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On the Weak Reflections Violating Body-Centered Symmetry in Scapolites

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With 5 Figures

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Summary

X-ray diffraction studies reveal that most scapolites belong to space group $P4_2/n$. The mean intensity of weak reflections violating body-centered symmetry, reaches a maximum around 37 per cent meionite and extrapolates to zero at the pure end-members. All intermediate scapolites of the marialite-meionite series are pseudobody-centered, and as the composition approaches that of the end-members the structure becomes truly body-centered ($I4/m$).

The weak $h + k + l$ *odd* reflections are directly related to (1) order-disorder of Al and Si in the tetrahedral framework and (2) structural distortion from body-centered symmetry.

Scapolites may be regarded as a continuous, homogeneous solid solution. The cell dimensions are only approximately linearly related to composition and there is a maximum deviation from linearity for those scapolites (25% Me ~45% Me) whose symmetry departs the most from body-centered symmetry. These phenomena are interpreted in terms of the structural characteristic of the scapolites.

Zusammenfassung

Über schwache Reflexe, welche der Raumzentrierung der Skapolithe widersprechen

Röntgenbeugungs-Untersuchungen zeigen, daß die meisten Skapolithe der Raumgruppe $P4_2/n$ angehören. Die durchschnittliche Intensität der schwachen Reflexe, welche der Raumzentrierung widersprechen, erreicht bei 37% Meionit-Komponente ein Maximum — für die reinen Endglieder nähert sie sich dem Wert Null. Alle intermediären Skapolithe der Marialith-Meionit-Reihe sind pseudo-raumzentriert und mit Annäherung der Zusammensetzung an jene der Endglieder wird die Struktur echt raumzentriert ($I4/m$).

Die schwachen $h + k + l$ *ungerade* Reflexe stehen (1) mit Ordnung-Unordnung von Al und Si im Tetradergerüst und (2) mit strukturellen Abweichungen von der Raumzentrierung in Beziehung.

Die Skapolithe können als kontinuierliche homogene Mischkristallreihe betrachtet werden. Die Zelldimensionen ändern sich nur ungefähr linear mit der Zusammensetzung; die stärkste Abweichung von der Linearität tritt bei jenen Skapolithen (25% Me bis ~45% Me) auf, deren Symmetrie am stärksten von der Raumzentrierung abweicht. Diese Phänomene werden aus den strukturellen Eigenheiten der Skapolithe interpretiert.

Introduction

Studies of the crystal structure of scapolites were initiated by *Gossner* and *Brückl* (1928) and extended by *Pauling* (1930), *Schiebold* and *Seumel* (1932), *Scherillo* (1939), *Papike* and *Zoltai* (1965), and *Papike* and *Stephenson* (1966). The last two studies basically confirmed the structural model proposed by *Schiebold* and *Seumel* (1932). Nevertheless, some problems still remain unresolved, e.g. the interpretation regarding the presence of the weak reflections violating body-centered symmetry. The space group of scapolite has long been disputed. *Papike* and *Stephenson* (1966) reported the presence of weak reflections violating body-centered symmetry, but they refined the structure according to the space group $I4/m$. In a preliminary survey the writers found that scapolites from the McMaster departmental collection showed distinct reflections of the type $h + k + l$ *odd* as did the marialite (ON8) of *Papike* and *Zoltai* (1965). A reinvestigation of the space groups and crystal structures of scapolites is therefore desirable. The crystal structure of several scapolites each with different compositions has been redetermined in the newly determined space group $P4_2/n$ (*Lin*, 1971; *Lin* and *Burley*, 1973). The present report concerns the space groups and cell parameters of scapolites and contains discussion of the relationship between the weak $h + k + l$ *odd* reflections and the crystal structure of scapolites (see abstract by *Lin* and *Burley*, 1971).

Previous Studies on the Space Group of Scapolite

Table 1 lists the unit cell dimensions and the seven different space groups previously reported. Recently, an abstract by *Ulbrich* (1971) also reported the space group $P4_2/n$ for some intermediate scapolites. Most previous workers failed to observe the weak $h + k + l$ *odd* reflections, perhaps because they used either powder methods or the highly absorbed Cu$K\alpha$ radiation with single crystal methods.

