COMPOSITION-DEPENDENCE OF LATTICE CONSTANT IN $Li_{0.5}Fe_{2.5-t}Al_tO_4$ SYSTEM

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Lattice constants have been measured for several lithium ferrites-aluminates of the series described by the formula $Li_{0.5}Fe_{2.5-t}Al_tO_4$. It was found that Vegard's rule is adhered to in this system. The possibility of anion-anion contact appearing in these compounds also considered.

1. Introduction

Lithium ferrites-aluminates of the formula $Li_{0.5}Fe_{2.5-t}Al_tO_4$ have been studied by many authors, *e.g.*, Refs [1–6]. Their results concerning changes in lattice constants with changes in chemical composition are compiled in Fig. 1. It is seen here that in the region of low aluminum content the lattice constants given by Blasse and Schulkes [1] distinctly exhibit a positive shift relative to the straight line expressing Vegard's rule. The data published by Strickler and Roy [2] appear to corroborate this dependence, although the large scatter of experimental points does not permit a definite conclusion to be reached. In contrast with these results, in his paper presenting the results of researches concerning lithium ferrites-aluminates, Zhilyakov [3] finds that the lattice constants in this system are in conformity with Vegard's rule. Unfortunately, the author did not give the values of lattice constants measured, limiting himself only to the initial and end values for the series of samples he investigated ($t = 0$ and $t = 1.00$).

The run of the dependence of lattice constant on chemical composition of lithium ferrites-aluminates is quoted as an argument for the occurrence of an anion-anion contact in these compounds [1]. It was reasonable, therefore, to examine this dependence once again, especially in the region of low aluminium content, for which the found deviations from Vegard's rule are the largest.

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2. Experimental

The method of sintering Fe_2O_3, Al_2O_3 and Li_2CO_3 powders was used in this work to obtain five samples of compositions with $t = 0$, 0.4, 0.8, 1.6 and 2.5.

An X-ray analysis of these samples showed that pure ferrite phases without impurities were obtained, except for a very small Al_2O_3 peak for the $t = 2.5$ sample. Chemical analysis did not reveal any essential deviations from the pre-assumed compositions. In particular, no loss of lithium was found to occur during the sintering.

Lattice constant measurements were performed with a diffractometer incorporating G–M counter with the use of K_α Co radiation passed through an iron filter. The obtained results are given in Table I. The error of measurement was estimated on the basis of the

TABLE I

t	Lattice constant [Å]
0	8.330
0.4	8.268
0.8	8.201 ± 0.003
1.6	8.060
2.5	7.911

maximum accuracy of Bragg angle measurements. The values of lattice constants determined from the various reflection maxima for the examined samples lie within the quoted error limits.

Supplementary measurements made for a check with an aluminum standard revealed excellent agreement with the value of 4.0496 Å quoted in the literature [7]. Results for the $t = 0$ sample are also in excellent agreement with values given by other authors.

3. Discussion of results

As is seen in Fig. 1, the results obtained in this experiment lie along a straight line, thus corroborating the results of Zhilyakov. It seems, therefore, that the dependence of lattice constant on composition in lithium ferrites-aluminates cannot be taken as an indication of the existence of an anion-anion contact in these compounds.

This kind of contact may occur in a spinel-type structure between the oxygen ions in the octahedrons. In most spinel compounds the oxygen parameter u describing the positions of the oxygen ions in the elementary cell is greater than 0.375. The oxygen octahedrons then have edges of two different lengths,

$$d_1 = a\sqrt{2}(1-2u) \tag{1}$$

$$d_2 = a\sqrt{\tfrac{11}{16} - 3u + 4u^2} \tag{2}$$

where a is the lattice constant. The anion-anion contact will appear in the case when the shorter of these edges, d_1, will be smaller than double the oxygen ion radius. If we accept the oxygen ion radius after Goldschmidt, this value is 2.64 Å. By substituting this value

