Chemical shifts in the K absorption discontinuities of Cr, Mn, Fe, Co and Cu in their oxidic spinels

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Abstract. Levine's theory of ionicity has been widely used to calculate the bond parameters in solids. For predominantly ionic solids this theory has been modified to show the equivalence between ΔE (the chemical shift) and C (the ionic energy) and has been successfully applied to spinels containing transition elements in different valence states.

1. Theoretical development

It has been shown by several workers (Adhyapak and Nigavekar 1976, Leonhardt and Meisel 1970, Gianturco and Coulson 1968, Batsanov and Ovsyannikova 1968, Ovsyannikova and Nasonova 1970, Sapre and Mande 1972, 1973, Kondawar and Mande 1976) that the chemical shifts ΔE in the x-ray spectra are governed by the effective charge on the absorbing ion. The effective charge can be calculated by various theories (Lindberg *et al* 1970, Suchet and Baily 1965, Clementi 1965, Jolly and Perry 1973, Lawaetz 1971) which are based on different physical concepts and have mostly been developed for binary compounds. The linear dependence of the ionic energy C on the chemical shift ΔE has been shown by Ballal and Mande (1976, 1977a, b). These workers have obtained different curves not only for different elements but also for different valencies of the same element.

The dielectric theory of ionicity developed by Phillips (1968, 1970) and Philips and Van Vechten (1969) has been successfully employed by several workers in order to understand the nature of chemical bonds in solids of the type $A^x B^{8-x}$. Levine (1973a) extended the above theory to some complex systems.

According to Levine's (1973a, b) theory of ionicity the energy gap E_g^μ of a given μ type of bond is expressed as

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2$$

where E_h^μ and C^μ are the covalent (or homopolar) and ionic (or heteropolar) energies, respectively. In the present study we are considering only one type of bond and hence for convenience the superscript μ has been deleted. It may be noted that the energy E_g does not correspond to the usual forbidden energy gap in the band picture but in fact is

an average over all the Brillouin zone. The fractional ionicity f_i and fractional covalency f_c of a particular bond are given by

$$f_i = C^2/E_g^2 \qquad f_c = E_h^2/E_g^2.$$

E_h and C are given by the relation $E_h = 39.74/d^{2.48}$ eV and

$$C = b \exp(-K_s r_0)(Z_\alpha/r_\alpha - Z_\beta/r_\beta)e^2 \qquad (1)$$

where r_α and r_β respectively, are the covalent radii of atoms α and β, $r_0 = d/2$ where d is the bond length, Z_α and Z_β respectively, are the valence electrons of atoms α and β, and $K_s = (4K_F/\pi a_0)^{1/2}$, where K_F is the Fermi wavevector and is given by the expression

$$K_F^3 = 3\pi^2 N_e$$

where N_e is number of valence electrons per unit bond volume given by the expression $N_e = N_v/V_b$. Here V_b (the bond volume) and N_v (the number of valence electrons per bond), respectively, are given by $V_b = (d^\mu)^3/\Sigma_v (d^v)^3 N_b^v$ and $N_v = Z_\alpha/N_{c_\alpha} + Z_\beta/N_{c_\beta}$ where N_{c_α} and N_{c_β} are the coordination numbers of α and β atoms, respectively, N_b is the number of bonds per unit volume and b is a constant for a particular structure. The denominator in the expression for V_b represents the required normalization (Levine 1973a). After extensive study of various crystalline materials, Levine (1973a) has shown that $b = 0.089\bar{N}_c^2$ where $\bar{N}_c$ is the average coordination number.

2. Modification of Levine's theory

The present model has been proposed only for predominantly ionic crystals such as transition metal oxide spinels. The ionicity of the compounds reported by Ballal and Mande (1976, 1977a, b) is in the range of 81–92%. In such strongly ionic crystals the homopolar contribution to the bond can be neglected. The magnitude of the chemical shift depends on the effective charge on the absorbing ion and in turn on the magnitude of the coulombic potential difference between the two atoms. Therefore in a purely ionic crystal the magnitude of the chemical shift can very well be attributed to the coulombic potential difference between the two atoms and in turn to the ionic energy C. Equation (1) has been interpreted by Levine (1973a) so that the ionic energy C may be considered as the coulombic potential difference between the two atoms taking part in the bond formation.

    In the present paper we have attempted to modify Levine's (1973a, b) theory of ionicity to take account of an atom in an element and in different chemical surroundings. As the spinels are predominantly ionic crystals, the ionic energy parameter C is expected to be related to the chemical shift ΔE. We observe that, for oxide spinels containing chromium, manganese, iron, cobalt and copper, good agreement exists between the theoretically calculated values of C and the chemical shifts reported earlier from this laboratory.

