Calcium Environment in Omphacitic Pyroxenes: XANES Experimental Data One Electron Multiple Scattering Calculations

Eleonora Paris[1], Ziyu Wu[2], Annibale Mottana[3] and Augusto Marcelli[2]

[1] Dipartimento di Scienze della Terra, Universita' di Camerino, I–62032 Camerino, Italy and Department of Geology, University of Bristol, Queen's Road, BS81RJ Bristol, UK

[2] INFN–Laboratori Nazionali di Frascati, Via E.Fermi 40, I–00044 Frascati, (Roma) Italy

[3] Dipartimento di Scienze Geologiche, Terza Università di Roma, Via Ostiense 169, I–00154 Roma, Italy

Abstract

One–electron multiple scattering calculations have been used to determine the calcium local environment in three pyroxenes (diopside, intermediate ordered omphacite, and jadeite–rich disordered omphacite) starting from their crystal structure data. The calculated Ca K–edge spectra agree well with the experimental X–ray absorption XANES spectra. The overall comparison of theory and experiment supports the model that in omphacite Ca distributes over two inequivalent sites, one with the same geometry as the Ca site in diopside, and the second one with that of Na in jadeite. The comparison of the measured XANES spectra with ab–initio calculated ones allows the achievement of full understanding of experimentally observed features and from them the crystal–chemical behaviour of individual cations present in a mineral structure is also determined.

(Submitted to European Journal of Mineralogy)

INTRODUCTION

The crystal chemistry of Ca–Na pyroxenes has been studied extensively in the last two decades, mainly on the basis of single–crystal structure refinements of natural samples (for a review see Rossi et al., 1983). Most recently, the character of the order–disorder transition occurring in this join has also been explained using Landau theory (Carpenter et al., 1990a,b). Ordering occurs in two distinct sets of sites: (i) Mg ($\pm Fe^{2+}$) and Al ($\pm Fe^{3+}$) are partitioned over two slightly distorted octahedral sites (M1 and M11) which are edge–connected so as to form a chain parallel to the tetrahedral T chain; (ii) Na and Ca are ordered over two large sites (M2 and M21) having eight–fold coordination and separated one from the other because of the interposition of the O2A and O2B oxygens that link the octahedra with the tetrahedra. In fact, only the ordering of the two M2 cations Na and Ca can directly be measured by X–ray single crystal diffraction because of their large difference of electronic density; ordering in the M1 and M11 (i.e. between Mg and Al) is inferred only (Rossi et al., 1983).

Ordering in the M2 and M21 sites was independently confirmed by Davoli et al. (1983, 1987) by the chemically selective XAS (X–ray Absorption Spectroscopy) technique. They measured the Ca K–edge of various Ca–Na pyroxenes by XANES (X–ray Absorption Near–Edge Structure) spectroscopy and found that Ca was located in two distinguishable sites, different in their absorption energy and environment. However, their interpretation of XANES spectra was not conclusive and dependent on models derived from the general knowledge of the structure. Ab–initio calculation methods based on the one–electron multiple–scattering theory allow precise computation of absorption spectra and their comparison with the experimental ones, thus making possible in practice the explanation of the observed XANES resonances. By performing such calculations on three samples of the Ca–Na pyroxene set measured by Davoli et al. (1987) for which full structural data were available, we could now confirm the initial interpretation, and bring independent support to their crystal–chemical model of solid–solution and ordering in the Ca–Na pyroxene series.

METHODS

The samples investigated in this paper are natural pyroxenes having different calcium contents: a nearly pure diopside (MMR18362, with Ca 0.982 atom per formula unit [apfu] and Na 0.018 apfu); an ordered P2/n omphacite of intermediate composition (M1, with Ca 0.493 apfu and Na 0.436 apfu); and a jadeite–rich disordered C2/c omphacite [or impure jadeite] (P1–25, with Ca 0.202 and Na 0.762 apfu) (Davoli et al., 1987). The crystal structures of the three samples were investigated by the Giuseppe Rossi (personal communication, 1987) to R ca. 0.02–0.03. Such structural refinements constitute the starting data for our calculations (Table 1). Identical results were found for diopside when using the positional parameters given by Cameron et al. (1973), and these will be used in preference later for the only sake of showing that the calculated spectra are not affected by small differences (< 0.003 Å) in the positional parameters of the atoms, but only by the chemistry of the cluster used.

