Al Coordination and Local Structure in Minerals: XAFS Determinations and Multiple–Scattering Calculations for K–Feldspars

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Abstract. – The Al K-edge spectra of three potassium feldspars $KAlSi_3O_8$: sanidine, microcline and orthoclase, all with four-fold–coordinated Al, have been measured by X-ray absorption near-edge structure spectroscopy and calculated according to the multiple-scattering formalism using clusters of different sizes and the X_α exchange-correlation potential. Although these structures are quite complex, and clusters as large as containing ca. 150 atoms are needed to calculate them, a significant agreement has been obtained between experimental spectra and calculated ones up to 60 eV above the threshold, both for energy positions and for relative intensities. Moreover, while the gross features of all spectra appear to be dominated mainly by the first coordination sphere around the absorber, effects due to higher shells are detected.

X-ray absorption near-edge structure (XANES) spectroscopy is a powerful tool to gain structural information [1] on condensed matter, *i.e.* coordination numbers, bond angles and distances. Moreover, this technique is orbital-momentum-selective and can probe the geometrical local arrangement around a selected element without the need of long-range order (LRO). However, when LRO is present, it has such consequences on the experimental spectrum as to be detectable and evaluated.

Very recently, high-resolution Al K-edge spectra of some aluminosilicate minerals have been reported [2]-[4], and we have published [5] a detailed experimental and theoretical comparison of the six-fold coordinated Al K-edge absorption spectra of some garnets where satisfactory matches were obtained using multiple-scattering (MS) calculations extending over 60 eV from the threshold. We present here new experimental and theoretical spectra at the Al K-edge for three four-fold coordinated Al compounds, and we attempt at the interpretation of their

characteristic features by means of an extended MS calculation, using clusters of increasing size around the excited Al atom. Aim of our entire project is to set up a number of new references for the interpretation of XANES spectra in even more complex cases, such as those where Al is in a mixed coordination, and to put forward an evaluation of the different geometrical order occurring around their Al sites.

The samples we measured are natural compounds, *i.e.* minerals. As representative for the four-fold Al case we have chosen the three $KAlSi_3O_8$ polymorphs having different degrees of order: a "disordered" sanidine from M. Somma, Italy; an "ordered" microcline ("amazonite") from U.S.A.; and an intermediate "orthoclase" from Norway. By "ordered" or "disordered" we mean the change in structural conditions by which the Bravais postulate that in an ideal ("ordered") crystalline solid a site repeats identically for its position, symmetry and chemical environments, up to infinity, is being perturbated in its regularity. Four types of disordering phenomena are normally described: 1) positional disorder, when the same atom occupies different mean positions in different unit cells; 2) rotational disorder, when the orientation of certain structural groups is not fixed but rotates around a common axis; 3) distortional disorder, when a structure oscillates between two or more alternative but equivalent orientations as a result of changes in the atom thermal motions; 4) substitutional disorder, when there is an interchange of different atoms over two or more sites, which are crystallographically distinct in the "ordered" phase, but equivalent (at least on average) in the "disordered" phase [6]. The case of $KAlSi_3O_8$ belongs to this fourth type.

The three $KAlSi_3O_8$ polymorphs belong to the sub-class of silicates known as framework or tecto-silicates [7]. They are characterized by having rings of four tetrahedra all interconnected via the apices so as to form a tridimensional framework; in the interstices of the framework the potassium atoms are located. The individual tetrahedra are centered either by Si or by Al, according to a distribution which is disordered in the ideal case of "high" sanidine and totally ordered in the opposite case of ideal "low" microcline. In the former, Si and Al are randomly distributed over two inequivalent tetrahedral sites, T1 and T2, which alternate within the four-membered ring, each tetrahedron thus having the theoretical occupancy $Al_{0.25}Si_{0.75}$. By contrast, in the latter, the Al atom occupies exclusively and entirely one tetrahedral site, T1(0), and Si occupies the remaining three sites, T1(m), T2(0) and T2(m). Intermediate conditions are common, and indeed this is the case of orthoclase, which contains domains of the ordered and disordered extreme phases.

The experimental data were collected at Stanford Synchrotron Radiation Laboratory (SSRL) at the SB03-3 beamline using the JUMBO monochromator equipped with YB_{66} crystals. Spectra acquisition was typically from 1540 to 1690 eV at 0.5 eV intervals, with 5 to 7 s counting times. The resolution of YB_{66} in this energy range is 0.46 eV [8].

