THE DEPENDENCE OF THE WAVELENGTH OF AlKα RADIATION FROM ALUMINO-SILICATES ON THE Al-O DISTANCE

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ABSTRACT

AlKα emission wavelengths from a range of substances are compared with that from aluminum metal. The wavelength shift, $\Delta\lambda$, and the angular shift $\Delta(2\theta)$ using a pentaerythritol analyzing crystal, are shown to be related primarily to the average Al-O distances rather than to coordination number as previously emphasized. The importance of this result in relation to the estimation of Al in 4- and 6-fold coordination is discussed.

INTRODUCTION

Over the past few years, many studies have been made of the wavelengths of characteristic X-radiation excited from certain cations in oxide materials in relation to their coordination number. The method has been applied particularly to the coordination of Al^{3+} ions in aluminosilicates by comparing the emitted wavelength with that from a particular substance, usually metallic aluminum. Since the wavelength change $\Delta\lambda$ is small, the results are often expressed by $\Delta(2\theta) = 2\theta(Al\ metal) - 2\theta(Al, sample)$, where 2θ is the diffraction angle for the measuring crystal.

The initial studies were concerned with showing that the $\Delta(2\theta)$ values fall mainly into two groups corresponding to the coordination numbers 4 and 6. When more than one coordination state occurs, then $\Delta(2\theta)$ is related to the weighted average of the two coordinations (White, McKinstry, and Bates, 1959; Brindley and McKinstry, 1961; Day, 1963). Subsequently measurements of $\Delta(2\theta)$ have been used to estimate the proportions of Al^{IV} and Al^{VI} in mixed systems, such as gels and glasses, on the basis of a linear variation of $\Delta(2\theta)$ between chosen end members. Some of the end members so chosen are kaolinite and $AlPO_4$ (DeKimpe *et al.*, 1961; Gastuche *et al.*, 1963), gibbsite and $AlPO_4$ (Leonard *et al.*, 1967), αAl_2O_3 and sanidine (White and Gibbs, 1969), and kaolinite and feldspar (Steinberg, 1970). The hazards of using this technique for estimating Al^{IV}/Al^{VI} ratios are discussed later.

The variations of $\Delta(2\theta)$ or $\Delta\lambda$ within a given coordination group have been attributed generally to variations of interatomic distances (Laputina and Narbutt, 1967; Shuvaev *et al.*, 1967; White and Gibbs, 1967; 1969). When the present work was completed, a paper by Läuger (1971) appeared in which the variations are discussed on the basis of the electronegativity of the cations in the second coordination shell.

In all these studies, $\Delta(2\theta)$ or $\Delta\lambda$ is considered to be primarily a function of coordination number.

It now appears, as will be shown in the present note, that $\Delta(2\theta)$ can be correlated with interatomic distances without reference to coordination number so that the primary variable seems to be the interatomic distance, a result which appears to be consistent with an approximate theoretical treatment by Shuvaev (1964).

Experimental

The $\Delta(2\theta)$ of the AlKα peak for several minerals was measured with respect to that for Al metal powder mixed with silica flour to give approximately the same Al concentration in the standard as in the samples (15–30 wt. percent). The samples were prepared as the front face of a methyl cellulose compact as often used for X-ray fluorescence analysis (Ingamells and Suhr, 1963). The spectra were recorded on a Siemens SRSI X-ray spectrometer with a chromium target at 40–45 kV and 12–16 mA. The analyzing crystal was pentaerythritol ($2d = 8.75$ Å) and a gas-flow counter was used. A vacuum of 0.1–0.2 torr was maintained to reduce absorption of the emitted AlKα radiation. The scanning speed was either 0.125° or 0.250° (2θ)/min. and the chart speed was chosen such that 1° (2θ) was equivalent to 8 cm. chart paper. Under these conditions the peak width at half maximum intensity was about 0.8° (2θ) and the peak position at half maximum intensity could be measured to ±0.003° (2θ). Readings of the Al metal standard and of the minerals studied were alternated so that any drift in the recording process could be taken into account.

Results and Discussion

The present results, Table 1 and Figure 1, show that a single curve can be drawn through almost all the data, certainly within the limits of experimental error, when $\Delta(2\theta)$ is represented as a function of the mean Al-O distance. For this purpose, accurately determined distances are necessary and the sources of the data used are indicated in the footnote to the table. To verify that this result is not peculiar to the present measurements, the $\Delta\lambda_m$ values given by Läuger have been converted to $\Delta(2\theta)$ values and plotted with triangles in Figure 1. That the two curves are not coincident is not surprising in view of the small shifts to be measured. The significant result is that Läuger's data show the same trend as the present results, with most of the $\Delta(2\theta)$ values falling on a single curve.