    In the spinel structure AB_2O_4, there are two or more types of metal atom linked to the oxygen atom either tetrahedrally or octahedrally. The former is usually referred to as an A site and the latter as a B site. The B-site cation is surrounded by six anions and each anion is surrounded tetrahedrally by metal ions. We have considered here a typical metal atom situated at an A site whose chemical shift is primarily decided by its valency. The change in the site of occupancy will cause a negligible change in ΔE, especially when the coordinating atoms (oxygen in the present case) remain the same.

The cation at site A is surrounded by four anions while the anion is surrounded by four cations of which one is from the A site and the remaining three are from the B site. This tetrahedron, however, is not regular owing to the different bond lengths arising because of the difference in the type of A and B cations. The average coordination number at an A site can therefore be written as $\bar{N}_c = (N_{c_\alpha} + N_{c_\beta})/2 = (4 + 1)/2 = 2.5$. Following Levine (1973a) we observe that the constant $b = 0.089\bar{N}_c^2 = 0.556$ and the term $\exp(-K_s r_0)$ is the Thomas–Fermi screening factor.

In an ideal ionic crystal it is assumed that the cation donates electrons equivalent to its formal valency to the anions. However, in reality a small number of valence electrons resides in the bond and the remaining electrons screen the ion core, reducing the charge by the Thomas–Fermi factor. According to Levine (1973a), the true screening behaviour in solids will be more complex than this simple Thomas–Fermi description. To account for this, Levine (1973a) has introduced a correction factor b of the order of unity, which is different for different structures. Even for compounds having a similar structure, the correction factor varies by $\pm 14\%$. This prompted us to see whether any equivalence between C and ΔE, independent of the above parameters, exists, if the screening constant is suitably modified.

Investigations into several cubic and tetragonal spinels have revealed that, if the screening constant $\exp(-k_s r_0)$ is changed to $\exp(-B_s r_0 N_e^{1/3})$ there is good agreement between the ionic energy C and the chemical shift ΔE.

It is well known that the chemical shift increases abruptly with increase in the oxidation state of the cation. This indicates that the magnitude of the screening constant should also increase abruptly with the oxidation state. A factor N, termed the fitting parameter, has therefore been introduced into the screening constant and can be expressed as $\exp(-B_s r_0 N_e^{1/3})^{1/N}$. In the modified expression, B_s is the dimensionless constant and has the value 2.1026 and N is a positive integer. Equation (1) can now be written as

$$C = b \exp(-B_s r_0 N_e^{1/3})^{1/N}(Z_\alpha/r_\alpha - Z_\beta/r_\beta)e^2. \tag{2}$$

If r_α, r_β and r_0 are expressed in ångströms, equation (2) can be written as

$$C = 14.4b \exp(-B_s r_0 N_e^{1/3})^{1/N}(Z_\alpha/r_\alpha - Z_\beta/r_\beta)\,\text{eV}. \tag{3}$$

Assuming that in the volume of a unit cell there is only one type of bond, one can determine the volume per bond by calculating the ratio of the volume of the unit cell to the possible number of bonds. A unit cell of a spinel can contain 64 A–O types of bond and hence the bond volume $V_b = a^3/64$ where a is the lattice constant for a cubic spinel. In the case of a tetragonal spinel, $V_b = a^2 c/64$. The B–O type of bond is not taken into account since the position of the metal ion in either the tetrahedral or the octahedral site does not affect the chemical shift considerably.

When one atom combines with another atom to form a solid, valence electrons per unit bond volume will change and the new value of the valence electrons per unit bond volume on the formation of a solid can be obtained by the relation

$$N_e' = N_v'/V_b \qquad N_v' = Z_\alpha'/N_{c_\alpha} + Z_\beta/N_{c_\beta}.$$

It should be noted that Z_α' refers to the number of valence electrons possessed by the cation.

Table 1. Data on the Cr–O bond: $Z = 6$, $Z_{Cr} = 1$, $Z_{Cr}^{3+} = 3$, $Z_O = 6$.