All our XANES calculations are based on the one-electron full multiple-scattering (MS) theory [9]-[12] using the XANES CONTINUUM code [13] which has been widely and successfully used to interpret the X-ray absorption spectra in different systems [14]. Lately, we set up a systematic procedure [5], [15] which enabled us to compare results on most possible structural arrangements and chemical systems. Starting data for our calculations are the atomic positional parameters of materials with crystal structure determined by single-crystal X-ray diffraction.

Sanidine, $(K_{0.8}Na_{0.2})AlSi_3O_8$, is monoclinic $C2/m$ with unit cell parameters: $a_0 = 8.546$ Å, $b_0 = 13.037$ Å, $c_0 = 7.178$ Å and $\beta = 116.0°$, the unit cell containing 4 formula units. It has a "disordered" structure, thus two independent sets of AlO_4 tetrahedra; the mean bond lengths Al-O are 1.6451(11) Å for the T1 site, and 1.6403(10) Å for the T2 site [15]. The top curve in the left panel of fig. 1 is the experimental Al K-edge spectrum. It consists of five features which combine the superimposed contributions of the Al atoms present in the two tetrahedral sites. In order to calculate the theoretical spectrum, the bottom curve of the left panel of fig. 1,
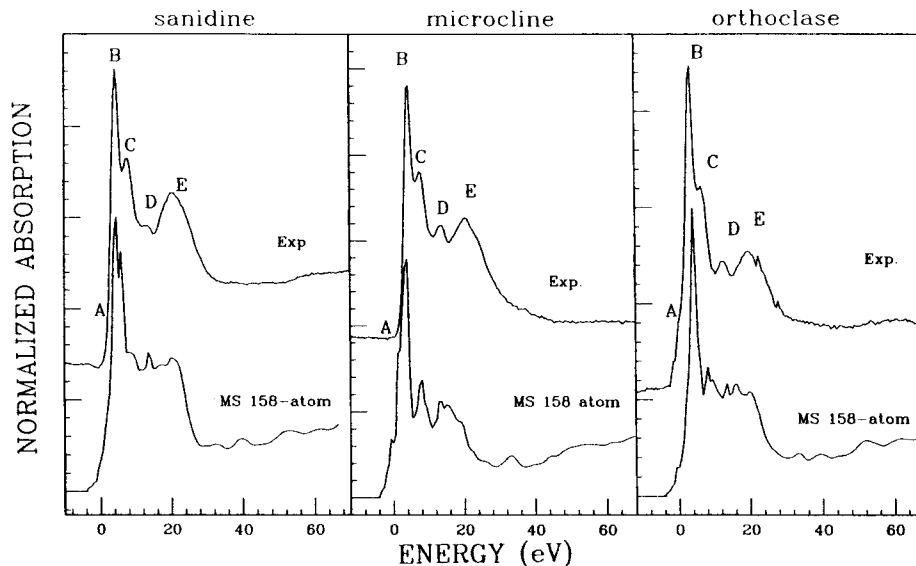
Fig. 1. – In the three panels, experimental (top curves) and MS-calculated (158-atom cluster, bottom curves) Al K-edge XANES spectra from left to right for sanidine, microcline and orthoclase, respectively.

we performed a calculation for the two independent sites using clusters of increasing size up to containing 158 atoms. Finally, we summed up the spectra of the calculated Al-T1 and Al-T2 clusters in the 1:1 proportion. For this large cluster the general characteristics are not well reproduced, in particular agreement appears poor in the region of the D and E features. The agreement in the energy positions (note A, B and C) is quite good; disagreement lies mostly in their relative intensities. Furthermore, the peaks in the experimental spectrum are at places sharper (*e.g.*, B) or elsewhere broader (D) than the calculated ones.

Microcline has a triclinic structure, and a unit-cell containing 4 formula units with parameters $a_0 = 8.573$ Å, $b_0 = 12.967$ Å, $c_0 = 7.223$ Å and $\alpha = 90.7°$, $\beta = 115.9°$, $\gamma = 87.60°$ [16]. The tetrahedral site T1(0), where Al is hosted, is much larger (average bond length 1.7376 (n.g.) Å) [16] than those hosting Si, and is also rather distorted. The final spectrum was obtained using a cluster of 158 atoms. There is a reasonable agreement between the experimental spectrum and our MS calculations (fig. 1, center panel). Features are pronounced, and there is correspondence in their energies positions. The relative intensities do not fail to achieve agreement: the major exception is in peak E, so that the intensity ratio between peak D and peak E is in fact reversed. However, this effect has to be carefully evaluated, because the theoretical spectra, in these large clusters, actually include many MS paths, *i.e.* certainly more than those allowed in the real case because of thermal or disorder effects. Actually, the experimental spectrum clearly shows that MS contributions in the region over 30 eV are essentially smeared out, and some reduction has to be considered also in near-edge energy region.