The computation of the XANES spectra is based on the one–electron multiple–scattering (MS) theory of Lee and Pendry (1975), and takes advantage of the refinements to the theory as well as to the computational methods progressively introduced by Natoli et al. (1980), Durham et al. (1982), Natoli and Benfatto (1986) and Durham (1988). In order to simulate the charge relaxation around the core hole in the photoabsorber of atomic number Z, we use the well screened Z+1 approximation (final state rule) of Lee and Beni (1977). In metallic and (nearly) covalent systems, this method is known to provide charge distributions quite close to those obtained by self–consistent calculations, at least within the muffin–tin model. For more details, the reader is referred to the multichannel MS theory description of Natoli et al. (1990).

RESULTS

The XANES experimental spectra at the Ca K–edge of our three pyroxenes are shown in Fig. 1. In diopside (curve (a)), the spectrum is composed of a strong absorption peak (labelled A) and minor features both on the low energy side of the edge (A' and A") and on the high energy side (B, C, D). In intermediate pyroxene, the spectra are similar in shape to that of diopside, but the single features differ in energy position and intensity. In fact, peak A shifts of 1.3 eV to high energy in passing from diopside (Fig. 1, curve (a)) to impure jadeite (curve (c)), and peaks A' and A" merge in only one peak in jadeite. Furthermore, peak B decreases in intensity with decreasing Ca content (from (a) to (c)) and shifts to higher energy as well. On the basis of the experimental spectra, the absorption features have been interpreted as a variation of the local environment around calcium atoms: in diopside CaO_8 cluster has a 4–2–2 configuration (i.e. four short, two intermediate and two long Ca–O bonds, nearly symmetrically distributed around the central M2 cation) whereas in jadeite the configuration of the M2 site (ideally centered by Na) is 6–2 (six short and two very long bonds) (Table 2). The shift in energy of peak A supports the idea that Ca in jadeite assumes the same configuration as Na with slightly shorter average bonds if compared to diopside but, more important, with six bonds at almost the same distance assuming therefore a more "regular" configuration.

The MS calculations have been carried out using clusters of increasing number of atoms (up to 95 atoms), taking into account all atoms within 6 Å from the absorber (Ca) as the center of the cluster. In this way, the structural significance of the cluster is assured, although a comparison with spectra obtained from smaller clusters shows that no substantial changes happen for this structure when increasing the cluster size from 58 to 95 atoms (Fig. 2). Most likely, this is due to the fact that the majority of the atoms involved in the clusters are low–Z atoms.

Figure 3 shows the calculated spectra of the three samples under investigation, using clusters of the same size for better comparison. All the spectra show a strong main peak A that compares well with the experimental one. In agreement with the experimental data, this peak shifts of about 1 eV toward high energy when passing from diopside (curve (a)) to impure jadeite (curve (c)). Peaks A' and A" have a more complex behavior: they both shift to higher