Compound	Valency	a (Å)	c (Å)	d (Å)	N	N_v	N_v'	C (eV)
ZnMnCrO$_4$	3	8.252	8.62	1.958	1	6.25	6.75	7.1
CuMnCrO$_4$	3	8.320	—	2.046	1	6.25	6.75	6.2
CoMnCrO$_4$	3	8.340	—	1.960	1	6.25	6.75	7.0
FeCoCrO$_4$	3	8.340	—	1.920	1	6.25	6.75	7.4

Table 2. Data on the Mn–O bond: $Z = 7$, $Z_{Mn} = 7$, $Z_{Mn}^{2+} = 5$, $Z_{Mn}^{3+} = 4$, $Z_{Mn}^{4+} = 3$, $Z_O = 6$.

Compound	Valency	a (Å)	c (Å)	d (Å)	N	N_v	N_v'	C (eV)
CoMnFeO$_4$	2	8.409	—	1.960	1	7.75	7.25	7.1
CoMnCrO$_4$	2	8.340	—	1.960	1	7.75	7.25	7.0
CuMn$_2$O$_4$	3	8.349	—	2.010	2	7.75	7.00	12.2
CuMnFeO$_4$	3	8.390	—	1.901	2	7.75	7.00	13.4
ZnMnCrO$_4$	3	8.252	8.62	1.958	2	7.75	7.00	12.8
ZnMnFeO$_4$	3	8.257	8.77	1.973	2	7.75	7.00	12.7
CuMnCoO$_4$	4	8.310	8.58	1.963	4	7.75	6.75	16.1
ZnMnCoO$_4$	4	8.407	—	1.960	4	7.75	6.75	16.1

We have, for convenience, defined Z_α^* (the effective valence electrons on the transition metal atom) and this can be calculated for the system under consideration by appropriately modifying the expression given by Levine (1973b) as

$$Z_\alpha^* = Z \exp(-B_s r_0 N_c^{1/3})^{1/N} / b \exp(-B_s r_0 N_c'^{1/3})^{1/N} \tag{4}$$

where Z is the number of valence electrons of an α atom, $\exp(-B_s r_0 N_c^{1/3})^{1/N}$ is an appropriate screening factor for an α atom and $b \exp(-B_s r_0 N_c'^{1/3})^{1/N}$ is very similar to the Thomas–Fermi (Levine 1973b) screening factor for the anion β on the formation of a solid.

Substituting Z_α^* for Z_α in equation (3) we get

$$C = 14.4b \exp(-B_s r_0 N_c^{1/3})^{1/N} (Z_\alpha^*/r_\alpha - Z_\beta r_\beta) \text{ eV}. \tag{5}$$

Levine (1973a), in order to reduce the spread of b values, has assumed that $r_\alpha = r_\beta = d/2 = r_0$. Equation (5) can therefore be written as

$$C = 14.4b \exp(-B_s r_0 N_c^{1/3})^{1/N} [(Z_\alpha^* - Z_\beta)/r_0] \text{ eV}. \tag{6}$$

As we are considering only the magnitude of the coulombic potential difference between α and β atoms, equation (6) can be written as

$$C = 14.4b \exp(-B_s r_0 N_c^{1/3})^{1/N} |(Z_\alpha^* - Z_\beta)/r_0| \text{ eV}. \tag{7}$$

The values of C for different compounds have been calculated using equation (7) and the data given in tables 1–5. The value of $b = 0.556$ has been taken as a constant for all the compounds.

Table 3. Data on the Fe–O bond: $Z = 8$, $Z_{Fe} = 8$, $Z_{Fe}^{2+} = 1$, $Z_{Fe}^{3+} = 5$, $Z_O = 6$.

Compound	Valency	a (Å)	c (Å)	d (Å)	N	N_v	N_v'	C (eV)
FeAl$_2$O$_4$	2	8.124	—	1.970	1	8.00	6.25	6.6
GeFe$_2$O$_4$	3	8.425	—	2.104	1	8.00	7.25	6.9
CdFe$_2$O$_4$	3	8.705	—	2.176	1	8.00	7.25	6.7
ZnMnFeO$_4$	3	8.275	8.770	1.973	1	8.00	7.25	8.5
CuMnFeO$_4$	3	8.390	—	1.904	1	8.00	7.25	9.4
CoMnFeO$_4$	3	8.409	—	1.960	1	8.00	7.25	8.6
FeCoCrO$_4$	3	8.340	—	1.920	1	8.00	7.25	9.0

Table 4. Data on the Co–O bond: $Z = 9$, $Z_{Co} = 9$, $Z_{Co}^{2+} = 7$, $Z_{Co}^{3+} = 1$, $Z_O = 6$.

