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A SINGLE-CRYSTAL NEUTRON-DIFFRACTION INVESTIGATION OF DIOPSIDE AT 10 K

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ABSTRACT

Single-crystal neutron-diffraction data, collected at 10 K on a natural sample of diopside, provided a structure that refined to *R* = 4.5% for 415 independent reflections. The structure refinement showed significant reduction of the *M*(2)–O(3C2),(3D2) bond lengths, resulting in a more regular *M*(2) polyhedron than at higher temperatures. A significant *zero-point* contribution to the atomic displacement parameters (*ADP*) was found. On average, it accounts for the 35% of the room-temperature determination. Such results confirm previous predictions based on lattice-dynamics calculations.

Keywords: diopside, neutron diffraction, low-temperature structure, zero-point motion.

SOMMAIRE

Des données en diffraction neutronique, prélevées à 10 K sur un cristal unique de diopside naturel, ont mené à une structure affinée jusqu'à un résidu *R* de 4.5% en utilisant 415 réflexions indépendantes. L'affinement de la structure indique une réduction importante de la longueur des liaisons *M*(2)–O(3C2),(3D2) et, par conséquent, un polyèdre *M*(2) plus régulier qu'aux températures plus élevées. Le mouvement des atomes au point zéro contribuerait de façon importante aux paramètres décrivant les déplacements atomiques. Par exemple, en moyenne, ce mouvement rend compte de 35% des valeurs établies à température ambiante. Ces résultats confirment les prédictions antérieures fondées sur les calculs de la dynamique du réseau.

Mots-clés: diopside, diffraction neutronique, structure à basse température, mouvements au point zéro.

INTRODUCTION

Clinopyroxenes are important rock-forming minerals. The reference clinopyroxene end-member is diopside ($CaMgSi_2O_6$); in fact, the composition of natural clinopyroxenes, for example augite, can be derived by solid solution in the cation sites of diopside. Therefore, several structural investigations have been performed on both natural and synthetic diopside to clarify its structural features in relation to those of other clinopyroxenes at room (Clark *et al.* 1969, Bruno *et al*. 1982) and non-ambient conditions (high pressure: Levien & Prewitt 1981, Zhang *et al*. 1997; high temperature: Cameron *et al*. 1973, Finger & Ohashi 1976). The main result of the cited papers was a description of the evolution of the average bond-lengths and distortion of polyhedra as a function of temperature (T), pressure (P) and composition.

At present, no data exist on the diopside structure at T close to 0 K; the purpose of this work is to provide structural data on diopside at low temperature. A refinement at low T is of interest (i) to show the structural variations that occur at low T with respect to the room-temperature and high-temperature data (Cameron *et al*. 1973, Finger *et al*. 1976); (ii) to evaluate experimentally the extent of *zero-point motion* in diopside and to compare these results with theoretical predictions provided by lattice dynamics (Pilati *et al*. 1996). Experi-

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mental investigations of several minerals at low T (Smith *et al.* 1986, Pavese *et al.* 1995, Lager *et al.* 1982) have shown that the contribution of the *zero-point motion* to the atomic displacement parameters (*ADP*s) may be between 30 and 60% of the observed *ADP*s at room temperature.

A neutron-diffraction single-crystal refinement at 10 K on diopside was done with these objectives in mind. The fortuitous occurrence of (100) non-merohedral twinning in the crystal chosen for study enabled us to test corrections and the reliability of results for this twin orientation, very common in clinopyroxenes.

EXPERIMENTAL

The collection of single-crystal neutron-diffraction data was performed on a crystal of diopside from a rodingitic rock sampled at Bellecombe, Aosta Valley, Italy; its dimensions are 4.6 × 5.8 × 1.0 mm. Its chemical composition, determined by electron-microprobe analysis (energy-dispersion spectrometry) at the end of the experiment, is $(Ca_{0.99}Na_{0.01})(Mg_{0.94}Fe_{0.07})Si_{1.99}O_6$.