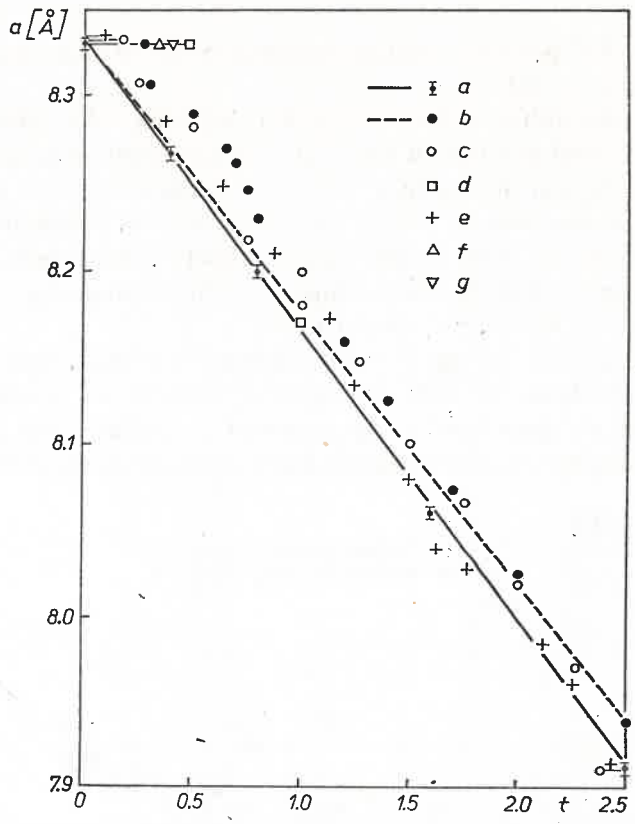

Fig. 1. Dependence of lattice constant on composition in $Li_{0.5}Fe_{2.5-t}Al_tO_4$ compounds; *a* — this work, *b* — [1], *c* — [2], *d* — [3], *e* — [4], *f* — [5], *g* — [6]

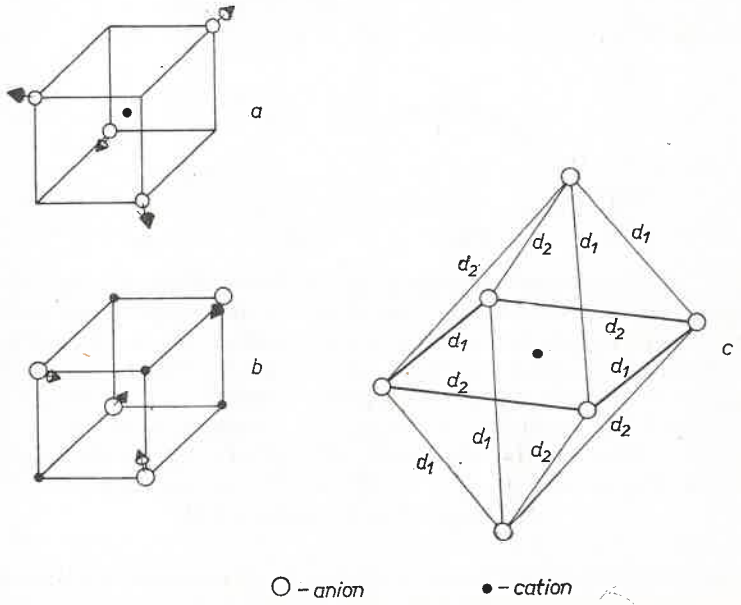

Fig. 2. Tetrahedral (a), (b) and octahedral (c) systems of oxygen ions in spinel structure. Arrows in figures (a) and (b) indicate shift of oxygen ions from "ideal" positions (oxygen parameter $u = 0.375$)

in the place of d_1 it is possible to plot an $a(u)$ curve, being the boundary of the occurrence of the anion-anion contact.

Figure 3 presents such a curve together with the experimental data for a certain number of compounds of spinel structure. It shows that for a majority of compounds the experimental points lie beyond the region in which anion-anion contact is possible.[1].

It can also be seen from the plotted accessible data that almost all compounds containing aluminum lie within the contact region. This may mean there is deformation of anions due to their contact in these compounds. Notwithstanding, our $Li_{0.5}Fe_{2.5}O_4$ ferrite lies fairly well beyond the contact region.