Compound	Valency	a (Å)	c (Å)	d (Å)	N	N_v	N_v'	C (eV)
FeCoCrO$_4$	2	8.340	—	1.920	1	8.25	7.75	11.3
CuMnCoO$_4$	2	8.310	8.58	1.963	1	8.25	7.75	10.7
CoCr$_2$O$_4$	2	8.320	—	1.987	1	8.25	7.75	10.1
CoMnAlO$_4$	2	8.260	—	1.950	1	8.25	7.75	10.5
Co$_2$MnO$_4$	2	8.276	—	1.934	1	8.25	7.75	10.8
CoMnCrO$_4$	3	8.340	—	1.960	2	8.25	6.25	18.3
ZnMnFeO$_4$	3	8.409	—	2.020	2	8.25	6.25	17.4

Table 5. Data on the Cu–O bond: $Z = 1$, $Z_{Cu}^{2+} = 9$, $Z_O = 6$.

Compound	Valency	a (Å)	c (Å)	d (Å)	N	N_v	N_v'	C (eV)
CuCr$_2$O$_4$	2	8.330	—	1.980	1	6.25	8.25	4.9
CuMn$_2$O$_4$	2	8.349	—	2.010	1	6.25	8.25	4.8
CuMnCoO$_4$	2	8.310	8.58	1.963	1	6.25	8.25	5.2
CuMnFeO$_4$	2	8.390	—	1.904	1	6.25	8.25	5.6
CuMnCrO$_4$	2	8.320	—	2.046	1	6.25	8.25	4.5

3. Typical calculation for ionic energy C

Consider as an example, a Cr–O bond in the spinel CuMnCrO$_4$, having a lattice parameter $a = 8.32$ Å and a bond length $d = 2.046$ Å, i.e. $r_0 = 1.023$ Å. The number of valence electrons of the Cr atom is six (i.e. $Z = 6$), out of which five form $3d^5$ as a stable configuration and hence Z_{Cr} can be assumed to be equal to 1. Therefore $N_v = Z_{Cr}/N_{cCr} + Z_O/N_{cO} = 1/4 + 6/1 = 6.25$. In the case of a cation Cr^{3+} the number of valence electrons is $6 - 3 = 3$, which gives $N_v' = Z_{Cr}^{3+}/N_{cCr} + Z_O/N_{cO} = 3/4 + 6/1 = 6.75$. The bond volume $V_b = a^3/64 = 8.9989$ Å^{-3}. $N_e = N_v/V_b = 0.6945$ Å^{-3} and $N_e' = N_v'/V_b = 0.7501$ Å^{-3}. $N = 1$, $Z = 6$, $b = 0.556$; $\exp(-B_s r_0 N_e^{1/3})^{1/N} = 0.1488$ and

Table 6. Theoretically calculated values of C and ΔE.

Sample	Compound	Bond	C (eV)	ΔE (±0.5 eV)	Sample	Compound	Bond	C (eV)	ΔE (±0.5 eV)
1	$ZnMnCrO_4$[a]	Cr^{3+}–O	7.1	6.3	17	$CuMnFeO_4$[a]	Fe^{3+}–O	9.4	9.3
2	$CuMnCrO_4$[a]	Cr^{3+}–O	6.2	6.5	18	$CoMnFeO_4$[a]	Fe^{3+}–O	9.6	9.7
3	$CoMnCrO_4$[b]	Cr^{3+}–O	7.0	7.1	19	$FeCoCrO_4$[a]	Fe^{3+}–O	9.0	9.9
4	$FeCoCrO_4$[a]	Cr^{3+}–O	7.4	7.4	20	$FeCoCrO_4$[c]	Co^{2+}–O	11.3	11.8
5	$CoMnFeO_4$[a]	Mn^{2+}–O	7.1	7.1	21	$CuMnCoO_4$[c]	Co^{2+}–O	10.7	10.9
6	$CoMnCrO_4$[b]	Mn^{2+}–O	7.0	6.9	22	$CoCr_2O_4$[f]	Co^{2+}–O	10.1	9.0
7	$CuMn_2O_4$[a]	Mn^{3+}–O	12.2	13.3	23	$CoMnAlO_4$	Co^{2+}–O	10.5	11.0
8	$CuMnFeO_4$[a]	Mn^{3+}–O	13.4	12.8	24	Co_2MnO_4	Co^{2+}–O	10.8	11.9
9	$ZnMnCrO_4$[a]	Mn^{3+}–O	12.8	12.1	25	$CoMnCrO_4$[c]	Co^{3+}–O	18.3	16.3
10	$ZnMnFeO_4$[a]	Mn^{3+}–O	12.7	12.7	26	$CoMnFeO_4$[c]	Co^{3+}–O	17.4	16.9
11	$CuMnCoO_4$[c]	Mn^{4+}–O	16.1	16.3	27	$CuCr_2O_4$[f]	Cu^{2+}–O	4.9	5.7
12	$ZnMnCoO_4$[a]	Mn^{4+}–O	16.1	16.1	28	$CuMn_2O_4$[c]	Cu^{2+}–O	4.8	5.2
13	$FeAl_2O_4$[a]	Fe^{2+}–O	6.6	5.3	29	$CuMnCoO_4$[c]	Cu^{2+}–O	5.2	5.9
14	$GeFe_2O_4$[c]	Fe^{3+}–O	6.9	7.6	30	$CuMnFeO_4$[a]	Cu^{2+}–O	5.6	4.9
15	$CdFe_2O_4$[c]	Fe^{3+}–O	6.7	7.8	31	$CuMnCrO_4$[a]	Cu^{2+}–O	4.5	3.9
16	$ZnMnFeO_4$[d]	Fe^{3+}–O	8.5	9.6					