The collection of neutron-diffraction single-crystal data was done on the four-circle diffractometer E5 at the BER II reactor of the Hahn-Meitner-Institut in Berlin. The crystal was mounted with [001] approximately parallel to the ω axis of the instrument and was cooled to 10 K using a closed-cycle refrigerator. Positions and intensities (I) of the diffracted beams were measured with a position-sensitive ^{3}He detector (PSD), 90 × 90 mm^2 in area. A Cu(220) monochromator was used, giving the neutron wavelength of $\lambda = 0.912$ Å. Data collection was performed on the whole reciprocal lattice sphere, up to $2\theta = 110°$, resulting in a total of 2471 reflections; data were corrected both for absorption and for extinction by using laboratory-supplied software. The Bragg peaks were integrated with the RACER program, which uses parameters to describe the shapes of the strong peaks to improve the precision of the standard deviation, $\sigma(I)/I$ (Wilkinson *et al.* 1988).

A few reflections with $h + k = 2n + 1$ (with n an integer) were found to have intensities higher than $10\sigma(I)$, thus violating the established *C*2/*c* symmetry of diopside. To test whether these apparent violations are due to some unknown phase-transition, a powder spectrum was collected at 4 K on the E2 diffractometer at the same neutron facility. Careful comparison of the low-T spectrum with the room-T one did not show any extra reflections violating the *C* lattice; a cell refined from the powder data [*a* 9.735(1), *b* 8.898(1), *c* 5.242(1) Å, β 105.72(1)°] was used for bond-length calculations. It was instead found during refinement (and subsequently optically confirmed) that the crystal used for the refinement is twinned along the (100) plane. This kind of orientation induces specific reflections on positions forbidden by *C2/c* symmetry; details concerning the corrections performed and discussion of the results obtained with the different models are given below.

The SHELX–93 package (Sheldrick 1993) was used for an isotropic refinement based on a total of 825 reflections, resulting in 415 independent ones, having $l = 0$, 2 and 4; a standard twin correction, as implemented in SHELX–97, was performed assuming an almost merohedral twinning (see below for a justification of this assumption). Neutron-scattering lengths $b(Ca) = 4.9$ fm, $b(Mg) = 5.375$ fm, $b(Si) = 4.149$ fm, $b(O) = 5.805$ fm were used (Ibers & Hamilton 1992). The effects of extinction were corrected according to Larson's (1970) model, as implemented in SHELX–93 (Sheldrick 1993). A fixed weighting scheme $[1/\sigma(F_o)^2]$ was used. The *agreement index* (*R*) and the *goodness of fit* (*GooF*) were found to be 4.6% and 1.07, respectively, for all 415 independent reflections (23 variables refined). Refined coordinates, bond lengths and angles are given in Tables 1 and 2, with the site labels used according to Burnham *et al.* (1967). A table of squared structure-factors is available from the Depository of Unpublished Data, Canada Institute for Scientific and Technical Information, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS AND DISCUSSION

Twinning

A correction for twinning on (100) was required. In principle, such twinning is non-merohedral, but in view of the particular cell-parameter values adopted, the misfit of the reciprocal lattices from the two twin components is almost negligible. With reference to one component (*A*), the twin law is such that a reflection of the second twinned component (*B*) with indices *hkl* takes the indices *–h–l.kl* in the reference reciprocal lattice of *A*. Taking into account the *C* centering of the lattice, reflections with indices *hkl* with (1) $h + k = 2n$, $l = 2m$ (where n and m are integers) receive contributions from both the *A* and *B* components (note that if $l = 0$, the *hk*0 reflections from *A* exactly overlap with *–hk*0

TABLE 1. POSITIONAL PARAMETERS AND ISOTROPIC-DISPLACEMENT FACTORS (Å^2) FOR DIOPSIDE AT 10 K

	Coordinates			B_{iso}		
	x/a	y/b	z/c	10 K	0 K[a]	298 K[a]
M(2)	0	0.3020(3)	0.25	0.26(4)	0.19	0.58
M(1)	0	0.9085(2)	0.25	0.11(6)	0.19	0.43
T	0.2865(2)	0.0936(2)	0.2293(6)	0.08(3)	0.13	0.32
O(1)	0.1155(2)	0.0880(2)	0.1425(5)	0.13(3)	0.23	0.47
O(2)	0.3612(2)	0.2504(2)	0.3193(5)	0.18(3)	0.26	0.59
O(3)	0.3510(1)	0.0180(2)	0.9946(4)	0.18(3)	0.21	0.53

[a] The isotropic-displacement parameters are calculated (at 0 K) and measured (at 298 K), from Pilati *et al.* (1996). Errors on the last digit, in parentheses.

