Reports of the Academy of Sciences of the USSR

D. Z. Brainina, A. N. Men, V. S. Chudakov,

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Volume 160, No. 2

PHYSICAL CHEMISTRY

D. Z. Brainina, A. N. Men, V. S. Chudakov,
Corresponding Member of the Academy of Sciences of the USSR G. I. Chufarov

ON THE CALCULATION OF THE "STABILIZATION" ENERGY OF IRON-GROUP IONS IN OXIDES WITH THE SPINEL STRUCTURE

Many important physical properties of ferrites depend on the distribution of cations over the tetrahedral $8(a)$ and octahedral $16(d)$ sites (sublattices) in the spinel structure. The distribution of cations over the $8(a)$ and $16(d)$ sites is characterized by the degree of inversion λ. A statistical calculation of the temperature and concentration dependence of λ was carried out in ([2]). In this calculation the ion energies at sites of the $8(a)$ and $16(d)$ types were used as parameters of the theory. In works ([1,8]), the distribution of iron-group ions over the sublattices for the simplest ferrites of the type MFe_2O_4 was determined, in the crystal-field approximation, from the assumption that the limiting point symmetry of the $8(a)$ and $16(d)$ sites is cubic, and that the Me–O distance in octahedra and tetrahedra is the same. In this case the energy levels of an ion with configuration $3d^n$ were determined by a single parameter D_q, whose value for different ions was taken from experiments on the optical spectra of hydrates and simple oxides. Taking as the "stabilization" energy (E_{st}) the difference between the energy of the free ion and the energy of the lower term in a field of cubic symmetry, the authors of ([1,8]) obtained qualitative agreement with experiment concerning the preference of an ion of a given kind for a site of a given type in simple ferrites.

However, a more careful investigation of the spinel structure showed ([3]) that the limiting point symmetry of the $8(a)$ sites is $\bar{4}3m$ (T_d), and that of the $16(d)$ sites is $\bar{3}m$ (D_{3m}). In this connection, a numerical calculation ([4]) was carried out (in the point-charge approximation) of the contribution to the splitting energy both from second neighbors and from the deviation of the parameter u from the value 0.375 (in the case of a nonideal spinel), which proved to be appreciable.

In the present work a consistent calculation is carried out of the "stabilization" energy of iron-group ions located at the $8(a)$ and $16(d)$ sites of the spinel. The

value of E_{st} and the explicit form of the parameters in the point-charge approximation are readily obtained from the general solutions given in Table 1. Table 1 gives values of E_{st} for the case in which the trigonal field is not taken into account (the approximation used in works [1,8]), E'_{st} in the approximation in which the trigonal field (V_{tr}) is much weaker than the cubic field (V_{cub}) created by oxygen ions in an ideal spinel, and the exact solution ($V_{cub} \sim V_{tr}$). In the last two columns (in the first and second rows), two values of E_{st} are given, since the ground level cannot be determined from the general expressions. As is seen from the data of Table 1, in order to obtain numerical values of E_{st} it is necessary to know two parameters, $\langle r^2 \rangle$ and $\langle r^4 \rangle$, which determine the mean value of the corresponding power (second or fourth) of the radius of the impurity ion. The remaining parameters a, δ, and $\tilde{q}$ can be determined (for the case of concentrated solutions) from x-ray and neutron-diffraction measurements (see Table 3). It should be noted that, generally speaking, in the case of solid solutions the limiting point symmetry will be lower than that considered in the work, but the magnitude of the splitting due to this factor will be of the order of 100 cm^{-1} [6], which is considerably smaller than E_{st}; therefore we take into account ···

