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Variation of displacement parameters in structure refinements of low albite

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Abstract

New X-ray diffraction measurements of a well-ordered Roc Tourné low albite (space group $C\bar{1}$) were refined in a variety of models. In addition, structural data for other low albites obtained from room-temperature X-ray and neutron diffraction refinements were retrieved from the literature. Comparison of refined structural parameters indicates that highly significant differences exist among anisotropic displacement parameters from different data sets and models. Such differences are largely systematic and were analyzed in terms of B_{eq} values. Significant differences were found between refinements with different $\sin\theta/\lambda$ cutoff ranges. Refinement models in which Si and Al scattering curves were not correctly assigned lead to erroneous B_{eq} values. Assumption of nonrealistic vacancies on tetrahedral sites decreases B_{eq} values for T sites but increases oxygen displacement parameters. Choice of ionic or neutral scattering factors, selection of a weighting scheme, and neglect of anomalous dispersion correction (Mo$K\alpha$ radiation) have only minor influence on B_{eq} values.

Introduction

Twenty years ago, Zachariasen (1969) criticized the quality of single-crystal structure refinements with the statement: "It is evident that positional parameters are reasonably good—even though the actual errors are probably five times greater than the experimental ones. However, the thermal parameters are all nonsense and must be done again in a sensible way." In spite of this pessimistic opinion, ORTEP drawings (Johnson, 1976) of "vibrational ellipsoids"—enclosing a surface of usually 50% probability—adorn many structure publications, and extensive tables of U_{ij} or β_{ij} are published in the literature.

Recently, Dunitz et al. (1988) summarized the present knowledge on displacement parameters as obtained from diffraction studies and showed that valuable physical information can be derived from them. These authors have also chosen the term "displacement parameters" instead of "vibrational parameters" or "thermal parameters" because numerous kinds of disorder, static or dynamic, may influence their magnitude. Anisotropic Gaussian displacement parameters, obtained from neutron and X-ray structure refinements, describe the second moments of atomic probability functions and hence provide information on averaged displacements of atoms from their mean positions. Unfortunately, displacement parameters are often biased by systematic experimental errors such as inadequate absorption or extinction correction, thermal diffuse scattering, or scan truncation.

The aim of the present paper is to estimate the quality and variation of displacement parameters in feldspar structures depending on experimental set-ups and refinement models. We have chosen low albite because there are several other structure refinements available and all data were collected on samples with similar chemical composition and degree of (Si,Al) ordering.

New X-ray diffraction data for a low albite from Roc Tourné, France (Rose, 1865) are reported and compared with data for other low albites. In a second paper (Kunz and Armbruster, 1990) the extent to which displacement parameters of (Na,K)-feldspars contain information on (Si,Al) ordering will be tested.

Structure of Roc Tourné low albite

X-ray data collection and refinement

An untwinned low albite crystal, $NaAlSi_3O_8$, space group $C\bar{1}$, (0.20 × 0.12 × 0.09 mm) from Roc Tourné, France, was selected. With the spindle-stage technique (Bloss, 1981), the optic axial angle $2V_X$ was determined from extinction positions under crossed polarizers at 540 nm to be 102.0(1)°, a value characteristic of highly ordered low albite (Su et al., 1986). Subsequently, 4079 unique reflection intensities ($\sin\theta/\lambda < 0.90$, $-14 \le h \le 14$, $-23 \le k \le 23$, $0 \le l \le 10$) were collected in Ω-scan mode using graphite monochromated Mo$K\alpha$ radiation on a CAD-4 Enraf Nonius diffractometer. Lattice constants (Table 1) were refined from the scattering vectors of 20

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TABLE 1. Composition and room-temperature cell dimensions of low albites

Locality and reference	Composition (mol%) Ab	An	Or	a (Å) α (°)	b (Å) β (°)	c (Å) γ (°)
Amelia, Virginia, U.S.A. (Harlow and Brown, 1980)	99.3	0.1	0.6	8.142(2) 94.19(2)	12.785(2) 116.61(2)	7.159(2) 87.68(2)
Cazadero, California, U.S.A. (Wenk and Kroll, 1984)	99.7	0.1	0.2	8.1354(7) 94.274(6)	12.7852(7) 116.600(5)	7.1582(7) 87.685(6)
Ramona, California, U.S.A. (Ferguson et al., 1958; Ribbe et al., 1969)	98.5	0.5	1.0	8.138 94.33	12.789 116.60	7.156 87.66
Roc Tourné, France (this paper)	99.9	0.1	0.0	8.137(1) 94.26(1)	12.785(1) 116.60(1)	7.1583(4) 87.71(1)
Tiburon, California, U.S.A. (Winter et al., 1977)	99.8	0.0	0.2	8.152(1) 94.28(2)	12.784(3) 116.67(2)	7.165(1) 87.74(2)