energy from curve (a) to curve (c). Peaks C and D are very weak in the theoretical spectra, although they have the same energy position in all the three spectra. However, these peaks show a peculiar behavior: by changing the chemical composition of the cluster (i.e., by substituting some Mg atoms in M1 with Al (in diopside, Fig. 4 (b) and of the Ca atoms in M2 with Na (in impure jadeite, Fig. 4 (d)) these peaks show some changes in energy position and intensity when compared with the starting clusters (Fig. 4 (a) and (c)). These effects are not related to changes in the first coordination shell (since Ca is always the absorber centering the cluster) but to higher–shell effects: they point out how changes in the chemistry of atoms well away from the absorber affect the XANES. In this regard, peak B (Fig. 3) is particularly interesting: in all three samples it has the same energy position and shows the same trend as seen in the experimental spectra (Fig.1) but in diopside (curve (a), Fig. 3) its intensity is slightly too strong with respect to that of the experimental spectrum (Fig. 1 (a)). In our case this fact has a simple explanation: the calculated spectrum is based on Cameron's et al. (1973) structure for a diopside synthetic crystal of pure $CaMgSi_2O_6$ composition, whereas the experimental spectrum was taken on a gem–quality natural diopside that, although very pure, contains minor Al substituting for Mg (see Fig. 4 (b)). Indeed, the presence of Al in M1 introduces detectable changes in the XANES spectrum, since the substitution of a chemical species with another having different atomic number strongly affects the charge density and, consequently, the potential calculated for the cluster. On the contrary, small differences in atomic position do not modify the features in the calculated spectra, allowing therefore the use of structural refinements obtained on different crystals for a general calculation of the spectra. The effects evidenced by our calculations point out the high sensitivity of XANES to even minor chemical variations in the cluster around the absorbing atom that could be suitable of extremely useful applications in the crystal–chemistry study of known and sometimes unknown structures.

CONCLUSIONS

1 – Interpretation of XANES spectra is greatly enhanced by the possibility of comparing the experimental spectra with calculated ones; in particular, by using the one–electron multiple–scattering theory in real space starting from the crystal–structural data of the minerals.

2 – The use of MS calculations allows to evidence directly the geometry and bond distribution of the first shells of atoms around the absorber.

3 – Combination of experimental and calculated spectra makes XANES a powerful probe to test the local crystal–chemical properties of some natural minerals, in which deviations from ideal composition are always present; these deviations reflecting the pressure–temperature–chemical environment where the mineral equilibrated.

4 – Specifically, these MS calculations confirm the interpretation of XANES spectra of intermediate Ca–Na pyroxenes (omphacites) already given by Davoli et al. (1987): Ca

distributes over two M2 sites, one close in geometry to that of Ca in diopside, and the second close to that of Na in jadeite. The average structure of omphacite is made up from a mosaic of two different polyhedra (M2 and M21) that remain essentially the same throughout the series but vary in their relative proportions. The stability of the overall structure is made possible by the fact that the octahedral and tetrahedral chains are flexible enough to bend around these rather rigid eight–fold coordinated units.

Dedicated XANES studies at the Na, Mg and Al K–edges are now under way to confirm these findings and to improve the knowledge of the crystal chemistry properties of these pyroxenes.

ACKNOWLEDGEMENTS

REFERENCES

Cameron, M., Sueno, S., Prewitt, C.T., Papike, J.J. (1973): High–temperature crystal chemistry of acmite, diopside, hedenbergite, jadeite, spodumene and ureyite. *Amer. Mineral.* **58**, 594–618.

Carpenter, M., Domeneghetti, M.C., Tazzoli, V.(1990a): Application of Landau theory to cation ordering in omphacite. I. Equilibrium behaviour. *Eur. J. Mineral.* **2**, 7–18.

Carpenter, M., Domeneghetti, M.C., Tazzoli, V.(1990b): Application of Landau theory to cation ordering in omphacite. II. Kinetic behaviour. *Eur. J. Mineral.* **2**, 19–28.

Davoli, I., Stizza, S., Durazzo, A., Mottana, A. (1983): Progress in EXAFS and XANES analysis of complex minerals (pyroxenes). *Per. Mineral* . **52**, 637–638.

Davoli, I., Paris, E., Mottana, A., Marcelli, A. (1987): XANES analysis on pyroxenes with different Ca concentration in M2 site. *Phys. Chem. Minerals* **14**, 21–25.

Durham, P.J. (1988): Theory of XANES. In: "X–ray absorption" Konigsberger D.C. and Prins, R. (eds.) Chemical Analysis Series **92**, 72–84, J. Wiley, New York.

Durham, P.J., Pendry, J.B., Hodges, C.H.(1982): Calculation of X–ray absorption spectra based on the multiple scattering theory. *Comput. Phys. Comm.* **25**, 193–205.