Table 1

Configuration	Ion types	$E_{st}^{8(d)}$	$E_{st}^{16(d)}$ (cub.)	$E_{st}^{16(d)}$ ($V_{cub} \gg V_{tr}$)	$E_{st}^{16(d)}$ ($V_{cub} \approx V_{tr}$)
d^1	Ti^{3+}, V^{4+}	$6(Dq)_T$	$4(Dq)_0$	$4(Dq)_0 - 30(b_4^T + b_4^T)$ "n"	$-30(b_2 + b_4)$ "n"
d^6	$\boxed{Fe^{2+}}$ Co^{3+}	$6(Dq)_T$	$4(Dq)_0$	$4(Dq)_0 + 5\left(3b_2^T + \frac{2}{3}b_4^T - \frac{2}{3}\sqrt{70}\,b_3^T\right)$	$\frac{5}{2}\left[3(b_2+b_4) + \sqrt{(5b_4-9b_2)^2+140b_3^2}\right]$
d^2	Ti^{2+}, V^{3+}	$12(Dq)_T$	$6(Dq)_0$	$6(Dq)_0 + \frac{1}{3}\left(9b_2^T + 65b_4^T - 20\sqrt{70}\,b_3^T\right)$	$\frac{1}{2}\left[3b_2 + 45b_4 + 3\sqrt{(9b_2-5b_4)^2+1400b_3^2}\right]$ "n"
d^7	$\boxed{Co^{2+}}$, Ni^{3+}	$12(Dq)_T$	$6(Dq)_0$	$6(Dq)_0 - \frac{1}{6}\left(9b_2^T + 170b_4^T + 10\sqrt{70}\,b_3^T\right)$ "n"	$-\frac{1}{2}\left[9b_2 + 30b_4 - \sqrt{(9b_2+40b_4)^2+1400b$
d^3	V^{2+} $\boxed{Cr^{3+}}$ $\boxed{Mn^{4+}}$	$\frac{1}{2}\left\{\Delta p + 6(Dq)_T - \sqrt{[\Delta p - 12(Dq)_T]^2 + 64(Dq)_T^2}\right\}$	$12(Dq)_0$	$\frac{70}{3}\left(b_4^T + \frac{2\sqrt{70}}{7}b_3^T\right)$	$\frac{1}{2}\left[3b_2 + 45b_4 - 3\sqrt{(9b_2-5b_4)^2+1400b$
d^8	$\boxed{Ni^{2+}}$	$\frac{1}{2}\left\{\Delta p + 6(Dq)_T - \sqrt{[\Delta p - 12(Dq)_T]^2 + 64(Dq)_T^2}\right\}$	$12(Dq)_0$	$\frac{70}{3}\left(b_4^T + \frac{2\sqrt{70}}{7}b_3^T\right)$	$\frac{1}{2}\left[3b_2 + 45b_4 - 3\sqrt{(9b_2-5b_4)^2+1400b$

Configuration	Ion types	$E_{\text{st}}^{8(d)}$	$E_{\text{st}}^{16(d)}$ (cub.)	$E_{\text{st}}^{16(d)}$ ($V_{\text{cub}} \gg V_{\text{tr}}$)	$E_{\text{st}}^{16(d)}$ ($V_{\text{cub}} \approx V_{\text{tr}}$)
d^4	$\boxed{\text{Mn}^{3+}}$ Fe^{4+}	$4(Dq)_T$	$6(Dq)_0$	$6(Dq)_0 - \frac{35}{3}\left(b_4^T + \frac{2\sqrt{70}}{7}b_3^T\right)$	$-\frac{5}{2}\left[3(b_2+b_4) - \sqrt{(5b_4-9b_2)^2+140b_3^2}\right]$
d^9	Cu^{2+}	$4(Dq)_T$	$6(Dq)_0$	$6(Dq)_0 - \frac{35}{3}\left(b_4^T + \frac{2\sqrt{70}}{7}b_3^T\right)$	$-\frac{5}{2}\left[3(b_2+b_4) - \sqrt{(5b_4-9b_2)^2+140b_3^2}\right]$

$$(Dq)_T = -\frac{4\sqrt{3}}{729}(1-40\delta)\left(\frac{8r_{\text{B}}}{a}\right)^5 \frac{\langle r^4\rangle}{r_{\text{B}}^4}\frac{l^2}{r_{\text{B}}}$$

