the thermodynamically most stable form.

Despite these cautions, the majority of compounds exhibit the predicted structures. The data in the Table indicate how small Δ(CFSE) is compared with ΔU: ΔU in turn is small compared with U which for 2–3 spinels is typically in the range 17–21 MJ mol^{-1}, of which the Madelung energy is the principal component; thus for $FeFe_2O_4$ and $CoCo_2O_4$, the experimental lattice energies are 18.90 MJ mol^{-1} and 19.57 MJ mol^{-1} respectively, while the respective Madelung energies are 22.02 MJ mol^{-1} and 24.42 MJ mol^{-1}. Consequently CFSE cannot be used as a reliable guide to site preference in spinels. The usual assumption that the change in lattice energy on inversion is approximately constant, leaving Δ(CFSE) as the determining factor, is unjustified because of the great sensitivity of ΔU to δ, which itself varies quite widely.

Closely related to the problem of cation distribution in spinels is that of octahedral–tetrahedral equilibria in solution. For a metal M^{+z}, complexed by an anionic ligand X^-, such as halide, the reaction may be written:

$$MX_4^{+(z-4)} + 2X^- \longrightarrow MX_6^{+(z-6)}$$

If it is assumed that the effective radii of the tetrahedral and octahedral complexes are identical, so that their solvation energies are identical, then

$$\Delta H^{\ominus} = +2\Delta H_{X^-}^{\ominus} + 4B(M^{+z}\text{–}X) - 6B'(M^{+z}\text{–}X) + CFSE(MX_4^{+(z-4)}) - CFSE(MX_6^{+(z-6)})$$

where $\Delta H_{X^-}^{\ominus}$ is the solvation enthalpy of X^-, and B and B′ represent bond energy terms in the tetrahedral and octahedral complexes respectively. For X = Cl, in aqueous solution, $2\Delta H_{X^-}^{\ominus}$ is +726 kJ mol^{-1}; Δ(CFSE) ranges for the 3*d* metal ions from zero when M = Mn(II) or Zn(II) to −139 kJ mol^{-1} when M = Cr(III). Values of B and B′ are unknown for X = Cl, but from values[24] when X is H_2O or CN^-, their order of magnitude, assuming B ≃ B′ is *ca.* 180 kJ mol^{-1} for M(II) and *ca.* 370 kJ mol^{-1} for M(III) (with an increase of 40–70 kJ mol^{-1} across the series), so that −2B is *ca.* −360 kJ mol^{-1} and −750 kJ mol^{-1} respectively, again prompting the suggestion that CFSE is not the dominant factor in determining the position of equilibrium. It may be noted that in chloride melts, octahedral $MCl_6^{+(z-6)}$ ions were formed[25] by 3*d* metals more readily when z = 3 than when z = 2: on changing from M(II) to M(III) for say chromium, Δ(CFSE) changes by *ca.* −70 kJ mol^{-1}, while the change in −2B is some five times this, *ca.* −370 kJ mol^{-1}.

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