Note: Numbers in parentheses are standard deviations and refer to the last digit.

reflections with $34° < \theta < 38°$. The crystal used in our experiment was so small that absorption ($\mu = 9.028$ cm^{-1}) should not significantly influence the results. This was also confirmed by a series of psi-scans. Data reduction, including background and Lorentz-polarization corrections, was carried out with the SDP program system (Enraf Nonius, 1983).

A total of 3370 reflections with $F_{obs} > 6\sigma(F_{obs})$ was employed in the refinement, which started from atomic parameters given by Harlow and Brown (1980) for low albite; the program system PROMETHEUS was used (Zucker et al., 1983). Structure factors were weighted on the basis of counting statistics ($w = 1/\sigma^2$). Neutral-atom scattering factors and real as well as imaginary anomalous-dispersion corrections were used. In addition to positional and anisotropic displacement parameters of all atoms, a scale factor and an isotropic extinction coefficient [$=0.24(3) \times 10^{-4}$; extinction type 1 on the basis of Lorentzian distribution of mosaic blocks according to Becker and Coppens (1974)] were refined to $R = 0.020$ and $R_w = 0.034$ (standard deviation of an observation of unit weight = 2.39; Table 5, model 8). Table 2[1] contains a list of observed and calculated structure factors.

Results

A final difference-Fourier synthesis revealed maximum residual density of 0.36 e Å^{-3} and -0.29 e Å^{-3} close to Na; residual density up to 0.23 e Å^{-3} was also found between (Si,Al) and oxygen. Final atomic coordinates and anisotropic displacement parameters are given in Tables 3 and 4. Several other models were also refined and discussed below.

Atomic coordinates and interatomic distances (not displayed) of the Roc Tourné low albite obtained from a variety of refinement models are not significantly different. However, corresponding anisotropic displacement parameters show significant and systematic differences.

The Na atom in the low albite structure shows highly anisotropic displacement parameters at room temperature. This anisotropy has been modeled either by splitting the Na position into two sites or by refining only one site with strongly anisotropic displacement parameters (Table 4). Although the maximum residual electron density for the Roc Tourné low albite is associated with this Na position, we prefer the one-site model because refinement of higher cumulants for Na did not improve the model. Furthermore, the anisotropic model yields smaller weighted R factors than the split atom model for both the neutron and X-ray data of Harlow and Brown (1980). Finally, the 13-K neutron refinement of Smith et al. (1986) also indicates the one-site model to be physically correct.

Other low albite data

Room-temperature crystal-structure refinements of low albite are available for several specimens with more than 98.5% albite content. For the purpose of diffraction experiments, these can be treated as chemically equivalent. The composition and cell parameters of the specimens

TABLE 3. Final atomic positional parameters and B_{eq} values of Roc Tourné low albite

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
$T_1O(Al)$	0.00887(4)	0.16846(2)	0.20805(4)	0.530(3)
$T_1m(Si)$	0.00375(3)	0.82051(2)	0.23737(3)	0.488(3)
$T_2O(Si)$	0.69162(3)	0.11021(2)	0.31466(4)	0.512(3)
$T_2m(Si)$	0.68129(3)	0.88190(2)	0.36076(4)	0.506(3)
Na	0.26799(8)	0.98865(6)	0.1465(1)	2.57(1)
O_{A1}	0.0049(1)	0.13103(5)	0.9666(1)	0.903(8)
O_{A2}	0.59176(8)	0.99756(5)	0.2804(1)	0.676(7)
O_BO	0.8123(1)	0.10966(6)	0.1901(1)	0.985(8)
O_Bm	0.8200(1)	0.85101(6)	0.2587(1)	1.25(1)
O_CO	0.01288(9)	0.30238(5)	0.2706(1)	0.883(8)
O_Cm	0.02329(9)	0.69368(5)	0.2291(1)	0.898(8)
O_DO	0.20780(9)	0.10896(5)	0.3890(1)	0.961(8)
O_Dm	0.1840(1)	0.86817(6)	0.4362(1)	1.112(9)

Note: Standard deviations in parentheses. $B_{eq} = \frac{8}{3}\pi^2 \Sigma_i[\Sigma_j(U_{ij}a_i^*a_j^*a_ia_j)]$. $\sigma(B_{eq})$: Schomaker and Marsh (1983).