$$\delta = u - \frac{3}{8},$$

where a is the lattice parameter,

u is the oxygen parameter,

$$\Delta p = E(4p) - E(4F)$$

$$(Dq)_0 = \frac{1}{96}\left(\frac{8r_{\text{B}}}{a}\right)^5 \frac{\langle r^4\rangle}{r_{\text{B}}^4}\frac{l^2}{r_{\text{B}}}$$

$$b_2^T = \frac{1}{70}\left(8\delta - \frac{3\sqrt{2}}{16}\tilde{q}\right)\left(\frac{8r_{\text{B}}}{a}\right)^3 \frac{\langle r^2\rangle}{r_{\text{B}}^2}\frac{l^2}{r_{\text{B}}}$$

$$b_3^T = -\frac{2\sqrt{35}}{630}\left(\sqrt{28} + \frac{\tilde{q}}{16^2}\right)\left(\frac{8r_{\text{B}}}{a}\right)^5 \frac{\langle r^4\rangle}{r_{\text{B}}^4}\frac{l^2}{r_{\text{B}}}$$

$$b_4^T = \frac{1}{5040}\left(-235\delta + \frac{13\sqrt{2}}{64}\tilde{q}\right)\left(\frac{8r_{\text{B}}}{a}\right)^5 \frac{\langle r^4\rangle}{r_{\text{B}}^4}\frac{l^2}{r_{\text{B}}}$$

$\tilde{q}$ is the mean charge in the octahedral site

$$b_2 = b_2^T$$

$$b_3 = -\frac{2\sqrt{35}}{630}\left[\frac{\sqrt{2}}{16} + \sqrt{28} + \frac{\tilde{q}}{16^2}\right]\left(\frac{8r_{\mathrm{B}}}{a}\right)^5 \frac{\langle r^4\rangle}{r_{\mathrm{B}}^4}\,\frac{l^2}{r_{\mathrm{B}}}$$

$$b_4 = \frac{1}{5040}\left[-7 - 235\delta + \frac{13\sqrt{2}}{64}\tilde{q}\right]\left(\frac{8r_{\mathrm{B}}}{a}\right)^5 \frac{\langle r^4\rangle}{r_{\mathrm{B}}^4}\,\frac{l^2}{r_{\mathrm{B}}}$$

this is possible only by introducing an average charge ($\tilde{q}$) in the octahedra ($\tilde{q}$ in the general case is determined by the composition of the solid solution and λ). The calculation scheme considered (in the case of concentrated solutions) also does not take into account the change in E'_{st} due to the energy of electron exchange between nearest-neighbor cations; however, such a neglect is justified by the fact that the magnitude of this effect is also considerably smaller than E'_{st} (thus, for example, for Co^{2+} it is 600 cm^{-1} ([7])). As for the parameters $\langle r^n\rangle$, there are several ways of determining them ([7], [15], [16]), which unfortunately give strongly differing values. It is therefore most consistent to determine $\langle r^n\rangle$ from experiment. Thus, to determine $\langle r^4\rangle$ we use formula (1), using data on the optical spectra of simple oxides and hydrates:

$$\frac{\langle r^4\rangle}{r_B^4} = \frac{3D_q}{R^2/r_B}\left(\frac{R}{r_B}\right)^5, \qquad (1)$$

where R is the equilibrium Me–O distance; r_B is the Bohr radius; D_q is a parameter characterizing the splitting in a cubic field. The results of calculations for several ions are given in Table 2. The situation is considerably worse for determining $\langle r^2\rangle$, since the necessary experimental data are lacking. For the ions listed in Table 3, only for the Cr^{3+} ion was it possible to find $\langle r^2\rangle$ and $\langle r^4\rangle$, using data on the optical spectra of Cr^{3+} in $MgAl_2O_4$ ([19]) (see in more detail ([4]) and ([5])); for the remaining ions, the values of $\langle r^2\rangle$ were chosen from ([15]), taking into account the corresponding values for $\langle r^4\rangle$ given in Table 2. Therefore the value of E_{st} given in Table 3 (for all ions except Cr^{3+}) is illustrative in character. Nevertheless, they make it possible to draw some general conclusions about the substantial importance of taking into account