TABLE 2. BOND LENGTHS (Å) AND ANGLES (°) FOR DIOPSIDE AT 10 K, AT ROOM TEMPERATURE, AND AT HIGHER TEMPERATURES

Bond	10 K	297 K^a	297 K^b	673 K^c	973 K^c	1123 K^c	1273 K^c
M(2)-O(1A1),(1B1)	2.356(2)	2.361(1)	2.360(1)	2.377(2)	2.391(2)	2.394(2)	2.399(2)
-O(2C2),(2D2)	2.343(2)	2.337(1)	2.353(3)	2.357(2)	2.366(2)	2.368(2)	2.370(2)
-O(3C1),(3D1)	2.557(2)	2.566(1)	2.561(2)	2.571(2)	2.578(2)	2.580(2)	2.586(3)
-O(3C2),(3D2)	2.706(2)	2.724(1)	2.717(1)	2.749(2)	2.773(2)	2.784(2)	2.797(2)
M(2)-O mean	2.490	2.497	2.498	2.514	2.527	2.532	2.538
Volume	25.55	25.73	25.76	26.19	26.58	26.69	26.87
Δ M(2)	0.287	0.303	0.292	0.314	0.328	0.337	0.345
M(1)-O(1A1),(1B1)	2.116(2)	2.125(1)	2.115(1)	2.135(2)	2.147(2)	2.150(2)	2.160(2)
-O(1A2),(1B2)	2.061(2)	2.060(1)	2.065(3)	2.067(2)	2.070(2)	2.069(2)	2.075(2)
-O(2C1),(2D1)	2.051(2)	2.057(1)	2.050(1)	2.063(2)	2.076(2)	2.081(2)	2.086(3)
M(1)-O mean	2.076	2.081	2.077	2.088	2.098	2.100	2.107
Volume	11.83	11.92	11.85	12.05	12.21	12.24	12.35
T-O(1)	1.603(2)	1.601(1)	1.602(2)	1.601(2)	1.600(2)	1.603(2)	1.602(2)
-O(2)	1.584(2)	1.585(1)	1.585(2)	1.586(2)	1.586(2)	1.583(2)	1.586(2)
Mean non brg.	1.594	1.593	1.593	1.593	1.593	1.593	1.594
T-O(3A1)	1.667(3)	1.667(1)	1.664(2)	1.671(2)	1.670(2)	1.670(2)	1.671(2)
-O(3A2)	1.686(3)	1.686(1)	1.687(2)	1.687(2)	1.688(2)	1.689(2)	1.690(2)
Mean brg.	1.676	1.676	1.676	1.679	1.679	1.680	1.681
T-O mean	1.635	1.635	1.635	1.636	1.636	1.636	1.637
Volume	2.22	2.22	2.22	2.23	2.23	2.23	2.24
O(3A2)-O(3A1)-O(3A2)	166.1(1)	166.1(1)	166.4(1)	167.1(1)	167.7(2)	168.2(2)	168.5(2)
T(A1)-O(3)-T(A2)	135.7(2)	136.0(1)	136.0(1)	136.3(1)	136.8(1)	137.0(1)	137.3(1)

The data at room temperature [(a) Bruno *et al*. (1982), (b) Clark *et al*. (1969)] and higher temperatures [(c) Cameron *et al*. (1973)] are compared with those from this work. Errors on the last digit, in parentheses.

reflections from B, which are equivalent in the point group $2/m$); (2) $h + k = 2n$, $l = 2m + 1$, receive a contribution from A only; (3) $h + k = 2n + 1$, $l = 2m + 1$, receive a contribution from B only and, finally (4) $h + k = 2n + 1$, $l = 2m$, are not present. Note that in case (3), apparent violations of the C lattice would result.