In both sets of data, the αAl_2O_3 results fall below the mean curves and this may well be due to the next nearest neighbor effect as explained by Läuger since the Al-Al distance is 2.65 Å (Newnham and DeHaan, 1962).

The $\Delta(2\theta)$ value for anhydrous $AlPO_4$ lies on the mean curve for the present results but is very greatly displaced from the mean curve through Läuger's data. Since $AlPO_4 \cdot 2H_2O$ gives a considerably larger $\Delta(2\theta)$ value, within the range of 6-fold coordinations (see Table 1), a possible explanation is that the $AlPO_4$ used by Läuger may have been partly hydrated.

TABLE 1. $\Delta(2\theta) = 2\theta$ (Al METAL) - 2θ (SUBSTANCE), MEAN Al-O DISTANCES,
$\overset{\circ}{A}$, AND Al COORDINATION NUMBERS FOR MINERALS STUDIED

	Substance	Composition (Ideal)	$\Delta(2\theta)^{\circ}$	Al-O Distance $\overset{\circ}{A}$	Coordination Number
1.	Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	0.131	1.94^a	6
2.	Kaolinite	$Al_2Si_2O_5(OH)_4$	0.124	1.93_0^b 1.938^c	6
3.	Aluminum phosphate hydrate	$AlPO_4 \cdot 2H_2O$	0.122	-	-
4.	Dickite	$Al_2Si_2O_5(OH)_4$	0.120	1.90_2^d	6
5.	Kyanite	Al_2SiO_5	0.116	1.912^e	6
6.	Gibbsite	$Al(OH)_3$	0.112	1.90^f	6
7.	Corundum	αAl_2O_3	0.111	1.917^g	6
8.	Andalusite	Al_2SiO_5	0.110	1.890^h	5,6
9.	Sillimanite	Al_2SiO_5	0.104	1.855^i	4,6
10.	Pyrophyllite dehydroxylate	$Al_2Si_4O_{11}$	0.091	-	-
11.	Metakaolin	$Al_2Si_2O_7$	0.081	-	4
12.	Microcline (max)	$KAlSi_3O_8$	0.081	1.741^j	4
13.	Albite* (low)	$NaAlSi_3O_8$	0.077	1.746^k	4
14.	Analcime	$NaAlSi_2O_6 \cdot H_2O$	0.076	-	4
15.	Aluminum phosphate anhydrous	$AlPO_4$	0.073	1.70^l	4

*X-ray examination suggests small proportion of high albite present.

[a] Wardle and Brindley (197-)
[b] Zvyagin (1960)
[c] Drits and Kashaev (1960)
[d] Newnham (1961)
[e] Burnham (1963b)
[f] Megaw (1935)

[g] Newnham and De Haan (1962)
[h] Burnham and Buerger (1961)
[i] Burnham (1963a)
[j] Brown and Bailey (1964)
[k] Ribbe et al. (1969)
[l] Mooney (1956)

Läuger's value for spinel, $MgAl_2O_4$, is plotted with Al-O = 1.927 Å, a value derived from the data of Bacon (1952) on the assumption that *all* Al is in the octahedral cation sites, but if the spinel is partly inverse with some Al in tetrahedral cation sites, then a smaller mean Al-O distance is required; this would move the spinel point nearer the mean curve.