[1] A copy of Table 2 may be ordered as Document AM-90-425 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 4. Anisotropic displacement parameters U_{ij} (Å²) of low albite (Roc Tourné)

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
T_1O(Al)	0.0074(1)	0.0068(1)	0.0061(1)	−0.00086(7)	0.00310(8)	0.00045(7)
T_1m(Si)	0.00679(9)	0.00646(9)	0.00552(8)	0.00111(6)	0.00299(7)	0.00080(6)
T_2O(Si)	0.00612(9)	0.00547(8)	0.00729(9)	−0.00023(6)	0.00247(7)	0.00040(6)
T_2m(Si)	0.00602(9)	0.00554(9)	0.00744(9)	0.00063(6)	0.00280(7)	0.00090(6)
Na	0.0136(2)	0.0471(4)	0.0315(3)	−0.0050(2)	0.0084(2)	−0.0219(3)
O_{A1}	0.0164(3)	0.0122(2)	0.0074(2)	−0.0002(2)	0.0067(2)	0.0014(2)
O_{A2}	0.0074(2)	0.0056(2)	0.0119(2)	0.0003(2)	0.0033(2)	0.0020(2)
O_BO	0.0117(2)	0.0130(3)	0.0162(3)	−0.0040(2)	0.0093(2)	−0.0017(2)
O_Bm	0.0134(3)	0.0179(3)	0.0216(3)	0.0046(2)	0.0129(3)	0.0020(6)
O_CO	0.0103(2)	0.0076(2)	0.0150(3)	−0.0020(2)	0.0052(2)	−0.0009(2)
O_Cm	0.0101(2)	0.0071(2)	0.0145(3)	0.0022(2)	0.0034(2)	0.0012(2)
O_DO	0.0120(3)	0.0129(3)	0.0080(2)	0.0024(2)	0.0013(2)	0.0015(2)
O_Dm	0.0140(3)	0.0140(3)	0.0084(2)	−0.0026(2)	−0.0002(2)	−0.0006(2)

Note: The thermal parameters are of the form

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

Numbers in parentheses are standard deviations and refer to the last decimal place.

described in the literature and in this paper are summarized in Table 1. The methods of intensity measurement include visual intensity estimation from films (Ferguson et al., 1958), four-circle X-ray diffractometry (Harlow and Brown, 1980; Wenk and Kroll, 1984) and 4-circle neutron diffractometry (Harlow and Brown, 1980). All X-ray diffraction data (Table 5) were obtained with Mo$K\alpha$ radiation, either graphite-monochromated or Zr-filtered, and were corrected for Lorentz and polarization effects. Additional parameters pertaining to experimental procedures are listed in Table 5 and discussed below.

In a fully ordered low albite, three of the four tetrahedrally coordinated positions (T sites) are occupied by Si (T_1m, T_2O, T_2m) and one by Al (T_1O). In some instances [neutron refinements by Harlow and Brown (1980) and Smith et al. (1986)], the refined occupancies of the four T sites indicated essentially all Al to be in T_1O.

Atomic coordinates[2] from various room-temperature

[2] Note that the atomic y coordinates of O_{A1} for X-ray and neutron data of Harlow and Brown (1980) are misprinted. The correct values (in agreement with their bond distances) are 0.13120(14) (X-ray) and 0.13115(4) (neutron).