The results of refinements using different groups of reflections are summarized in Table 3: the first two columns refer to refinements done using only the reflections $h + k = 2n$, $l = 0$. In this case, since reflections from B overlap with equivalent ones from A, the refinement could be performed without taking twinning into account; the overall scale-factor (SF) reflects the scattering from the whole crystal ($A + B$); the volume fraction of the B individual (Fr) and the z coordinate were not refined (since $l = 0$).

The refinement done using all the reflections $h + k = 2n$, $l = 0, 2, 4$ is summarized in column 3: the overall scale-factor reflects the scattering from the whole crystal, but the contributions from the two twin components had to be separated; from the refinement of Fr, the B component constitutes nearly 90% of the crystal. This is the *reference* refinement, on which the later discussion about the structural features of diopside is based. Column 4 summarizes the results for a refinement with all the reflections having $l = 2m$ (m up to 4); since reflections with higher l are weaker, a higher error in the refinement is expected, as reflected in the higher agreement-factors. Moreover, the misfit between the A and B reciprocal lattices increases at higher l, so that the *merohedral approximation* becomes less effective.

Refinements using only reflections $h + k = 2n$, $l = 2m + 1$ are summarized in columns 5 (a) and 6 (b): in this case, since the diffracted intensities receive a contribution from the A component only, which amount to about 10% of the whole crystal, the overall scale-factor [$SF(A)$] is lower. Owing to the low intensity of the reflections from the smaller component, the refinement ended with agreement factors that are significantly worse than those of the other refinements.

Results from a refinement with reflections belonging to the B individual only (reflections $h + k = 2n + 1$, $l = 2m + 1$) are summarized in column 7; these reflections were originally collected to test for the C centering, but turned out to be useful in establishing the fraction of the B component of the twin.

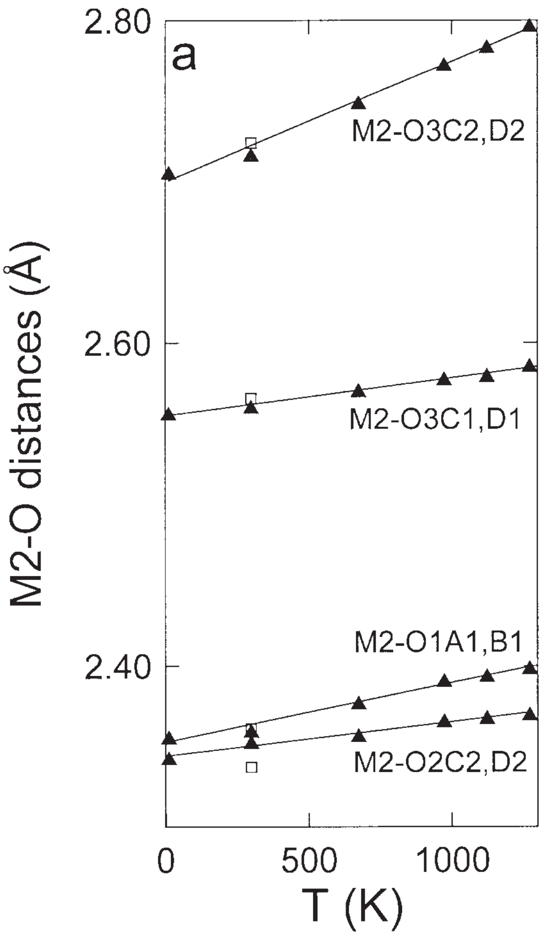
Refinements using all reflections with l odd (not overlapping reflections from both A and B) and all the reflections collected ($A + B$ with and without overlap) are shown in the last three columns.

