UDC 549.02 : 548.32

A.N. Platonov[1], V.S. Urusov[2], K. Langer[3]

[1] M.P. Semenenko Institute of Geochemistry, Mineralogy
  and Ore Formation of the NAS of Ukraine, Kyiv
  34, Palladina Prospect, 03680, Kyiv-142, Ukraine
  E-mail: platonov@i.com.ua

[2] Lomonosov Moscow State University, Russia
  1, Vorobievy Gory, GSP-1, 119991, Moscow, Russia

[3] Institute für Angew. Geowissenschaften, Techn. Univ., Berlin, Deuschland
  Ernst-Reuter-Platz, 1, D-10623, Berlin, Germany

A REMARK ON CORRELATION BETWEEN RELAXATION PARAMETER AND COVALENCE OF Cr^{3+}—O BONDS IN SOME MINERAL STRUCTURES

The local interatomic distances $R^{loc}_{<Cr-O>}$ and the local lattice relaxation coefficient ε for low-chromium members of solid solution series corundum — escolaite, spinel — magnesiochromite, $YAlO_3$ — $YCrO_3$ (perovskites), pyrope — knorringite, grossular — uvarovite, jadeite — kosmochlore, spodumene — $LiAlSi_2O_6$ were calculated. The correlation between relaxation coefficient ε and Racah parameter B_{35} of Cr^{3+}, which reflects the covalent character of the respective (Cr^{3+}—O)-bonds was firstly revealed. The observed dependence could be preliminary explained by the so-called "rule of mutual influence of different bonds in the crystal structure".

As it was demonstrated by Urusov [22] in his model of binary solid solutions the local lattice relaxation coefficient, ε, reflects the response of the mineral structures on the incorporation of substituting foreign ions different in sizes comparing with the substituted host ions.

It has been shown that local mean ($O—M^{3dN}$)-distances, $R^{loc}_{<M-O>}$, can be determined from electronic absorption spectra of M^{3dN}-ions-bearing mineral solid solutions [9]. The presupposition is that $R^{loc}_{<M-O>}$ and the crystal field parameter $10Dq$ for the end members are known as reference values. A local relaxation parameter, ε, can also be calculated from the data obtained from electronic absorption spectra using the following equations [9]:

$$(R^{loc}_{<M-O>})_{xi} = (R_{<M-O>})_{x=1} \cdot [(10Dq)_{x=1}/(10Dq)_{xi}]^{1/5},$$

and

$$\varepsilon = (R^{loc}_{<M-O>xi} - R_{<M-O>x=0})/$$
$$(R_{<M-O>x=1} - R_{<M-O>x=0}).$$

Here we show that the local relaxation, ε, around the substituting $^{VI}Cr^{3+}$ depends on the Racah parameter B_{35} of Cr^{3+}, which reflects the covalent character of the respective (Cr^{3+}—O)-bonds.

The data to check for such possible effects are, except of the B_{35}-values, mostly taken from the literature (Table). Columns 1, 2, 6 and 7 of Table give the reference values, needed to calculate the data in columns 3 and 4.

In Figure the results of our calculations of the local relaxation coefficient, ε, for some Cr^{3+}-bearing minerals noted in Table are shown as a function of the Racah parameter values, B_{35}, of Cr^{3+} in the respective structural matrix. This Figure demonstrates a strong dependence of the local lattice relaxation coefficient, ε, on the character of the Cr—O bond in the oxide structures of type (1), (2), and (3). This strong dependence becomes weak in the case of the chain silicate structures (6), (7), which exhibit high relaxation coefficients. Data for orthosilicates, e. g. garnets, (4) and (5), plot in an intermediate range.
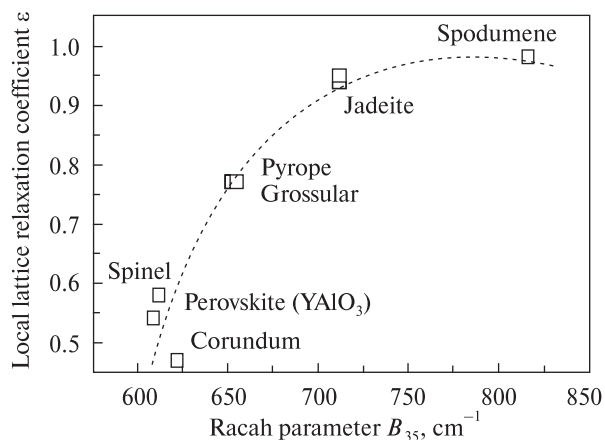
Fig. 8. The dependence of the lattice relaxation parameter ε on the Racah parameter of interionic interaction B_{35}

In the chain silicate structures the substitution of Cr^{3+} in $M1$-sites obviously approaches the "hard sphere" concept. The values of $R^{loc}_{<Cr-O>}$ in these minerals are very close to the sum of ionic radii $^{[6]}Cr^{3+}$ and O^{2-} [18]: the ratio $R^{loc}_{<Cr-O>}/\sum(rCr^{3+}+ + rO^{2-}) \geq 0.99$, and the corresponding relaxation parameter is equal in average 0.95.