TABLE 5. Experimental conditions and refinement models for low albites

Model	No. of reflections	sin θ/λ	Correction		Scattering factor	Anomalous dispersion	Model type for Na position	T sites		Weighting (w)	R (%)	R_w (%)
			Abs.	Ext.				Population = 1.0	(Si,Al) scattering factors			
Tourné low albite*												
1	3370	<0.90	no	yes	neutral	yes	single	yes	individual	$1/\sigma^2$	2.0	3.4
2	3370	<0.90	no	no	neutral	yes	single	yes	individual	$1/\sigma^2$	2.0	3.4
3	3370	<0.90	no	yes	neutral	yes	single	yes	individual	1	2.0	2.5
4	3370	<0.90	no	yes	neutral	no	single	yes	individual	$1/\sigma^2$	2.0	3.4
5	1602	>0.70	no	yes	neutral	yes	single	yes	individual	$1/\sigma^2$	1.6	2.1
6	1768	<0.70	no	yes	neutral	yes	single	yes	individual	$1/\sigma^2$	2.0	3.7
7	1768	<0.70	no	yes	ionic	yes	single	yes	individual	$1/\sigma^2$	2.0	3.7
8	3370	<0.90	no	yes	neutral	yes	single	refined	individual	$1/\sigma^2$	2.0	3.2
9	1786	<0.70	no	yes	neutral	yes	single	refined	individual	$1/\sigma^2$	1.9	3.2
10	3370	<0.90	no	yes	neutral	yes	single	yes	all Si	$1/\sigma^2$	2.2	3.9
11	3370	<0.90	no	yes	neutral	yes	single	yes	all Al	$1/\sigma^2$	2.1	3.3
Amelia low albite (Harlow and Brown, 1980)												
12†	1633	<0.69	n.s.	yes	neutron	yes	single	yes	individual	n.s.	2.1	2.4
13*	2441	<0.76	yes	yes	neutral	n.s.	single	yes	individual	n.s.	3.5	4.0
Cazadero low albite (Wenk and Kroll, 1984)*												
14	2538	<0.90	yes	yes	ionic	yes	split	refined	individual	$1/\sigma^2$	2.79	4.55
15	2528	<0.90	yes	yes	neutral	yes	split	refined	individual	$1/\sigma^2$	2.62	3.67
16	1148	>0.65	yes	fixed	neutral	yes	split	refined	individual	$1/\sigma^2$	2.54	3.13
Ramona low albite (Ferguson et al., 1958; Ribbe et al., 1969)‡												
17	1994	n.s.	n.s.	n.s.	half-ion	n.s.	single	yes	average	n.s.	6.8	n.s.
Tiburon low albite (Wainwright in Winter et al., 1977)*												
18	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	single	yes	individual	n.s.	n.s.	n.s.

Note: Abs. = absorption. Ext. = extinction. n.s. = not specified by authors of the original work.
* X-ray four-circle method.
† Neutron four-circle method.
‡ X-ray film method.