The results in columns 2, 6 and 9 were obtained after processing the data with the program EQUIV (Prencipe 1998), which replaces the standard deviations of F_o^2 derived from the counting statistics by those

TABLE 3. STATISTICS OF REFINEMENTS OF THE STRUCTURE OF DIOPSIDE USING DIFFERENT DATASETS, AS DISCUSSED IN THE TEXT

	A+B, $l = 2n$				A, $l = 2n + 1$		B	A+B, $l = 2n + 1$		A+B
	$l = 0$, a	$l = 0$, b	$l = 0, 2, 4$	all	a	b	$l = 2n + 1$	a	b	all
N	336	336	825	989	841	841	110	951	951	1940
N_4	320	305	815	979	685	781	108	793	702	1772
SF	6.3(1)	6.2(1)	6.1(1)	6.2(1)	2.3(1)	2.1(1)	6.1(2)	6.3(1)	6.2(1)	6.2(7)
Fr	-	-	0.88(1)	0.89(1)	-	-	-	0.89(1)	0.90(1)	0.89(2)
Ex	18(2)	16(2)	19(2)	21(2)	10(2)	8(1)	16(3)	24(4)	23(4)	21(2)
R	4.7	4.5	4.6	7.6	16.9	15.4	5.0	14.6	13.5	9.4
R_4	4.4	3.6	4.5	7.5	13.9	12.4	4.9	12.4	11.1	8.7
$GooF$	1.24	1.19	1.07	1.16	1.29	1.32	1.31	1.26	1.31	1.19
$Equiv$	N	Y	N	N	N	Y	N	N	Y	N

N is the total number of reflections. N_4 is the number of reflections with $F_o \geq 4\sigma(F_o)$. *SF* is the refined overall scale-factor. *Fr* is the refined volume-fraction of the *B* individual (see text). *Ex* is the refined extinction-factor. *R* and R_4 are, respectively, the agreement factors based on all the reflections and on the subset of those with $F_o \geq 4\sigma(F_o)$. *GooF* is the Goodness of Fit. The *Equiv* flag (N/Y; *a* and *b* columns, respectively) indicates whether or not the dataset has been processed with the program EQUIV (see text). For the refined values of *SF*, *Fr* and *Ex*, errors on the last digit are given in parentheses.



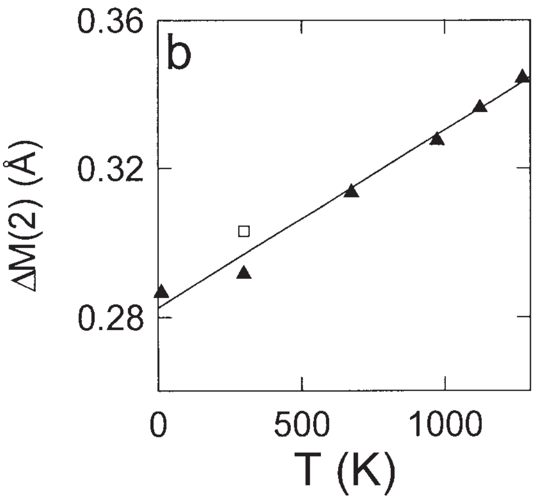


FIG. 1. a) *M*(2)–O bond lengths, and b) Δ*M*(2) for diopside at various temperatures. Triangles: at 10 K (this work), 298 K (Clark *et al.* 1969), and higher temperatures (Cameron *et al.* 1973). The square refers to synthetic diopside (Bruno *et al.* 1982).

obtained from the distribution of F_o^2, within each set of equivalent reflections.

As far as coordinates and displacement parameters (available from the authors) are concerned, the refinements based on the various datasets did not show any significant difference; this result supports the conclusion that the structural parameters refined are not greatly affected by the presence of twinning and, therefore, they can be used confidently for the subsequent discussion.