The observed correlation could be preliminary explained by the so-called "rule of mutual influence of different bonds in the crystal structure" [21]. According to this rule, the ionicity of the given bond, in our instance Al—O or Cr—O, turns to be higher when the neighboring bonds become to be more covalent. In the discussed set of the mineral structures, they form the following range in order of Cr—O bond ionicity increase (covalency decrease): perovskite — spinel — corundum — garnets — pyroxenes. Besides that, in this range of structures the O coordination number n and especially a number of the nearest Al(Cr) neighbors are remarkably decreasing: $4Y + 2Al$ ($n = 6$) in perovskite, $4Al$ ($n = 4$) in corundum, $3Al + 1Mg$ ($n = 4$) in spinel, $1Al + 2Mg + Si$ ($n = 4$) in garnets, $2Al + Na + + Si$ (O1), $1Al + 2Na + Si$(O2), $2Na + 2Si$ (O3)

Experimental data (columns 1, 2, 6 and 7) used this note for calculating the mean local distances, $R^{loc}_{<Cr-O>}$, and lattice relaxation coefficient, ε, around substituting chromium in some $^{[6]}Cr^{3+}$-bearing minerals (columns 3 and 4)

$R_{<Al-O>}$, Å	$10Dq$, cm^{-1}	$R^{loc}_{<Cr-O>}$, Å	ε	B_{35}, cm^{-1}	$R_{<Cr-O>}$, Å	$10Dq$, cm^{-1}
1	2	3	4	5	6	7
(1) *Corundum*, Al$_2$O$_3$, ($x_{Cr} = 0.09$)				*Eskolaite*, Cr$_2$O$_3$		
1.914[1]	18060	1.954	0.47	622	1.986[2]	16650[3]
(2) *Spinel*, MgAl$_2$O$_4$, ($x_{Cr} = 0.01$)				*Magnesiochromite*, MgCr$_2$O$_3$		
1.926	18520[4]	1.968	0.58	612	1.984[5]	17150[6,7]
(3) *Perovskite-type*, YAlO$_3$, ($x_{Cr} = 0.02$)[8]				YCrO$_3$, ($x_{Cr} = 1$)[8]		
1.911	17870	1.950	0.54	609	1.984	16400
(4) *Pyrope*, Mg$_3$Al$_2$Si$_3$O$_{12}$, ($x_{Cr} = 0.02$)				*Knorringite*, Mg$_3$Cr$_2$Si$_3$O$_{12}$		
1.886[9]	18000[10]	1.944	0.77	653	1.96[11]	17290[12]
(5) *Grossular*, Ca$_3$Al$_2$Si$_3$O$_{12}$, ($x_{Cr} = 0.005$)				*Uvarovite*, Ca$_3$Cr$_2$Si$_3$O$_{12}$		
1.926[9]	16590[13]	1.978	0.77	655	1.994[14]	15930[14]
(6) *Jadeite*, NaAlSi$_2$O$_6$, ($x_{Cr} = 0.02$)				*Kosmochlor*, NaCrSi$_2$O$_6$		
1.928[15]	15740[16]	1.996	0.94 / 0.95	712	1.998[15] / 2.000[17]	15570[18] / 16000[19]
(7) *Spodumene*, LiAlSi$_2$O$_6$, ($x_{Cr} = 0.004$)				LiCrSi$_2$O$_6$		
1.919[15]	16100[20]	1.988	0.98	817	1.992[21]	15955[18]

N o t e. [1]Finger & Hazen (1978), [2]Finger & Hazen (1980), [3]McClure (1963), [4]Wood et al. (1968), [5]O'Neill & Dollase (1994), [6]Reinen (1969), [7]Cervelle et al. (1984), [8]Cruciani (2009), [9]Geiger (2004), [10]Geiger et al. (2000), [11]Novak & Gibbs (1971), [12]Taran et al. (2004), [13]Langer et al. (2004), [14]Wildner & Andrut (2002), [15]Clark et al. (1969), [16]Khomenko & Platonov (1987), [17]Origlieri et al. (2003), [18]Taran et al. (2010), [19]White et al. (1971), [20]Platonov et al. (1984), [21]Ohashi & Sato (2003).