[a] From Kulkarni (1970).
[b] From Kulkarni and Mande (1971).
[c] From Kanetkar (1978).
[d] From Mande et al (1969).
[e] From Kulkarni and Mande (1974).
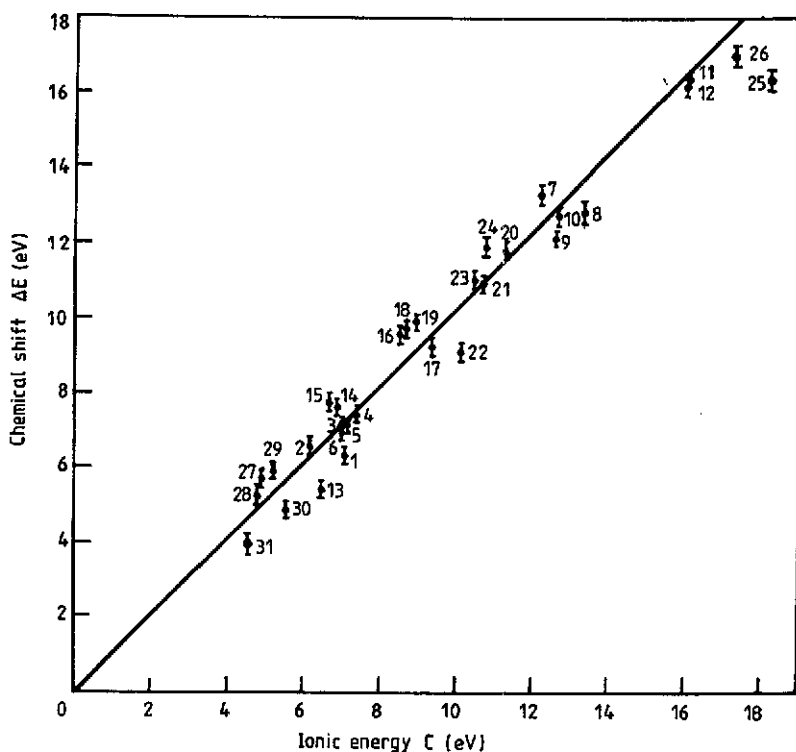[f] From Ballal and Mande (1977b).

Figure 1. Variation in chemical shift with ionic energy.

$\exp(-B_s r_0 N_e'^{1/3})^{1/N} = 0.1417$. Putting these values in equation (4), we get $Z_\alpha^* = 11.34$, which gives $C = 6.2 \, \text{eV}$.

The crystallographic data are taken from the work of Kulkarni (1970), Kanetkar (1970) and Kulkarni and Mande (1970, 1971).

4. Results and discussion

In table 6 are given the theoretically calculated values of the ionic energy C and the chemical shift ΔE for the spinel with cubic and tetragonal structures as reported in some of the earlier publications from our laboratory.

One observes that the values of ΔE and C for all the compounds are in good agreement. One may therefore conclude that the ionic part of the energy is responsible for the chemical shift. We have plotted in figure 1 the experimental values of chemical shift ΔE versus the theoretically calculated ionic energy C for all the compounds. All the points lie more or less on a straight line. The value of N, however, does not seem to depend on the oxidation state of absorbing ion, e.g. $N = 1$ for Cr^{3+} and Fe^{3+} as well as for Cu^{2+} and Mn^{2+} and $N = 2$ for Mn^{3+} and Co^{3+}. Further work, both theoretical and experimental, is necessary to understand the exact screening mechanism.

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