TABLE 6. B_{eq} (Å²) values for various refinement models

	Model 1 Tourné $w = 1/\sigma^2$	Model 2 Tourné No ext.	Model 3 Tourné $w = 1$	Model 4 Tourné No anom.	Model 5 Tourné High	Model 6 Tourné Low	Model 7 Tourné Ionic	Model 10 Tourné Si s.c.	Model 11 Tourné Al s.c.	Model 12 Amelia neutron	Model 13 Amelia X-ray	Model 17 Ramona average	Model 18 Tiburon
T_1O	0.530(3)	0.522(3)	0.540(3)	0.512(3)	0.499(3)	0.573(6)	0.566(6)	0.800(4)	0.609(3)	0.599(11)	0.44(1)	0.81(2)	0.54(1)
T_1m	0.488(3)	0.478(3)	0.498(3)	0.466(3)	0.460(3)	0.523(6)	0.523(5)	0.466(3)	0.277(3)	0.512(9)	0.44(1)	0.48(2)	0.55(1)
T_2O	0.512(3)	0.502(3)	0.521(3)	0.490(3)	0.479(3)	0.551(6)	0.550(6)	0.489(3)	0.300(3)	0.532(9)	0.46(1)	0.54(2)	0.51(1)
T_2m	0.506(3)	0.496(3)	0.515(3)	0.483(3)	0.474(3)	0.544(7)	0.543(6)	0.483(3)	0.295(3)	0.532(9)	0.46(1)	0.50(2)	0.52(1)
O_{A1}	0.90(1)	0.89(1)	0.91(1)	0.91(1)	0.877(6)	0.94(2)	0.91(2)	0.88(1)	0.98(1)	0.946(7)	0.92(3)	1.07(6)	0.99(1)
O_{A2}	0.67(1)	0.67(1)	0.69(1)	0.68(1)	0.646(6)	0.72(2)	0.65(1)	0.65(1)	0.74(1)	0.720(7)	0.75(3)	0.80(6)	0.73(1)
O_BO	0.98(1)	0.98(1)	1.00(1)	0.99(1)	0.962(6)	1.02(2)	0.99(2)	0.96(1)	1.07(1)	1.040(8)	1.03(3)	1.16(6)	1.02(1)
O_Bm	1.25(1)	1.24(1)	1.26(1)	1.25(1)	1.236(6)	1.27(2)	1.25(2)	1.22(1)	1.33(1)	1.319(8)	1.26(3)	1.37(6)	1.29(1)
O_CO	0.88(1)	0.87(1)	0.90(1)	0.89(1)	0.860(6)	0.91(2)	0.87(1)	0.86(1)	0.95(1)	0.918(8)	0.95(3)	1.01(6)	0.97(1)
O_Cm	0.90(1)	0.89(1)	0.91(1)	0.90(1)	0.877(6)	0.93(2)	0.88(1)	0.87(1)	0.97(1)	0.935(8)	0.98(3)	1.08(6)	0.93(1)
O_DO	0.96(1)	0.95(1)	0.97(1)	0.97(1)	0.940(6)	0.99(2)	0.96(1)	0.94(1)	1.03(1)	1.020(8)	1.05(3)	1.18(6)	1.01(1)
O_Dm	1.11(1)	1.10(1)	1.12(1)	1.12(1)	1.096(6)	1.13(2)	1.11(2)	1.09(1)	1.18(1)	1.153(8)	1.19(3)	1.35(6)	1.14(1)

Note: Standard deviations in parentheses. For description of the models, consult Table 5. ext. = extinction correction. anom. = anomalous dispersion. High = high-angle data. Low = low-angle data. Ionic = ionic scattering factors. s.c. = scattering curves.

refinements (Table 5) agree within 5σ. The T-O distances averaged over a tetrahedron (not corrected for thermal motion) agree within 2σ. The distances for T_1O are in the range 1.740 to 1.746 Å, those for T_1m, T_2O, and T_2m are in the range 1.610 to 1.615 Å. The former values are typical for Al-O distances and the latter for Si-O distances. Thus, essentially complete (Si,Al) ordering can be assumed for all low albites studied. In a well-refined feldspar structure, the detection limit of (Si,Al) ordering based on tetrahedral distances is in the range of 5%.

For simplification, B_{eq} values (Hamilton, 1959) instead of anisotropic displacement parameters are used for a comparative analysis. Systematic effects in U_{ij} values build up in B_{eq} and can be analyzed more easily. B_{eq} values of Na are not considered because of the arbitrary choice of a split or single Na model. Corresponding B_{eq} values for Si, Al, and oxygen atoms in low albites (Table 6) agree in some cases only to within 20σ.

VARIATION IN DISPLACEMENT PARAMETERS

Effect of sin θ/λ limit and radiation type

Displacement parameters from single-crystal neutron diffraction experiments describe the time- and/or space-averaged distribution of an atomic nucleus, whereas those from X-ray diffraction may contain contributions from nonspherical valence-electron density that is not considered explicitly in most refinements (Hirshfeld, 1976). However, X-ray reflections at high sin θ/λ values should be largely free of bonding effects and reflect, to an extent that is comparable to neutron data, the smearing of the atomic core densities (Hirshfeld, 1976).

B_{eq} values obtained from high-angle data (model 5), low-angle data (model 6), and all data (model 1) are given in Table 6. The low-angle data yield B_{eq} values that are systematically ~0.07 Å² (up to 12σ) larger than those from high-angle refinements. Thus, it must be assumed that bonding electrons in the low-angle refinements are partly modeled by increased displacement parameters.

Two low-angle data sets were collected on different low albites by different groups, but comparable models were used in the refinements (Table 5, models 6 and 13). A third similar data set (model 18), refined with isotropic B values, is added for comparison. Values of B_{eq} for oxygen in these three refinements agree within 3σ. The same good agreement is found between B and B_{eq} values for Si and Al in models 18 and 6. The values for Si and Al in model 13 are ~0.1 Å² (up to 8σ) lower than in the other two refinements (models 6 and 18), however. The cause of this difference is not yet understood.