Piezoelectric experiments (except *Greenwood*, 1935) and statistical tests of centrosymmetry (*Burley* et al., 1961; *Papike* and *Zoltai*, 1965) support the presence of a center.

Table 1. *Cell Dimensions and Space Groups of Scapolites Reported Previously*

Composition (% Me)[1]	Cell edges (Å) *c*	*a*	Space group	Reference	Sample Locality
41	7.65	12.21	$I4/m$ or $I4_1/a$	*Gossner* and *Brückl* (1927)	Grasse Lake N.Y.
41	7.65	12.21	$P4_2/m$ or $P4_2/n$	*Gossner* and *Brückl* (1928)	Grasse Lake N.Y.
90	7.66	12.27	$I4/m$, $I4$	*Pauling*	Vesuvius and
50	—	—	or $I4$	(1930)	Bedford, Ont.
69	7.54	12.13	$I4/m$	*Jakob* et al. (1931)	Tessin
47	7.580	12.09	$I4/m$, $I4$	*Schiebold* and	Arendal, Norway
84	7.619	12.19	or $I4$	*Seumel* (1932)	Mt. Somma, Italy
87	7.59	12.24	$I4/m$	*Scherillo* (1935)	Vesuvius
66	7.51	12.055	$P4/m$	*Burley* et al.	Quebec
50	7.571	12.095		*Gibbs* and	Grenville, Canada
70	7.569	12.163	$I4/m$	*Bloss* (1961)	Arendal, Norway
20	7.572	12.060	$I4/m$	*Papike* and *Zoltai* (1965)	Gooderham, Ontario
70	7.569	12.169	$I4/m$	*Papike* and *Stephenson* (1966)	Grenville, Quebec

[1] % Me = 100 (Ca + Sr + Fe + Mn + Mg + Ba)/(Na + K + Ca + + Sr + Fe + Mn + Mg + Ba), see *Shaw* (1960) and *Deer* et al. (1963).

Experiments and Results

Specimen Descriptions

Table 2 describes the specimens. Most were of good quality. However, inhomogeneities (inclusions, alteration zoning or intimate intergrowths) were noted in some specimens. Specimen M730 appears to be the most seriously affected in this manner. Many of the specimens have been chemically analyzed (Table 3) either by conventional chemical method, by microprobe or both. Where there was a significant discrepancy or contamination was suspected, such as in the case of M730, the microprobe data were preferred. For those specimens which were not analyzed, their meionite contents were estimated by optical methods (*Shaw*, 1960) and checked by X-ray methods.

Determination of Space Group

These specimens were studied mainly by the precession method, using Mo$K\alpha$ radiation. Weissenberg and rotation methods were also employed. It was concluded that the space group of all the scapolite

Table 2. *Occurrence and Localities of Scapolite Samples*

Sample	Appearance	Mineral Assemblage	Occurrence	Locality
ON8	Bluish grey; massive; compact	Scapolite Feldspar Nepheline	Syenite-pegmatite	Glamorgan Twp., Ontario
GL	Blue with whitish spots	Scapolite Amphibole Plagioclase	Zoned skarn in marble	Pontefract Twp., Quebec
ON6A	Colorless to slightly yellowish, transparent	Scapolite Pyroxene Sphene	Scapolite-pyroxene granulite	Monmouth Twp., Ontario
ON70	Pale-yellow, transparent, single-crystal; gem-quality	Scapolite Quartz	Druses in quartzo-feldsparthic gneiss	Mpwapwa, Tanzania
M637	Coarse, columnar, aggregates white, massive	—	Pegmatite?	New York, U.S.A.
XL	Honey-yellow transparent single, prismatic crystal, gem-quality	Scapolite Beryl Radioactive minerals	Pegmatite	Tsarasaotra, Madagascar
Q85	White, brittle non-transluscent	Calcite Amphibole Diopside	Pegmatitic skarn	Huddersfield Twp., Quebec
M730	Honey-yellow, translucent; altered	—	Pegmatitic skarn	Granville, Quebec
ON47	White, brittle, bladed	—	—	Slyndyanka Siberia U.S.S.R.
ON45	Tiny, prismatic single crystal, colorless	—	Ejected block in tuff with lava flow	Monte Somma, Italy

specimens except ON45 is $P4_2/n$. It should be noted that the space group $P4_2/n$ is uniquely determinable by extinctions.