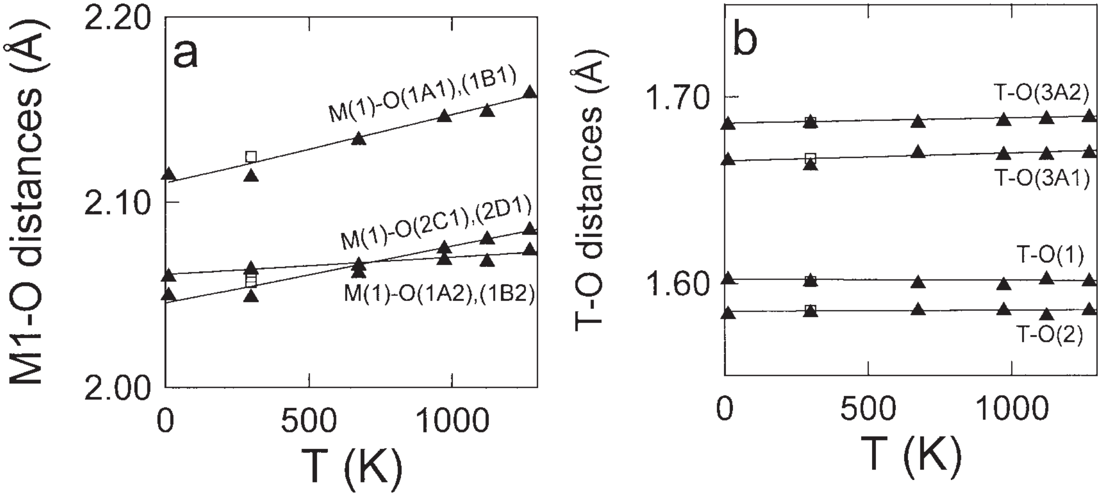


FIG. 2. a) *M*(1)–O bond lengths, and b) *T*–O bond lengths for diopside at various temperatures. Symbols as in Figure 1.

Average structure at 10 K

In Figure 1 and 2, the bond lengths for the *M*(1), *M*(2) and *T* polyhedra at high T and 10 K are shown. The overall trend of the average structural parameters follows the behavior that could be expected by extrapolation from higher-temperature data.

In the case of the *M*(2) polyhedron, a significant decrease of the *M*(2)–O(3C2),(3D2) bond lengths is observed with decreasing temperature, whereas the other *M*(2)–O bonds are only slightly shorter (2.422 *versus* 2.425 Å, on average). As an effect, a decrease in the polyhedron distortion is observed, as shown by the decrease in the distortion parameter (Fig. 1b) $\Delta M(2) = M(2)\text{–O(3C2)} - [M(2)\text{–O(3C1)} + M(2)\text{–O(2)} + M(2)\text{–O(1)}]/3$ (Dal Negro *et al*. 1982). This behavior confirms previous findings from *in situ* high-temperature measurements (Cameron *et al*. 1973, Benna *et al*. 1990, Tribaudino 1996); these indicate a greater approach of the furthermost and least strongly bonded O(3) oxygen atom to *M*(2) with decreasing temperature and an evolution toward an *eightfold* coordination for the *M*(2) cation at low T. From the geometrical point of view, the regularization of polyhedra is obtained by a shift in the chains of tetrahedra facing the *M*(2) polyhedron (Benna *et al*. 1988, 1990).

A comparison with higher-T data for the *M*(1) site of diopside confirms the minimal expansion of the *M*(1)–O(1A2),(1B2) distance with T, which results in an inversion in the shortest *M*(1)–O bond length: at low T the *M*(1)–O(1A1),(1B1) bonds are longer than *M*(1)–O(2C1),(2D1) whereas at higher T, the situation is reversed. Such behavior was observed only in diopside and in $Di_{80}En_{20}$ (Benna *et al*. 1990) and, extrapolating data from relatively low T, can be predicted to occur also in hedenbergite at a temperature close to its melting point (Cameron *et al*. 1973). On the other hand, in pyroxenes where the *M*(1) site is partly occupied by trivalent cations, such features were not observed or extrapolated, even in cases where only 0.3 Al substitutes for Mg in the *M*(1) site, as in the $Di_{70}CaTs_{30}$ clinopyroxene (Tribaudino 1996).