Lee, P.A., Beni, G.(1977): New method for the calculation of atomic phase shifts: application to extended X–ray absorption fine structure (EXAFS) in molecules and crystals. *Phys. Rev.* **B15**, 2862–2867.

Lee, P.A., Pendry, J.B.(1975): Theory of extended X–ray absorption fine structure. *Phys. Rev.* **B11**, 2795–2801.

Natoli, C.R. Misemer, D.K., Doniach, S., Kutzler F.W. (1980): First–principles calculation of X–ray absorption–edge structure in molecular clusters. *Phys. Rev.* **A22**, 1104–1107.

Natoli, C.R., Benfatto M., Brouder C., Ruiz Lopez M.Z., Foulis D.L. (1990): Multichannel multiple–scattering theory with general potentials. *Phys. Rev.* **B42**, 1944–1968.

Natoli, C.R., Benfatto, M. (1986): A unifying scheme of interpretation of X–ray absorption spectra based on the multiple scattering theory. *J. Phys.* (Paris) **47**, C8, 11–23.

Rossi, G., Smith, D.C., Ungaretti, L., Domeneghetti, M.C. (1983): Crystal–chemistry and cation ordering in the system diopside–jadeite: a detailed study by crystal structure refinement. *Contrib. Mineral. Petrol.* **83**, 247–258.

TABLE 1 – Structural and chemical data of the samples used for MS calculations.

sample	chemistry		positional parameters		
space group			x	y	z
(a)	Ca 0.982	M2	0.0000	0.3015	0.2500
C2/c	Na 0.018	M1	0.0000	0.9082	0.2500
		T	0.2862	0.0933	0.2293
		O1	0.1156	0.0873	0.1422
		O2	0.3611	0.2500	0.3180
		O3	0.3505	0.0176	0.9953
cell parameters a(Å) 9.510(4); b(Å) 8.686(4); c(Å) 5.238(3); β(°) 107.09(3)					
(b)	Ca 0.493	M2	0.2500	0.9504	0.7500
P2/n	Na 0.436	M2	0.2500	0.5526	0.2500
		M1	0.2500	0.3480	0.7500
		M1	0.2500	0.1598	0.2500
		T1	0.5394	0.3481	0.2266
		T2	0.5372	0.1631	0.7309
		O1	0.3634	0.3382	0.1232
		O2	0.3621	0.1767	0.6475
		O3	0.6138	0.5090	0.3091
		O4	0.6063	0.9974	0.8054
		O5	0.6057	0.2663	0.0037
		O6	0.5981	0.2398	0.4984
cell parameters a(Å) 9.552(9); b(Å) 8.780(8); c(Å) 5.209(5); β(°) 106.59(5)					
(c)	Ca 0.202	M2	0.0000	0.3000	0.2500
C2/c	Na 0.762	M1	0.0000	0.9048	0.2500
		T	0.2897	0.0928	0.2292
		O1	0.1115	0.0807	0.1422
		O2	0.3610	0.2578	0.3180
		O3	0.3522	0.0112	0.9953
cell parameters a(Å) 9.7496(4); b(Å) 8.9206(3); c(Å) 5.2509(2); β(°) 105.81(3)					

(a) synthetic diopside, structural refinement by Cameron et al.(1973); (b) ordered intermediate omphacite, M1 Biella (Italy), structural refinement by G.Rossi (pers. comm., 1987); (c) jadeite–rich disordered omphacite, P1–25 (Garnet Ridge, Arizona), structural refinement by G.Rossi (pers. comm., 1987).

TABLE 2 – Oxygens distribution around the Ca absorber for three pyroxenes described in the text.