The reflections $h + k + l = 2n + 1$ are systematically weaker than $h + k + l = 2n$ spectra, and insufficient exposure time could be one of the reasons why these extra weak reflections have not been reported previously. Smaller crystals require exposures up to one week or more

Table 3. *Atomic Proportions and Physical Properties of Scapolites* [Based on Si + Al = 12000]

Atom	ON8	GL[a]	ON6A	ON70	M637	XL	Q85	M730	ON47	ON45
Si	8334	8017	8044	7919	7643	7522	7272	5864	6790	6270
Al	3666	3983	3956	4081	4357	4478	4729	5136	5109	5730
Fe	8	0	11	21	—	—	5	1	9	19
Mn	1	0	1	2	—	—	0	0	1	0
Mg	7	2	2	4	—	—	11	7	16	19
Ca	744	1340	1382	1580	2001	2072	2568	2982	3080	3699
Na	2934	2581	2400	2213	1856	1703	1332	919	762	196
K	214	20	190	181	144	225	57	95	47	95
Ba	0	4	0	0	—	—	0	0	0	0
Sr	1	7	7	6	—	—	26	14	17	7
Cl	721	575	570	480	351	367	212	5	8	27
S	3	21	36	123	0	191	164	167	188	26
C	218	379[b]	339[b]	444	649[c]	443[c]	555[b]	597[b]	673	—
H	422	—	—	79.6	—	—	—	—	—	—
Σ Na[d]	3148	2601	2590	2394	2000	1928	1383	1014	809	291
Σ Ca	760	1349	1403	1607	2001	2072	2610	3004	3123	3744
AN	942	975	945	1047	1000	1001	931	769	870	—
% Me	19.4	34.2	35.1	40.3	50.0	51.8	65.3	74.2	79.4	92.8
n_m	1.545	1.553	1.554	1.558 H,e	1.558 L,e	1.560 L,e	1.569	1.571	1.576	1.580
Sp. Gr.	2.619	—	2.660	2.67 H,e		2.69 L,e	2.705	2.703	—	2.79 L,e

a Microprobe analyses of GL, ON6A, Q85, M730 and ON45 are from *Evans* et al. (1969); chemical analyses of ON70 and ON47 are from *Haughton* (1967); chemical analysis of ON8 is from *Shaw* (1970); and the microprobe analyses of M637 and XL are from *Lin* (1971).

b Data available from conventional wet chemical analyser (see *Evans* et al., 1969).

c Data derived by using the crystal-chemical relationship that the total atomic proportions of C, S and Cl is equal to 1.0, based on Si + Al = 12.0.

d Σ Na = Na + K; Σ Ca = Ca + Fe + Mn + Sr + Ba + Mg; AN = C + Cl + S + F; % Me = [Σ Ca/(ΣCa + ΣNa)] × 100; n_m = mean refractive index.

e L = measurement done by writers; H = done by *Haughton* (1967) and the rest done by *Shaw* (1960, 1965).

to reveal the weak reflections. Regardless of differences in composition or size of samples, the weak reflections $h + k + l$ *odd* are always present. Further these $h + k + l$ *odd* reflections have the same relative order of intensities, e.g., (067) reflection is the strongest $h + k + l$ *odd* reflection in all specimens. However, the intensity of the $h + k + l$ *odd* reflections relative to the $h + k + l$ *even* reflections varies with composition.

Using the Weissenberg method one month exposures were taken of the $(00l)$ reflections, with l up to 20. The result confirmed the conclusion from the precession method that reflections with $l \neq 2n$ are extinct.