50

ISSN 0204-3548. Mineral. Journ. (Ukraine). 2011. 33, No 4

$(n_{av} = 3.5)$ in jadeite and 2Al + Li + Si (O1), 1Al + Li + Si (O2), Li + 2Si (O3) $(n_{av} = 3.2)$ in spodumene. In average, only 1Al is the nearest neighbor of O atoms in the pyroxene structure. Remember that the relaxation of a crystal structure is mostly dependent on the shift of non-substituted structural unit from its regular position [22, 23]; in all the cases under consideration these are O atoms. The mentioned crystal chemical features are needed in further refinement and discussion.

1. *Cervelle B., Coutures J.-P., Malezieux J.-M., Priou B.* Crystallochimie des chromites : etude sur des produits de synthese du systeme Mg(Al, Cr)$_2$O$_4$ // Bull. Miner. — 1984. — **107**. — P. 627—634.

2. *Clark J.R., Appelman D.E., Papike J.J.* Crystal chemical characterization of clinopyroxenes based on eight new structure refinements // Miner. Soc. Amer. Spec. Pap. — 1969. — No 2. — P. 31—50.

3. *Cruciani G., Ardit M., Dondi M. et al.* Structure relaxation around Cr^{3+} in YAlO$_3$—YCrO$_3$ perovskites from electron absorption spectra // J. Phys. Chem. — 2009. — **113**. — P. 13772—13778.

4. *Finger L.W., Hazen R.M.* Crystal structure and compression of ruby to 46 kbars // J. Appl. Phys. — 1978. — **49**. — P. 5823—5826.

5. *Finger L.W., Hazen R.M.* Crystal structure and isothermal compression of Fe$_2$O$_3$, Cr$_2$O$_3$, and V$_2$O$_3$ to 50 kbars // Ibid. — 1980. — **51**. — P. 5362—5367.

6. *Geiger C.A.* Spectroscopic investigation related to the structural, crystal-chemical and lattice-dynamic properties (Fe^{2+}, Mn^{2+}, Mg, Ca)$_3$Al$_2$Si$_3$O$_{12}$ garnets. A review and analysis // EMU Notes in Mineralogy. — 2004. — **6**. — P. 589—645.

7. *Geiger C.A., Stahl A., Rossman G.R.* Single-crystal IR- and UV/VIS-spectroscopic measurements on transition-metal-bearing pyrope : the incorporation of hydroxide in garnets // Eur. J. Mineral. — 2000. — **12**. — P. 259—271.

8. *Khomenko V.M., Platonov A.N.* The rock-forming pyroxenes : optical spectra, the colour and pleochroism. — Kiev : Nauk. dumka, 1987. — 214 p. (in Russian).

9. *Langer K.* A note on mean distances, R[MO$_6$], in substituted polyhedra [(M$_{1-x}$M$_x$)O$_6$] in the crystal structures of oxygen-based solid solutions : local versus crystal averaging methods // Z. Kristallogr. — 2001. — **216**. — P. 87—91.

10. *Langer K., Platonov A.N., Matsyuk S.S.* Local mean chromium-oxygen distances in Cr^{3+}-centered octahedra in natural grossular-uvarovite garnet solid solutions from electronic absorption spectra // Ibid. — 2004. — **219**. — P. 272—277.

11. *McClure D.S.* Comparison of the crystal fields and optical spectra of Cr$_2$O$_3$ and ruby // J. Chem. Phys. — 1963. — **38**. — P. 2289—2294.

12. *Novak G.A., Gibbs G.V.* The crystal chemistry of the silicate garnets // Amer. Miner. — 1971. — **56**. — P. 791—825.

13. *O'Neill H.St.C., Dollase W.A.* Crystal structures and cation distribution in simple spinels from powder XRD structure refinements : MgCr$_2$O$_4$, ZnCr$_2$O$_4$, Fe$_3$O$_4$ and the temperature dependence of the cation distribution in ZnAl$_2$O$_4$ // Phys. and Chem. Minerals. — 1994. — **20**. — P. 541—555.

14. *Ohashi H., Sato A.* Studies on P21/c LiMSi$_2$O$_6$ pyroxenes // X-ray study of Si—O bonding / Ed. H. Ohashi. — Tokyo : Maruzen Publ. Serv. Center, 2003. — P. 229—243.

15. *Origlieri M.J., Downs R.T., Thompson R.M. et al.* High-pressure crystal structure of kosmochlor, NaCrSi$_2$O$_6$, and systematics of anisotropic compression in pyroxenes // Amer. Miner. — 2003. — **88**. — P. 1025—1032.

16. *Platonov A.N., Taran M.N., Balitsky V.S.* The nature of colour of gemstones. — Moscow : Nedra, 1984. — 196 p. (in Russian).