For a transition into the region where anion-anion contact exists to be feasible in lithium ferrites-aluminates of high iron content, the oxygen parameter would have to increase quickly to about 0.385 at the parameter t increasing from zero. This can be concluded when taking any of the present lattice constant *versus* composition relations

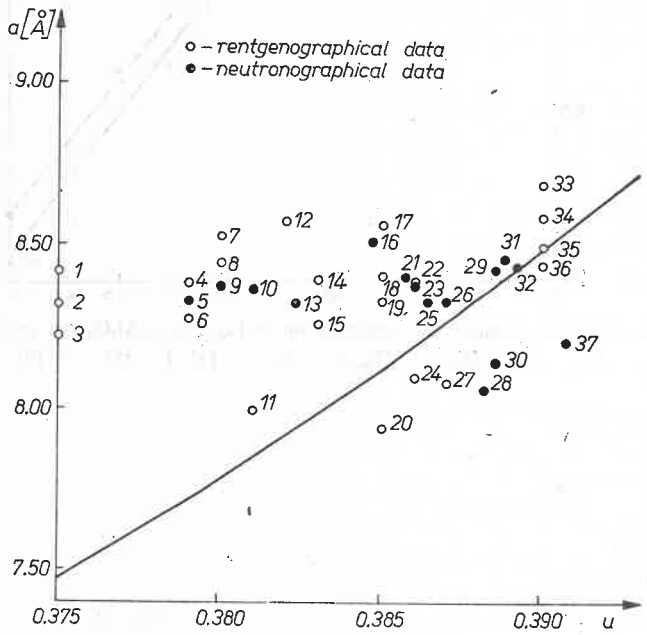

Fig. 3. Dependence of lattice constant a on oxygen parameter u for 37 compounds possessing spinel structure. Full line is boundary below which anion-anion contact exists at an assumed oxygen ion radius of 1.32 Å *1*–$Ge\,Fe_2O_4$ [21], *2*–$GeCo_2O_4$ [22], *3*–$GeNi_2O_4$ [22], *4*–Fe_3O_4 [23], *5*–$Li_{0.5}\,Fe_{2.5}O_4$ [8], *6*–$MgGa_2O_4$ [24], *7*–$Sb_{2/3}Co_{7/3}O_4$ [25], *8*–$TiZn_2O_4$ [22], *9*–$Ga_{1.1}Fe_{1.9}O_4$ [9], *10*–$MgFe_2O_4$ [10], *11*–$NiAL_2O_4$ [22], *12*–VMn_2O_4 [26], *13*–$NiFe_2O_4$ [11], *14*–$NiMn_2O_4$ [27], *15*–$NiGa_2O_4$ [28], *16*–$MnFe_2O_4$ [17], *17*–CdV_2O_4 [29], *18*–MgV_2O_4 [30], *19*–$MgCr_2O_4$ [29], *20*–$Li_{0.5}Al_{2.5}O_4$ [29], *21*–$ZnFe_2O_4$ [12], *22*–VMg_2O_4 [31], *23*–$FeCr_2O_4$ [13], *24*–$CoAl_2O_4$ [20], *25*–$ZnCr_2O_4$ [12], *26*–$CoCr_2O_4$ [14], *27*–$MgAl_2O_4$ [32], *28*–Co_3O_4 [15], *29*–$MnGa_2O_4$ [16], *30*–$FeAl_2O_4$ [20], *31*–$MnFeCrO_4$ [18], *32*–$MnCr_2O_4$ [19], *33*–$CdFe_2O_4$ [33], *34*–$Sb_{2/3}Zn_{7/3}O_4$ [25], *35*–$TiFe_2O_4$ [34], *36*–$TiMg_2O_4$ [22], *37*–$MnAl_2O_4$ [20]

[1] It must be remembered that the error in u found from rentgenographical data is of the order of 0.003. Neutronographical data are several times more accurate.

into account. Our unpublished estimative calculations indicate that such a situation may indeed occur in the compound with $t = 0.8$. Hence, any possible anion-anion contact in lithium ferrites-aluminates may be achieved in the low aluminum content region only when the value of the oxygen parameter is appropriate. Incidentally, these ferrites possess additional ordering in the octahedral sub-lattice and a single oxygen parameter can therefore only approximately describe the positions of the oxygen ions. It seems, however, that the additional deformation of the octahedrons due to this ordering is rather insignificant for the matter on hand.