Orthoclase has a monoclinic structure with unit-cell constants $a_0 = 8.563$ Å, $b_0 = 12.963$ Å, $c_0 = 7.210$ Å and $\beta = 116.1°$[17]. The right panel of fig. 1 shows the good agreement between the experimental spectrum and the calculated curve. However, again the MS peak E is narrower than the experimental one. Also in this system the weak MS features in the region over 30 eV above the threshold are not to be detected in the experimental spectrum. The lack of the weak features in the intermediate multiple-scattering region (IMS) may be interpreted as due to a small distortion of the local structure. It might imply the existence of a definite degree of
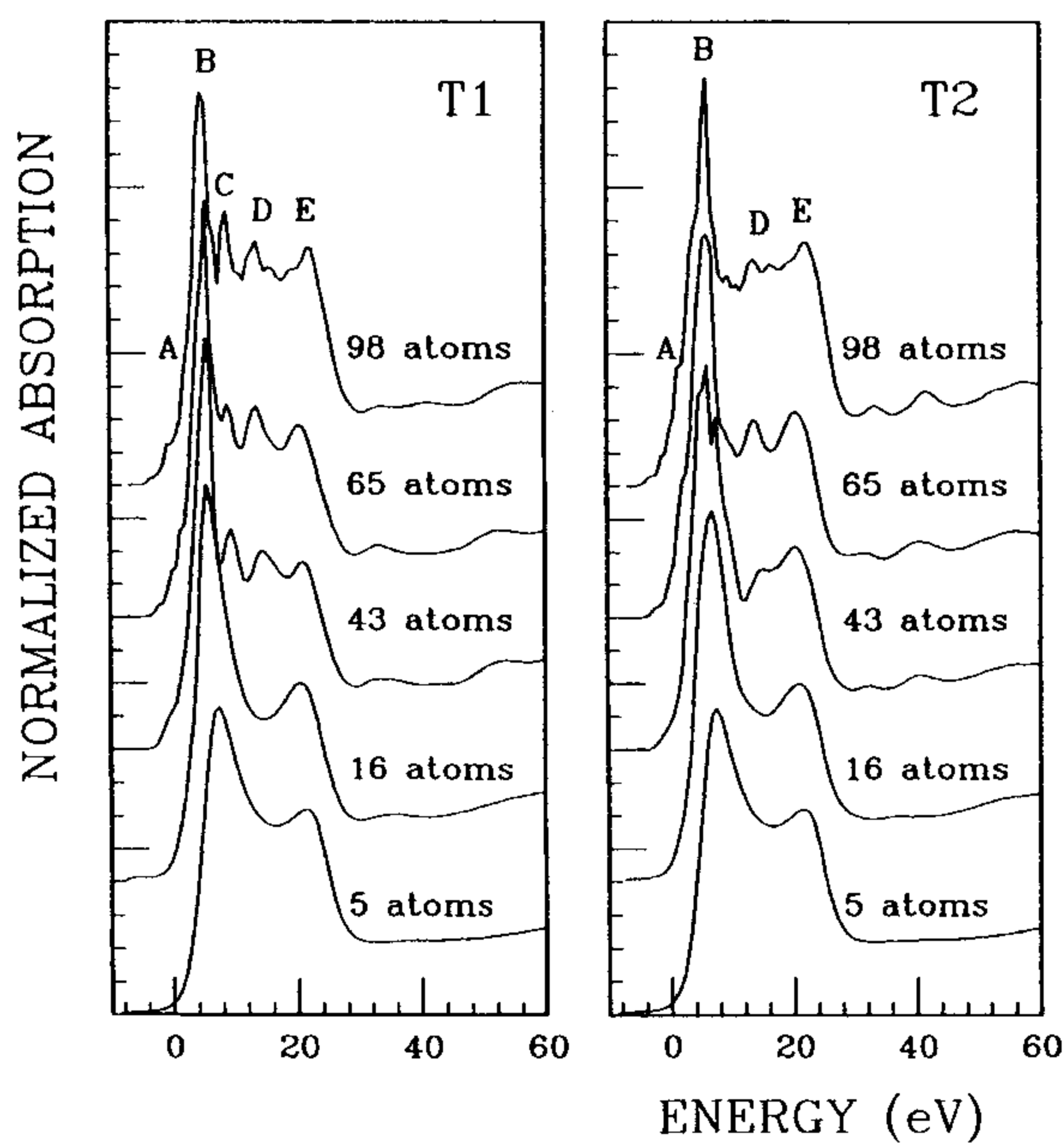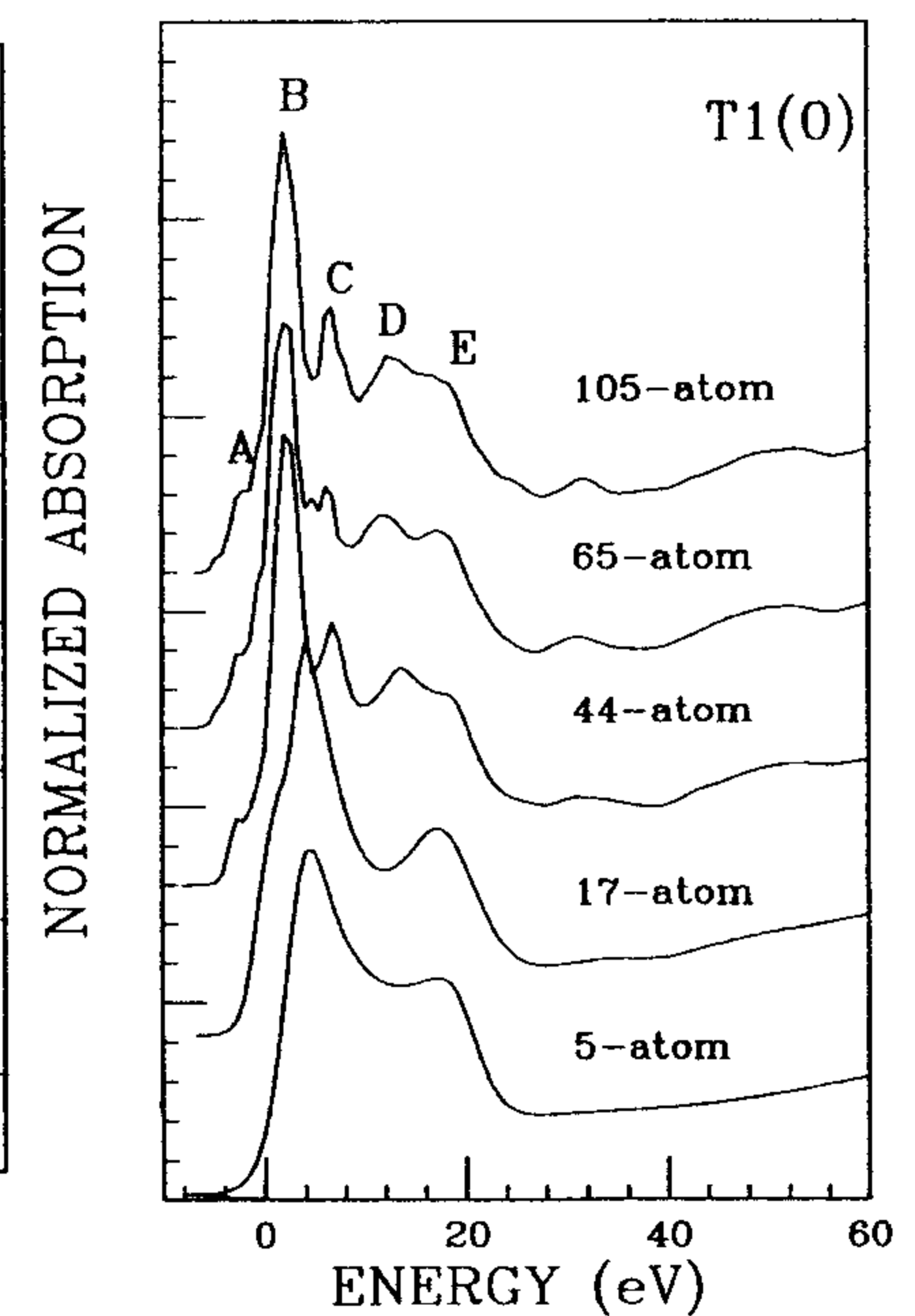
Fig. 2