In the case of the *T* polyhedron, the individual bond-lengths have, within error, the same values from 10 K to 1273 K, indicating almost no thermal expansion, at least for bond lengths not corrected for *libration* effects (Downs *et al*. 1992), following the well-known apparent lack of volume expansion of the tetrahedra (Hazen & Finger 1982).

Displacement parameters and zero-point motion

Table 1 presents the isotropic-displacement parameters of the atoms in the 10 K refinements for diopside, with comparison to those of a diopside sample refined at 298 K by Pilati *et al*. (1996) and with theoretical predictions from lattice-dynamics calculations at 0 K. Our results indicate the presence of a significant *zero-point motion*, which ranges from 25 to 35% of the room-T value, apart from the *M*(2) cation, which has a higher value (45%), in reasonable agreement with the predictions by Pilati *et al*. (1996).

The observed differences between calculated and measured *ADP*s at 10 K are of the same order of magnitude as those found by Pilati *et al*. (1996) at higher temperatures. A similar *zero-point* contribution was found in albite (Smith *et al*. 1986), anorthite (Kalus 1978) and pyrope (Pavese *et al*. 1995).

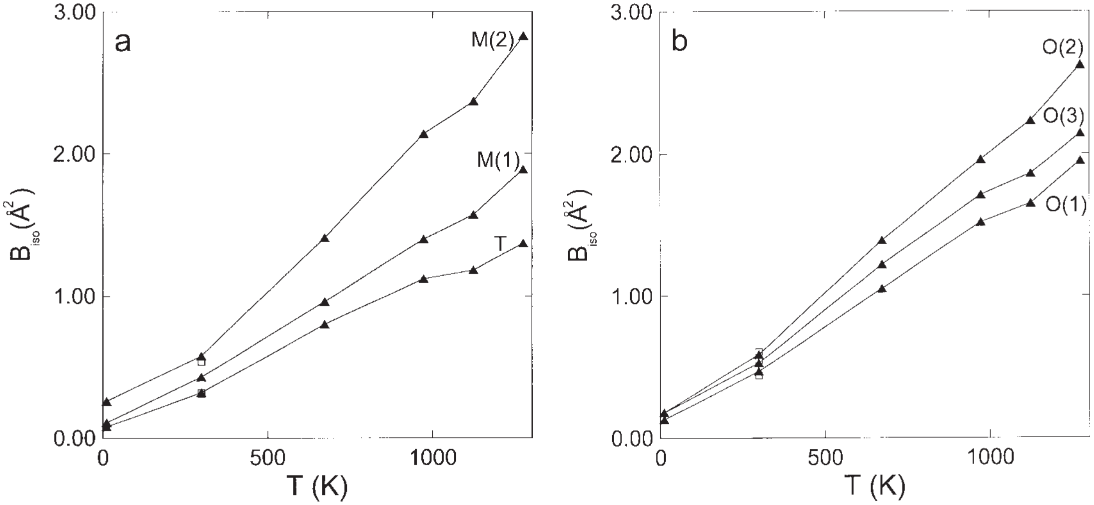


FIG. 3. Isotropic-displacement parameters *versus* temperature for a) *M*(2), *M*(1) and *T* sites, and b) O(1), O(2) and O(3) sites. Symbols as in Figure 1.

The twinning problem does not seem to have had an impact on the above conclusion: different selections of reflections included in the refinements, as discussed above (Table 3), could give individual *ADP*s, which may change significantly (up to 3σ). The average *zero-point* contribution, however, is not significantly changed. This is shown in Figures 3a and 3b, where the curves of isotropic-displacement parameters (*B*) *versus* T for diopside are provided: the *B* values at 10 K are ranked in the same order observed at room and higher T (Pilati *et al.* 1996), with $B_T < B_{M(1)} < B_{O(1)} < B_{O(3)} \leq B_{O(2)} \leq B_{M(2)}$; note also that for all the atoms, the *ADP versus* T curve flattens at lower T, in agreement with theoretical predictions of a trend, which approximates a linear fit only at a temperature higher than room temperature (Pavese *et al.* 1995).

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