The result that $\Delta(2\theta)$ appears to be a function of the Al-O distance is generally consistent with a theoretical discussion given by Shuvaev (1964) who points out that in compounds of elements in Period 2 if all the valence shell electrons are bonding, that is, no lone pairs of electrons, the shift of the $K\alpha_{1,2}$ lines relative to their position in the metal or pure element must be approximately proportional to the change in electron
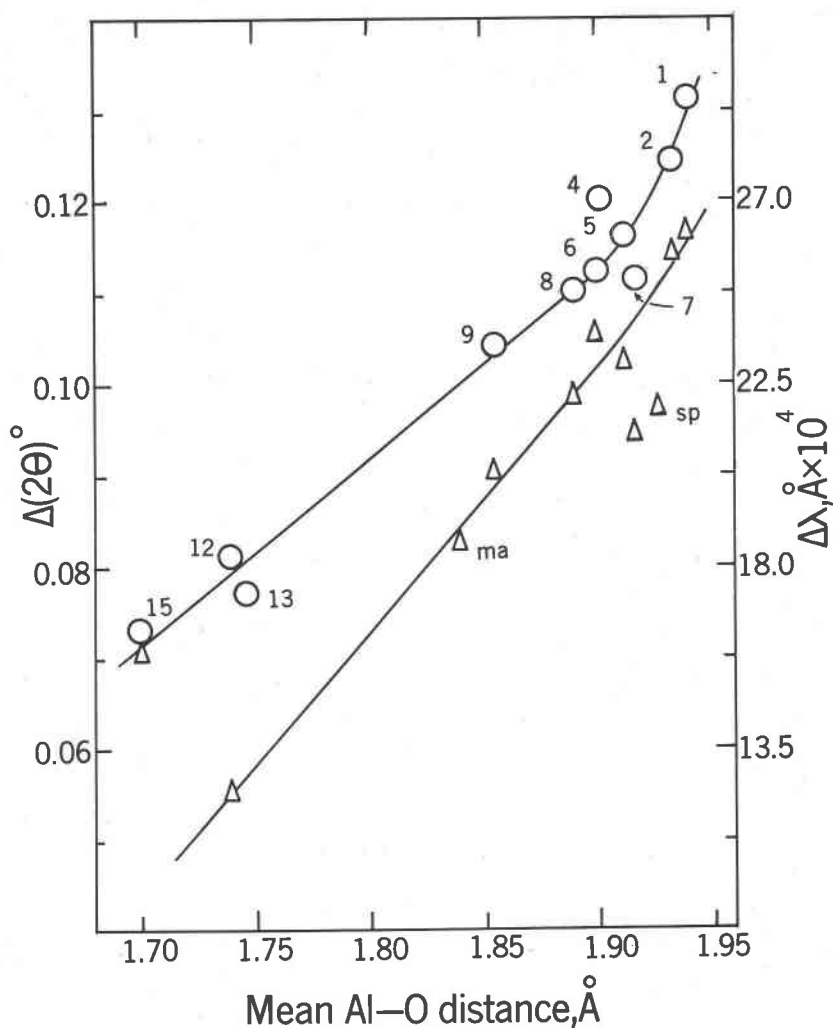
Fig. 1. $\Delta(2\theta)° = 2\theta°$(Al metal) $- 2\theta°$(Al, substance), and $\Delta\lambda$ plotted against Al-O distances, Å. Upper curve and circles, present data, lower curve and triangles, from data of Läuger (1971). The numbers correspond to the numbers in Table 1. In addition in Läuger's data sp = spinel, Al-O = 1.927 (Bacon, 1952), and ma = margarite, Al-O = 1.841 (Takéuchi, 1966).

density of the valence electrons. This electron density can be calculated over the whole volume of the ion which in turn introduces the ionic radius and hence the interatomic distance.

It is proper to sound a note of caution regarding the use of $\Delta(2\theta)$

values to estimate the proportions of Al ions in 6-fold and 4-fold coordination in mixed systems by interpolating on a straight line joining particular end members, often called "standards." This procedure is reasonable only if the Al-O distances in the calibrating substances and in the particular system studied are closely similar. An example of the kind of error which could arise in unfavorable circumstances would be to use pyrophyllite and $AlPO_4$ as calibrating substances to estimate the Al coordinations in gibbsite; the data in Table 1 would lead to the conclusion that gibbsite has 33 percent of the Al ions in 4-fold coordination.

The question whether the Al-O distances in feldspars vary with the degree of order may possibly be resolved by measurements of $\Delta(2\theta)$ if the experimental accuracy can be improved. The possibilities of this approach are under consideration.

Conclusions

It is concluded that $\Delta(2\theta)$ for $AlK\alpha$ emission from oxide systems measured with respect to emission from Al metal is related primarily to the mean Al-O distance and only indirectly to coordination number. The result is generally consistent with the theoretical discussion of Shuvaev (1964). Care is needed in using $\Delta(2\theta)$ values to estimate the proportions of Al ions in 4-fold and 6-fold coordination in mixed systems.

References

Bacon, G. E. (1952) A neutron-diffraction study of magnesium aluminium oxide. *Acta Crystallogr.* **5,** 684–686.

Brindley, G. W., and H. A. McKinstry (1961) The kaolinite-mullite reaction series: IV, The coordination of aluminum. *J. Amer. Cer. Soc.* **44,** 506–507.

Brown, B. E., and S. W. Bailey (1964) The structure of maximum microcline. *Acta Crystallogr.* **17,** 1391–1400.

Burnham, C. W. (1963a) Refinement of the crystal structure of sillimanite. *Z. Kristallogr.* **118,** 127–148.

———— (1963b) Refinement of the crystal structure of kyanite. *Z. Kristallogr.* **118,** 337–360.

————, and M. J. Buerger (1961) Refinement of the crystal structure of andalusite. *Z. Kristallogr.* **115,** 269–290.