(a)		(b)		(c)	
Ca		Ca		Ca	
O2	2.3489	O4	2.3840	O2	2.3132
O2	2.3489	O4	2.3840	O2	2.3132
O1	2.3647	O2	2.3904	O1	2.3265
O1	2.3647	O2	2.3904	O1	2.3265
O3	2.5633	O5	2.4800	O3	2.4480
O3	2.5633	O5	2.4800	O3	2.4481
O3	2.7223	O6	2.7748	O3	2.7174
O3	2.7223	O6	2.7748	O3	2.7174
(a),(b),(c) as in Table 1. Numbers refer to the distance in Å from the absorber.					
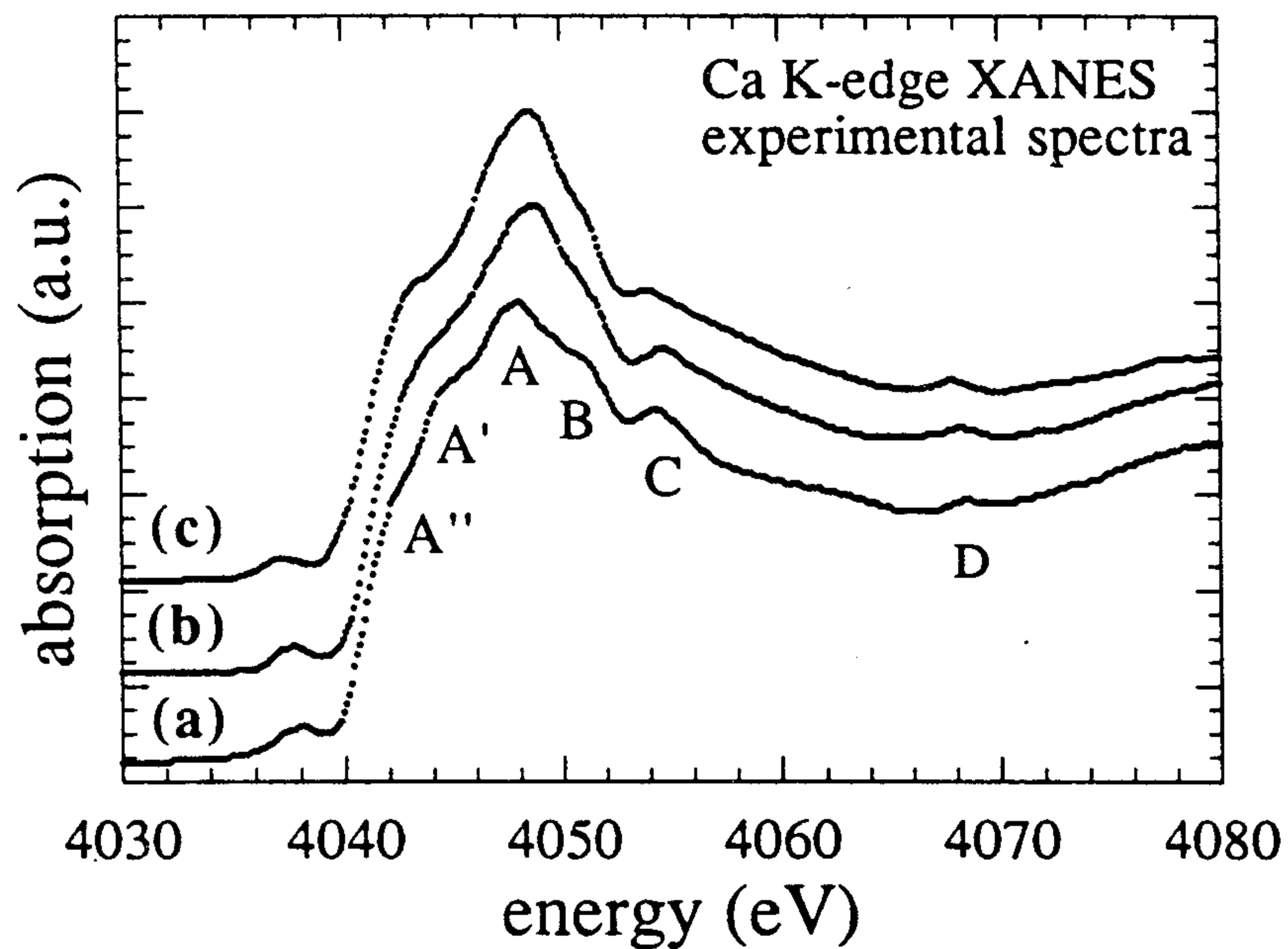
FIG. 1 – Experimental Ca K–edge XANES spectra of natural clinopyroxenes (Davoli et al., 1987). (a) diopside; (b) ordered intermediate omphacite; (c) jadeite–rich disordered omphacite.
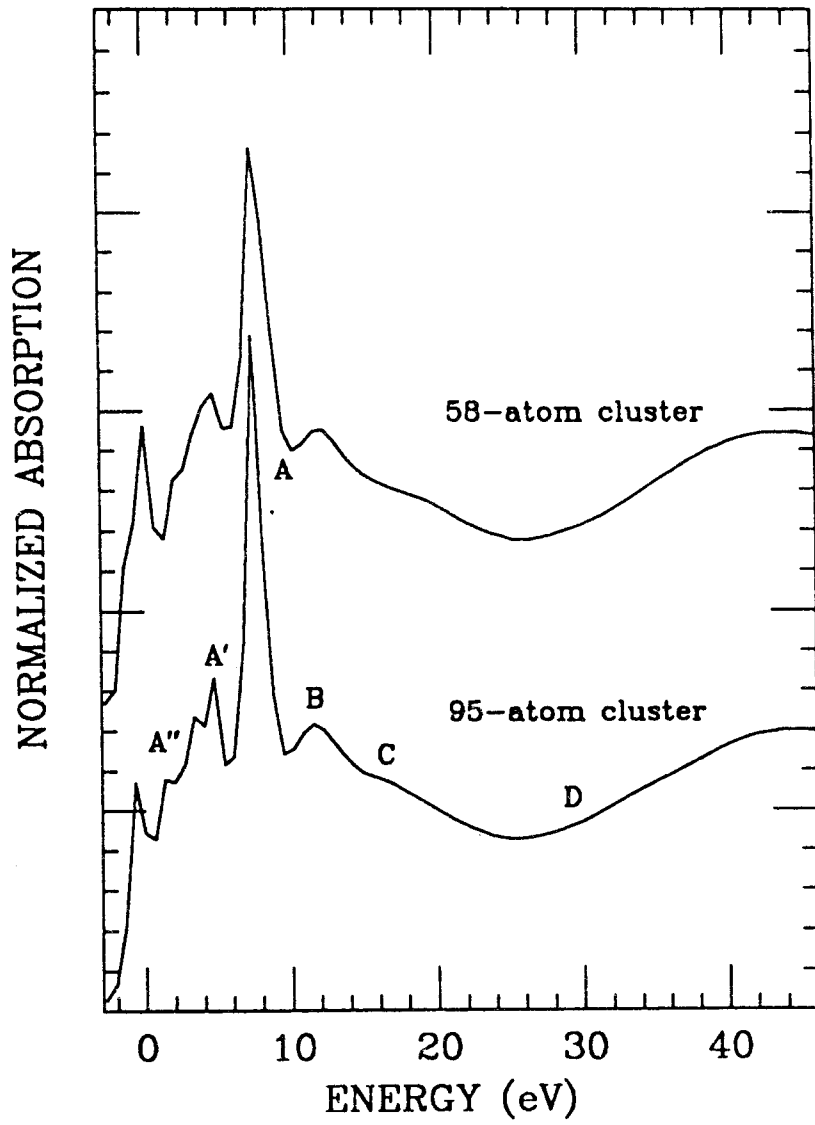