Following the ideas of Hirshfeld (1976), good agreement should be obtained between displacement parameters from neutron data and those from high-angle X-ray data. However, the neutron data of Harlow and Brown (1980) (model 12) yield values of B_{eq} that are systematically ~0.07 Å² higher than obtained from our high-angle X-ray data (model 5).

Effect of population refinement of tetrahedral sites

Apparently precise single-crystal measurements were performed by Wenk and Kroll (1984) on a Cazadero low albite (models 14, 15, and 16; Tables 5 and 7). The resulting anisotropic displacement parameters or the corresponding B_{eq} values (Table 7) are, nevertheless, significantly different from the comparable models discussed above. In general, Wenk and Kroll (1984) refined significantly lower displacement-parameter values for Si and Al but larger values for oxygen. This observation is not in agreement with the trend that various refinement models or data sets lead to systematic variations of B_{eq} values in the same direction for cations and anions. Wenk and Kroll (personal communication) indicated that populations of cations on tetrahedral sites were also refined, yielding values significantly below 1.0 (Table 7). Wenk and Kroll (1984) stated that these low occupancies may be artifacts due to correlations with the displacement parameters or the extinction coefficient. To understand the effect of low occupancies on displacement parameters, we

TABLE 7. B_{eq} (Å²) values for models with refined site populations on tetrahedral sites

	Model 1 Tourné	Model 15 Cazadero	Model 8 Tourné	Model 16 Cazadero	Model 9 Tourné	Model 14 Cazadero
		All data	All data	High	Low	Ionic
T_2O	0.530(3)	0.457(3)	0.518(3)	0.493(3)	0.550(6)	0.459(3)
Pop.	1.0	0.957	0.966(2)	0.957	0.955(2)	0.985
T_1m	0.488(3)	0.451(3)	0.478(3)	0.439(3)	0.493(6)	0.409(3)
Pop.	1.0	0.953	0.967(2)	0.953	0.961(2)	0.980
T_2O	0.512(3)	0.454(3)	0.492(3)	0.484(3)	0.503(6)	0.478(3)
Pop.	1.0	0.962	0.963(2)	0.962	0.949(2)	0.997
T_2m	0.506(3)	0.420(3)	0.476(3)	0.453(3)	0.479(6)	0.440(3)
Pop.	1.0	0.955	0.959(2)	0.955	0.950(2)	0.988
O_{A1}	0.90(1)	0.97(1)	0.97(1)	0.97(1)	1.06(2)	0.91(1)
O_{A2}	0.67(1)	0.77(1)	0.73(1)	0.76(1)	0.84(2)	0.67(1)
O_BO	0.98(1)	1.08(1)	1.06(1)	1.06(1)	1.15(2)	0.98(1)
O_Bm	1.25(1)	1.33(1)	1.33(1)	1.34(1)	1.41(2)	1.24(1)
O_CO	0.88(1)	0.97(1)	0.97(1)	0.94(1)	1.03(2)	0.85(1)
O_Cm	0.90(1)	0.97(1)	0.95(1)	0.95(1)	1.05(2)	0.87(1)
O_DO	0.96(1)	1.04(1)	1.03(1)	1.04(1)	1.12(2)	0.97(1)
O_Dm	1.11(1)	1.19(1)	1.18(1)	1.19(1)	1.26(2)	1.11(1)

Note: For description of the models, consult Table 5. High = high-angle data. Low = low-angle data. Ionic = ionic scattering factors.

refined the Roc Tourné data with variable populations of T sites (models 8 and 9; Tables 5 and 7). Data sets containing low-angle data refined to tetrahedral vacancies in the range of ~4–5%. The supposed vacancies on tetrahedral positions lead to lower B_{eq} values for Si and Al but higher values for oxygen, in agreement with the trend observed in the Wenk and Kroll (1984) results. Low cation occupancies on tetrahedral positions obtained from low-angle X-ray data are incorrect, however. This effect is caused by the bonding electrons that cannot be properly modeled by the refinement model. Only high-angle X-ray data should be used for precise populations. In the case of Roc Tourné low albite, a data set with reflections above $\sin\theta/\lambda = 0.7$ yielded occupancies of 1.00(2) for all tetrahedral sites.