Table 2

ion	D_q (oxide)	R	$\langle r^4\rangle/r_B^4$
Fe^{2+}	1040 ([9])	2.16	16.17
Co^{2+}	942 ([10])	2.12	13.34
Ni^{2+}	885 ([1])	2.10	11.95
Mn^{3+}	1890 ([9])	2.02	21.02

Table 3

Ion	$\langle r^4\rangle/r_B^4$	$\langle r^2\rangle/r_B^2$	$\tilde{q}$	a	δ	$\langle D_q\rangle_T$	$\langle D_q\rangle_0$	$E_{\rm st}^{(\alpha)}$	$E_{\rm st}^{16(d)}$ (K)	$E_{\rm st}^{(1)}$	$E_{\rm st}^{16(d)}$ (V)	$\langle V_{\rm K}\rangle_{\rm st}^{16(d)}$ (V)	$\langle V_{\rm K}\rangle \simeq$
Fe^{2+}	Fe_3O_4	16.17	2.24	2.5	8.396 (12)	0.008 (11)	500	1200	2700	4900	4200	23700	21600	
Fe^{2+}	$MnFe_2O_4$	16.17	2.24	2.9	8.508 (14)	0.010 (13)	500	1200	2700	4900	4200	23700	23200	
Fe^{2+}	$FeCr_2O_4$	16.17	2.24	3.0	8.377 (13)	0.009 (15)	500	1200	2700	4900	4200	23700	25300	
Co^{2+}	$CoFe_2O_4$	18.34	1.92	2.5	8.36 (13)	0.006 (13)	800	900	9000	5600	7700	5700	8200	
Ni^{2+}	$NiFe_2O_4$	10.95	1.65	2.5	8.325 (18)	0.006 (13)	700	900	3300	11100	10200	13100	14700	
Cr^{3+}	$MgCr_2O_4$	26.10	4.03	3.0	8.312 (13)	0.010 (13)	600	2000		24400	18700	26100	27000	
Mn^{3+}	$MnFe_2O_4$	21.02	2.515	2.9	8.508 (14)	0.010 (13)	600	1500	2400	9300	11300	11600	21600	
Mn^{4+}	$MnFe_2O_4$	21.02	2.515	2.9	8.508 (14)	0.010 (13)	600	1500	3100	18600		13800	24200	

the trigonal field and of the particular crystal for calculating $E'_{\rm st}$. The ions for which numerical calculations were carried out are enclosed in boxes in Table 1. For the Fe^{2+} and Co^{2+} ions, the lower terms yielded terms marked in the corresponding rows of Table 1 by the index "H."

The general formulas given in Table 1 can be used to calculate $E_{\rm st}$ for other systems as well, if the limiting island symmetry coincides with $43m$ or $\bar{3}m$; however, the parameters b_i must be calculated anew. To calculate $E_{\rm st}$ of ions in spinel, one must use the formulas given in the third and last columns of Table 1.

As for the numerical values given in Table 3, as well as in works ([1], [8], [19]), they should be used with great caution, remembering that they too have a qualitative character. More reliable val—

···can be obtained within the framework of this model when the availability of experiment makes it possible to determine $\langle r^2\rangle$ and $\langle r^4\rangle$, as was done in ([4]).