17. *Reinen D.* Ligand-field spectroscopy and chemical bonding in Cr^{3+}-containing oxide solids // Struct. and Bond. — 1969. — **6**. — P. 30—51.

18. *Shannon R.D.* Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides // Acta Crystallogr. A. — 1976. — **32**. — P. 751—767.

19. *Taran M.N., Langer K., Abs-Wurmbach I. et al.* Local relaxation around [6]Cr^{3+} in synthetic pyrope-knorringite garnets, [8]Mg$_3$[6](Al$_{1-x}$Cr^{3+}$_x$)$_2$[4]Si$_3$O$_{12}$, from electronic absorption spectra // Phys. and Chem. Minerals. — 2004. — **31**. — P. 650—657.

20. *Taran M.M., Ohashi H., Langer K., Vishnevsky A.A.* High-pressure electronic absorption spectroscopy of natural and synthetic Cr^{3+}-bearing clinopyroxenes // Mineral. Journ. (Ukraine). — 2010. — **32**, No 1. — P. 14—26 (in Ukrainian).

21. *Urusov V.S.* Energetic Crystal Chemistry. — Moscow : Nauka, 1975. — 333 p. (in Russian).

22. *Urusov V.S.* A geometric model of deviations from Vegard's rule // J. Solid State Chem. — 1992. — **98**. — P. 223—236.

23. *Urusov V.S., Tauson V.L., Akimov V.V.* Geochemistry of solids. — Moscow : GEOS, 1997. — 500 p. (in Russian).

24. *White W.B., McCarthy G.L., Scheetz B.E.* Optical spectra of chromium, nickel and cobalt-containing pyroxenes // Amer. Miner. — 1971. — **5**. — P. 72—89.

25. *Wildner M., Andrut M.* The crystal chemistry of birefringent natural uvarovites. : Pt. III. Application of the superposition model of crystal field with a characterization of the synthetic cubic uvarovite // Phys. and Chem. Minerals. — 2002. — **29**. — P. 595—608.

26. *Wood D.L., Imbusch G.F., Macfarlane R.M. et al.* Optical spectrum of Cr^{3+} ions in spinels // J. Chem. Phys. — 1968. — **48**. — P. 5255—5263.

А.Н. Платонов, В.С. Урусов, К .Лангер

ЗАМЕТКА О КОРРЕЛЯЦИИ
МЕЖДУ ПАРАМЕТРОМ РЕЛАКСАЦИИ
И КОВАЛЕНТНОСТЬЮ СВЯЗЕЙ Cr^{3+}—О
В СТРУКТУРАХ НЕКОТОРЫХ МИНЕРАЛОВ

Приведены расчеты локальных межатомных расстояний $R^{loc}_{<Cr-O>}$ и локального коэффициента решеточной релаксации ε для минералов изоморфных рядов корунд — эсколаит, шпинель — магнезиохромит, $YAlO_3$ — $YCrO_3$ (структура перовскита), пироп — кнорринигит, гроссуляр — уваровит, жадеит — космохлор, сподумен — $LiAlSi_2O_6$. Впервые установлена корреляция между коэффициентом релаксации ε и параметром Рака́ B_{35}, отражающим степень ковалентности связей Cr^{3+}—О. Выявленную зависимость можно объяснить в первом приближении эффектом взаимного влияния различных связей катион—лиганды в кристаллической структуре, содержащей примесные ионы.

О.М. Платонов, В.С. Урусов, К. Лангер

ЗАМІТКА ПРО КОРЕЛЯЦІЮ
МІЖ ПАРАМЕТРОМ РЕЛАКСАЦІЇ
Й КОВАЛЕНТНІСТЮ ЗВ'ЯЗКІВ Cr^{3+}—О
У СТРУКТУРАХ ДЕЯКИХ МІНЕРАЛІВ

Наведено розрахунки локальних міжатомних відстаней $R^{loc}_{<Cr-O>}$ і локального коефіцієнта граткової релаксації ε для мінералів ізоморфних рядів корунд — есколаїт, шпінель — магнезіохроміт, $YAlO_3$ — $YCrO_3$ (структура перовскіту), піроп — кнорингіт, гросуляр — уваровіт, жадеїт — космохлор, сподумен — $LiAlSi_2O_6$. Вперше встановлено кореляцію між коефіцієнтом релаксації ε і параметром Рака́ B_{35}, що відбиває ступінь ковалентності зв'язків Cr^{3+}—О. Виявлену залежність можна пояснити в першому наближенні ефектом взаємного впливу різних зв'язків катіон—ліганди у кристалічній структурі, що містить домішкові іони.

52

ISSN 0204-3548. Mineral. Journ. (Ukraine). 2011. 33, No 4