Fig. 3

Fig. 2. – MS-calculated spectra for sanidine at site T1 (left panel), site T2 (middle panel). Summations of these two contributions as a function of cluster size are reported in the right panel, where the top curve is the experimental spectrum. Clusters larger than 98 atoms are not shown because the differences in the MS region are only very subtle and in any case do not improve the comparison.

Fig. 3. – MS-calculated spectra for the T1 site of microcline as a function of cluster size. Clusters larger than 98 atoms are not shown because the differences in the MS region are very subtle.

disorder in the real atomic arrangement of all three measured samples which now cannot be included in the MS calculation.

The three experimental spectra markedly differ in the relative intensities of peaks C and D. In order to explain the results and to relate the measured and calculated features to the geometrical properties of the local structure around the Al atom, we present the theoretical spectra obtained by using clusters of different size for sanidine (fig. 2) and microcline (fig. 3), the two extreme cases of order/disorder. Comparing these two different cluster calculations is interesting to the aim of recognizing the similar behaviour of increasing the number of atoms. Indeed, all observed differences are internal to the Al atom sites.

In both sanidine and microcline, and in all types of tetrahedral structures, the first-shell cluster, which consists of 4 O atoms plus the central Al absorber, already gives rise to a definite, strong but broad peak at +4 eV above the threshold corresponding to B, the white-line. In terms of scattering, therefore, B mainly arises from MS within the first oxygen coordination shell. There is a second feature, a peak at about +17 eV (corresponding to E) that is dominantly derived from single scattering from the same oxygen shell, as suggested by resonance scattering arguments [18]. This type of MS spectrum is indeed typical of tetrahedral Al, and occurs in all minerals containing the AlO_4 tetrahedron [19].

The changes observed by increasing the cluster size up to containing 17 atoms (2 Al + 3 Si + 2 K + 10 O up to 4 Å distance) are by far less important than those to be seen later, in the calculation referred to the cluster containing 43 atoms (8 Al + 7 Si + 3 K + 25 O). It is in this medium-size cluster, extending to 5 Å the distance from the absorber, that peaks A, C and D develop, as do other features in the IMS region which are not detected in the experimental

spectra. Therefore these features arise from intershell multiple scattering and determine the convergence criterion.

Figure 2 clearly shows that the MS contributions are different between the T1 and T2 tetrahedral sites of sanidine, and these, in turn, refer to T2 mainly, as T1 is similar in both sanidine and microcline (fig. 3). Peak C begins to appear only in the T1 contribution, while peaks D and E are present in both configurations. Calculations were made without taking disorder into account, so that the discrepancies of the theoretical spectra of sanidine from the experimental ones may be now referred to different degrees of local order around the two Al sites. The T1 site is more ordered than T2, as it appears just from looking at the intensity of peak C which occurs only in T1. Furthermore, there is a lower degree of order compared to the microcline and orthoclase feldspars as demonstrated by the strong reduction of peak D (fig. 2 and 3).

Indeed, the 43-atom cluster spectrum contains all the features recorded in the experimental spectrum; increasing the cluster to a total number of 65 atoms, then to 105 atoms, and finally to 158 atoms, (fig. 1, left) *i.e.* to a distance of 8 Å from the absorber, does not produce a better agreement in the relative intensity distribution, *e.g.* peak C, or the ratio D/E. However, the pre-peak A becomes well-defined only after addition of the last two oxygen coordination shells, indicating that the final state reached in the core electron transition is not a simple atomic or molecular state [20], but that this region is also sensitive to long-range effects. On the contrary, cluster calculations for microcline (fig. 3) demonstrate a high degree of order around the only tetrahedral site occupied by Al and the need to use very large clusters to improve the comparison with experimental data.

A striking characteristic of the feldspar spectra, both the experimental ones and those reproduced by MS calculation, is peak E at ca. +17 eV above the threshold. This peak is never present in garnets [5], where Al is in a regular octahedral coordination with 6 oxygens at average distances 1.886-1.924 Å depending on the species [21]. Rather, a peak at ca. +18 eV occurs in other tetrahedral structures such as in the Si K-edge spectra of some SiO_2 polymorphs [22]. In garnets, as well as in other compounds where Al is in six-fold coordination [2], [3], [5], [19], peak E either does not occur, or is very weak, probably because the smaller O-Al-O angle implies different contibutions to MS. In this way, the presence of peak E helps in assessing the Al coordination in an unknown compound.

In conclusion:

1) the general shape of the Al K-edge is qualitatevely determined by the interaction of photoelectrons with the first coordination sphere around the absorber;

2) detailed information can be obtained only by performing calculations with large clusters containing up to 100 atoms or more, *i.e.* having a size extending to 7-10 Å from the absorber; it is only when this mean free path is allowed that important MS contributions begin to appear;

3) ordering is maximum in T1 for both microcline and sanidine; the state of structural disorder of the latter results mostly from Al being displaced in T2;

4) a relationship between the structural arrangement of feldspars and the position, shape and intensity of the different features in the spectra exists; in particular, the intensities of peak C (at ca. 1575 eV) and D (at ca. 1580 eV) appear to be a function of the degree of order of the aluminosilicate framework;

5) for unknown structures, the presence of peak E (at ca. 1584 eV) gives information about the Al coordination in the first shell, as well as about the polyhedral linkage.

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