Let us also note that in papers ([1,8,19]), in calculating the stabilization energies, the level shift was not taken into account. The calculation of the shift reduces to calculating the potentials φ created by the remaining ions at positions $8(a)$ and $16(d)$, respectively. The potentials are readily calculated using the Ewald method ([20]) or Hund functions ([21]).

$$\begin{aligned}\varphi_{8(a)} &= -5.387q_T - 3.336q_0 + 3.2(1+72\delta),\\ \varphi_{16(d)} &= -1.668\,q_T - 6.332\,q_0 - 4(1.09+38.40\delta),\end{aligned} \tag{2}$$

where q_T and $q_0(=\tilde{q})$ are the mean charges at positions $8(a)$ and $16(d)$, respectively. Using (2), it is easy to obtain for the shift energy E'_{shift}

$$E_{\text{shift}}^{8(a)} = -\frac{e^2}{a}\, n_d \varphi_{8(a)}, \qquad E_{\text{shift}}^{16(d)} = -\frac{e^2}{a}\, n_d \varphi_{16(d)}, \tag{3}$$

where n_d is the number of $3d$ electrons in the ion under consideration. Thus, for example, in ferrite $MnFe_2O$, $E_{\text{shift}}^{8(a)}(Fe^{3+}) = E_{\text{shift}}^{8(a)}(Mn^{2+}) = 1.0 \cdot 10^6$ cm^{-1}; $E_{\text{shift}}^{16(d)}(Fe^{3+}) = E_{\text{shift}}^{16(d)}(Mn^{2+}) = 1.3 \cdot 10^6$ cm^{-1}.

The value of the shift is comparable with the Coulomb energy, and therefore, in order to take account of the influence of the shift on the ion' s preference energy for a given site, one must also take into account other energy terms (the Coulomb energy, the repulsion energy, etc. ([19])) and otherwise define the very concept of "stabilization" energy ([22]).

Institute of Metallurgy
Sverdlovsk

Received
29 VII 1964

CITED LITERATURE

1. D. McClure, J. Phys. Chem. Sol., 3, 311 (1957).
2. A. N. Men' , Fiz. tverd. tela, 3, 1054 (1961); 4, 14 (1962).
3. A. N. Men' , V. E. Naish, Fiz. tverd. tela, 5, 2477 (1963).
4. V. I. Cherepanov, A. N. Men' , Fiz. tverd. tela, 6, 1939 (1964).
5. M. Tachiki, Progr. Theoret. Phys., 23, 1055 (1960).
6. J. C. Slonczewski, Phys. Rev., 110, 1341 (1958).
7. C. Burns, Phys. Rev., 128, 2121 (1962).
8. J. D. Dunitz, L. E. Orgel, J. Phys. Chem. Sol., 3, 318 (1957).
9. G. W. Pratt, R. Coelho, Phys. Rev., 116, 281 (1959).
10. T. G. Dvoryankina, Z. G. Pinsker, DAN, 132, 110 (1960).
11. V. I. Mikheev, *X-ray Determinative Tables for Minerals*, Moscow, 1957.

12. S. Hafner, Schweiz. mineral. u. petrogr. Mitt., 40, 207 (1960).

13. D. Z. Brainina, B. D. Averbukh et al., ZhFKh, 38, 7, 1811 (1964).

14. M. I. Simonova, Dissertation, Sverdlovsk, 1964.

15. N. F. Lan, C. C. Lin, Ann. Phys., 20, 234 (1962).

16. S. A. Altshuler, B. M. Kozyrev, *Electron Paramagnetic Resonance*, Moscow, 1961.

17. J. H. van Vleck, Phys. Rev., 41, 208 (1932).

18. S. V. Grum-Grzhimailo, Zap. Vsesoyuzn. min. obshch., 2nd ser., 87, issue 2, 129 (1958).

19. A. Miller, J. Appl. Phys. Suppl., 30, 245 (1959).

20. A. N. Men' , Dissertation, Sverdlovsk, 1956.

21. Y. Sukamoto, V. Tokanasi, J. Sci. Hiroshima Univ., Ser. A, II, 26, 67 (1962).

22. M. T. Zhuravleva, A. N. Men' , G. I. Chufarov, DAN, 159, No. 4 (1964).

Note: Figure translations are in progress. See original paper for figures.