4. *Conclusions*

These measurements of the lattice constants of $Li_{0.5}Fe_{2.5-t}Al_tO_4$ compounds testify that Vegard's rule is adhered to. No conclusions regarding the existence of anion-anion contact in these compounds can be arrived at from the shape of the lattice constant *versus* composition curve. Such contact may occur only when oxygen parameter takes on appropriate values.

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REFERENCES

[1] J. A. Schulkes, G. Blasse, *J. Phys. Chem. Solids*, **24**, 1651 (1963).
[2] D. W. Strickler, Rustum Roy, *J. Amer. Ceram. Soc.*, **44**, 225 (1961).
[3] S. M. Zhilyakov, *Izv. VUZ Fiz.*, **11**, 21 (1967).
[4] A. Vassiliev, *These l'Université de Paris*, 1962.
[5] E. Kato, *Bull. Chem. Soc. Japan*, **31**, 113 (1958).
[6] E. W. Gorter, *Philips Res. Rep.*, **9**, Table XII (1954).
[7] M. S. Straumanis, *J. Appl. Phys.*, **30**, 1965 (1959).
[8] E. Prince, *J. Phys.*, **25**, 503 (1964).
[9] A. Oleś, *C. R. Acad. Sci.* (France), **260**, 6075 (1965).
[10] L. M. Corliss, J. M. Hastings, F. G. Brockman, *Phys. Rev.*, **90**, 1013 (1953).
[11] S. I. Youssef *et al.*, *J. Phys. Chem. Solids*, **30**, 1941 (1968).
[12] A. Oleś, *Phys. Status Solidi*, **3**, 569 (1970).
[13] G. Shirane, D. E. Cox, J. Pickart, *J. Appl. Phys.*, **35**, 954 (1964).
[14] N. Menyuk, K. Dwight, A. Wold, *J. Phys.*, **25**, 528 (1964).
[15] W. L. Roth, *J. Phys. Chem. Solids*, **25**, 1 (1964).
[16] B. Boucher, A. Oleś, *J. Phys.*, **27**, 519 (1966).
[17] J. M. Hastings, L. M. Corliss, *Phys. Rev.*, **104**, 328 (1956).
[18] S. J. Pickart, R. Nathans, *Phys. Rev.*, **116**, 317 (1959).
[19] J. M. Hastings, L. M. Corliss, *Phys. Rev.*, **126**, 556 (1962).
[20] W. L. Roth, *J. Phys.*, **25**, 507 (1964).
[21] A. Durif-Varambon *et al.*, *Ann. Chim.*, **1**, 525 (1956).

[22] F. C. Romeijn, *Philips Res. Rep.*, **8**, 304, 321 (1953).
[23] S. C. Abrahams, B. A. Calhoun, *Acta Cryst.*, **6**, 57 (1953).
[24] M. Huber, *C. R. Acad. Sci.* (France), **244**, 5583 (1963).
[25] J. Dulac, A. Durif, *C. R. Acad. Sci.* (France), **251**, 747 (1960).
[26] I. C. Bernier, *C. R. Acad. Sci.* (France), **256** 5583 (1963).
[27] P. K. Baltzer, J. G. White, *J. Appl. Phys.*, **29**, 445 (1958).
[28] S. Greenwald *et al.*, *J. Chem. Phys.*, **22**, 1597 (1954).
[29] E. J. W. Verwey, E. L. Heilman, *J. Chem. Phys.*, **15**, 174 (1947).
[30] R. Plumier, A. Fardieu, *C. R. Acad. Sci.* (France), **257**, 3858 (1963).
[31] W. Rüdorff, B. Reuter, *Z. Anorg. Chem.*, **253**, 222 (1947).
[32] E. G. Bacon, *Acta Cryst.*, **5**, 684 (1952).
[33] E. Jarocki, W. Kubeł, J. Wenda, *Phys. Status Solidi*, **34**, K17 (1969).
[34] T. W. F. Barth, E. Posnjak, *Z. Kristallogr.*, **82**, 325 (1932).