Effect of atomic scattering factors

In most X-ray structure refinements, neutral-atom scattering factors are used. For the ionic model of Roc Tourné low albite (model 7 in Tables 5 and 6; to be compared with model 6), the extra electrons on oxygen (O^{2-} instead of O) lead to slightly smaller oxygen displacement parameters, whereas the electron deficit for cations (Si^{4+},Al^{3+}) does not lead to higher B_{eq} values. The ionic and neutral-atom scattering-factor model by Wenk and Kroll (1984) should not be compared in this context because different populations on T sites (Table 7) were assumed. As shown above, varying populations have a strong influence on B_{eq} values.

When a feldspar structure is refined, it is not known from the beginning what the individual Si/Al ratio for each T site will be and which scattering curves should be assigned. Therefore, two extreme models were tested. All tetrahedral cations in low albite were modeled by either exclusively Si (model 10) or Al (model 11), respectively. Corresponding positional parameters vary only within 2σ and are not displayed. If Si is arbitrarily assigned to all T sites, B_{eq} of T_1O (Al site) increases by ~50% (compare models 1 and 10 in Table 6). If Al is attributed to all T sites (model 11), B_{eq} values of T_1m, T_2O, and T_2m (Si sites) decrease by ~40%. Both models also show significant differences in the B_{eq} values for oxygen. Ribbe et al. (1969) used an average scattering factor (¼Al + ¾Si) for all tetrahedral positions in the refinement of Ramona low albite (model 17). The displacement parameters of T_1O, the Al site, converged at much higher values (Table 6) than those of the Si positions (T_1O, T_1m, and T_2m). This also indicates that the assumption of a scattering power that is too high at T_1O (13.75 electrons instead of 13 electrons) causes B_{eq} to increase significantly.

Effect of anomalous-dispersion correction

Several investigators do not state explicitly whether an anomalous-dispersion correction (f', f'') was included during refinement. Therefore, neglect of anomalous-dispersion correction is tested in model 4 (Tables 5 and 6). Anomalous-dispersion parameters of Si and Al for Mo radiation [$f'(\mathrm{Si}) = 0.072, f'(\mathrm{Al}) = 0.056, f''(\mathrm{Si}) = 0.071, f''(\mathrm{Al}) = 0.052$] are higher than those for oxygen ($f' = 0.008$, $f'' = 0.006$). Neglect of anomalous dispersion causes B_{eq}(Si,Al) to decrease by ~0.02 Å² (~7σ), while oxygen displacement parameters are hardly affected.

Effect of additional experimental differences

The Roc Tourné low albite shows minor extinction effects. B_{eq} values refined from the data set not corrected for extinction (model 2) are systematically lower (by ~0.01 Å²) than those from the corrected data set (model 1). The influence of a weighting scheme was tested by comparison of $w = 1/\sigma^2$ and $w = 1$ refinements (models 1 and 3). Unit weights lead to values of B_{eq} that are systematically higher by 0.01 Å² relative to the values obtained in the $w = 1/\sigma^2$ model.

Conclusions

(1) Atomic coordinates from various low albite refinements agree within 5σ. (2) The agreement between corresponding B_{eq} values is much poorer with differences up to 20σ. (3) Highly significant and systematic differences in B_{eq} values (up to 10σ) are observed for refinements with different sin θ/λ cutoff ranges. High-angle data lead to lower displacement parameters than low-angle data. (4) Refinements with neutral-atom and ionic scattering factors yield similar (within 2σ) B_{eq} values. (5) If average (Si,Al) scattering factors are applied for all positions instead of individual values (e.g., derived from T-O distances), T sites to which too much Al is assigned have values of B_{eq} that are too low. Correspondingly, T positions to which too much Si is assigned have increased values of B_{eq}. (6) If, because of correlation problems, physically nonrealistic vacancy concentrations are refined on T sites, lower B_{eq} values for Si and Al and higher values for oxygen are obtained. (7) Neglect of anomalous-dispersion correction causes B_{eq} values for Si and Al to decrease slightly. (8) Provided that correct scattering curves are assigned and that the tetrahedral population is 1.0, variations in displacement parameters obtained from various models are either systematic or only of minor significance.

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