Day, D. E. (1963) Determining the coordination number of aluminium ions by X-ray emission spectroscopy. *Nature* **200,** 649–651.

DeKimpe, C., M. C. Gastuche, and G. W. Brindley (1961) Ionic coordination in alumino-silicic gels in relation to clay mineral formation. *Amer. Mineral.* **46,** 1370–1381.

Drits, V. A., and A. A. Kashaev (1960) An X-ray study of a single crystal of kaolinite. *Sov. Phys. Crystallogr.* **5,** 207–210.

Gastuche, M. C., F. Toussaint, J. J. Fripiat, R. Touilleaux, and M. van Meersche

(1963) Study of intermediate stages in the kaolin-metakaolin transformation. *Clay Min. Bull.* **5**, 227–236.

INGAMELLS, C. O., AND N. H. SUHR (1963) Chemical and spectrochemical analysis of standard silicate samples. *Geochim. Cosmochim. Acta* **27**, 897–910.

LAPUTINA, I. P., AND K. I. NARBUTT (1967) X-ray emission spectra of aluminum in some minerals. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **31**, (6) 912–918. [English transl., 926–932, *Chem. Abstr.* **68**:8262ot].

LÄUGER, K. (1971) Über den Einfluss der Bindungsart und der Kristallstruktur auf das $K\alpha_{1,2}$-Röntgenspektrum von Aluminium. *J. Phys. Chem. Solids* **32**, 609–622.

LÉONARD, A. J., F. VAN CAUWELAERT, AND J. J. FRIPIAT (1967) Structure and properties of amorphous silicoaluminas. III. *J. Phys. Chem.* **71**, 695–708.

MEGAW, H. D. (1934) The crystal structure of hydrargillite $Al(OH)_3$. *Z. Kristallogr.* **87**, 185–204.

MOONEY, R. C. L. (1956) The crystal structure of aluminum phosphate and gallium phosphate, low cristobalite type. *Acta Crystallogr.* **9**, 728–734.

NEWNHAM, R. E. (1961) A refinement of the dickite structure and some remarks on polymorphism in kaolin minerals. *Mineral. Mag.* **32**, 683–704.

——, AND Y. M. DE HAAN (1962) Refinement of the αAl_2O_3, Ti_2O_3, V_2O_3 and Cr_2O_3 structures. *Z. Kristallogr.* **117**, 235–237.

RIBBE, D. H., H. D. MEGAW, W. H. TAYLOR, R. J. TRAILL, AND R. B. FERGUSON (1969) Albite structures. *Acta Crystallog.* **25B**, 1503–1518.

SHUVAEV, A. T. (1964) Determination of the charge of ions in compounds of period 2 elements from X-ray emission spectra. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **28**, 758-764. [English transl. 667–673, *Chem Abstr.* **61**:12786h].

——, M. A. BLOKHIN AND E. A. IZRAILEVICH (1967) X-ray spectrographic determination of the valence of titanium and the coordination number of aluminum in titanobarium glass and ceramic. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **31**, 919–921. [English transl., 933–935; *Chem. Abstr.* **68**:82623w].

STEINBERG, M. (1970) Distinction de l'aluminium tétracoordonné et hexacoordonné par fluorescence X. Premiers résultats. *Bull. Gr. Franç. Argiles* **22**, 115–126.

TAKÉUCHI, Y. (1966) Structures of brittle micas. *Clays Clay Minerals* **13**, 1–25.

WHITE, E. W., H. A. MCKINSTRY, AND T. F. BATES (1959) Crystal chemical studies by X-ray fluorescence. *Proc. Conf. Ind. Appl. X-ray Analysis, 7th, Denver, 1958,* 239–245.

——, AND G. V. GIBBS (1967) Structural and chemical effects on the $SiK\beta$ X-ray line for silicates. *Amer. Mineral.*, **52**, 985–993.

——, AND ——— (1969) Structural and chemical effects on the $AlK\beta$ X-ray emission band among aluminum containing silicates and aluminum oxides. *Amer. Mineral.* **54**, 931–936.

ZVYAGIN, B. B. (1960) Electron-diffraction determination of the structure of kaolinite. *Kristallografiya* **5**, 40–50 (1960) [*Sov. Phys. Crystallogr.* **5**, 32–42.]

Note added in proof: A paper by A. J. Léonard, P. N. Semaille, and J. J. Fripiat, *Proc. Brit. Cer. Soc.* (1969) 103–116, inadvertently overlooked in the review, discusses the Alkα shift for amorphous silico-aluminas in relation to the average Al-O distances determined by radial X-ray analysis.