FIG. 2 – Diopside spectra calculated using two clusters of different sizes.
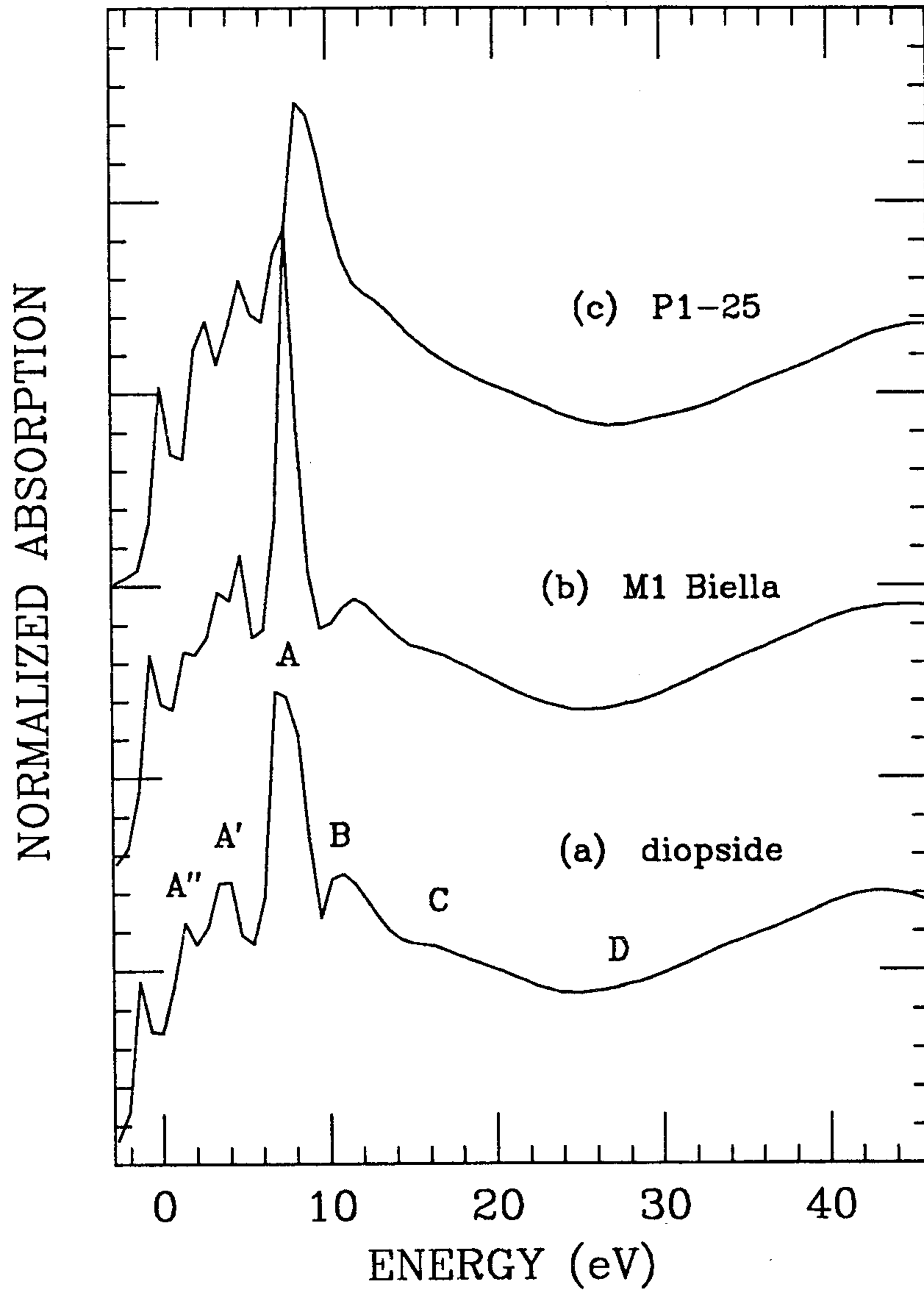
FIG. 3 – Theoretical MS calculation of the clinopyroxenes at the Ca K–edge. (a) diopside; (b) ordered intermediate omphacite; (c) jadeite–rich disordered omphacite.
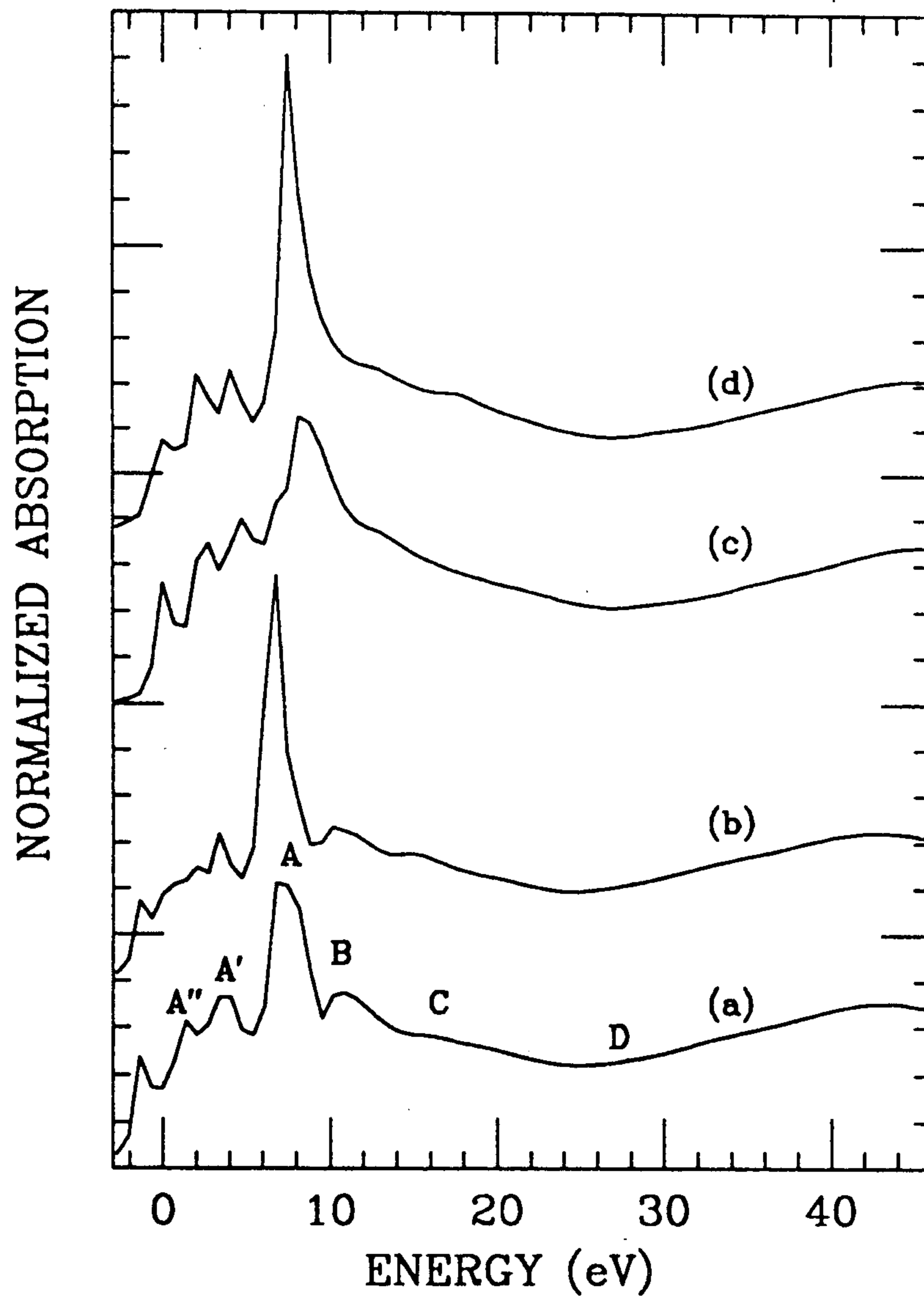
FIG. 4 – Effect of chemical composition of the cluster on the XANES resonances. (a) diopside, (b) same cluster with 2 Mg atoms substituted by Al; (c) jadeite–rich disordered omphacite, (d) same cluster with all the Mg atoms substituted by Al and all the Ca atoms substituted by Na, except the central absorbing atom.