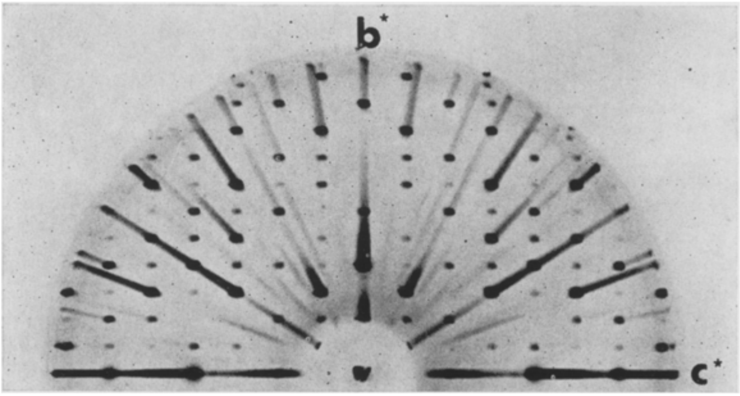

Fig. 1. An $0kl$ precession photograph of scapolite (M637, 50% Me), Mo$K\alpha$ radiation, $\mu = 20°$, 16 hrs.

Fig. 1 illustrates that the reflections $h + k + l$ *odd* are rather strong for specimen M637.

Specimen ON45 is the most Ca-rich scapolite (93% Me) ever found in nature. It is the only scapolite that does not exhibit weak reflections violating body-centered symmetry, even in photographs with a 10-day exposure. This does not necessarily mean that ON45 is body-centered. The writers believe that the $h + k + l$ *odd* reflection of ON45 may be less intense than the detection limit of the method employed. The crystal structure of scapolite ON45 could be refined for 3 dim. data in space group $I4/m$ to $R = 0.079$, in space group $P4_2/n$, however, to $R = 0.072$ (*Lin*, 1971).

Unit Cell Dimensions of Scapolites

The cell dimensions (Table 4) of each specimen were measured from peaks on powder diffractograms or from Debye-Scherrer photographs (for small specimens), and refined with a least-squares technique. In both methods Cu$K\alpha$ radiation was used. The diffractograms were prepared on a scale 1″/°2θ, using α-quartz as an internal standard and the precision in measurement of 2θ is ± 0.01°.

The cell parameters are plotted in Fig. 2. There is no indication of an abrupt structural change in the solid solution series. However, the effect of the structural distortion on the cell dimensions will be discussed later.

Table 4. *Unit Cell Parameters of the Scapolites*

Specimen	%Me	*a* (Å)	*c* (Å)	*V* (Å^3)	Method
ON8	20	12.059 (1)[a]	7.587 (2)	1103.22	chart
GL	34	12.060 (3)	7.589 (5)	1103.83	chart
ON6A	35	12.071 (4)	7.582 (4)	1104.83	chart
ON70	40	12.063 (3)	7.585 (3)	1103.77	chart
M637	50	12.107 (2)	7.577 (3)	1110.70	chart
XL	52	12.116 (1)	7.581 (2)	1112.98	chart
Q85	65	12.147 (1)	7.576 (2)	1117.69	chart
M730	74	12.156 (4)	7.556 (6)	1116.47	film[b]
ON47	80	12.168 (3)	7.571 (4)	1120.86	chart
ON45	93	12.194 (4)	7.557 (4)	1123.68	film

a Estimated standard deviation in parentheses refers to the last digit.
b Data may be not so reliable due to the poor quality of sample.

Measurements of the Intensity of the $h+k+l$ *odd* Reflections of Scapolites

As stated previously, the same $h+k+l$ *odd* reflections are present in all specimens, although their intensities relative to those with $h+k+l$ *even* vary with composition. Moreover, the order of intensities among the $h+k+l$ *odd* reflections remain nearly the same from specimen to specimen. This important relationship may be shown by plotting the ratio (r) of the total intensity (or mean intensity) of the $h+k+l$ *odd* reflections to the total intensity (or mean intensity) of the $h+k+l$ *even* reflections within the same reciprocal space for each specimen against its chemical composition. In order to reduce the labour only the ($0kl$) level of reciprocal space was used in this study. The photometrically measured intensities for specimens ON8, GL, ON70, XL, Q85, M730 and ON47 were collected by an integrating precession film technique using Zr-filtered Mo radiation and were corrected for Lorentz and polarization effects, but no absorption corrections were made; 30 $h+k+l$ *odd* and 66 $h+k+l$ *even* reflexions were considered. The data for specimen XL were also collected on a single-crystal diffractometer and these compare well with the film data.

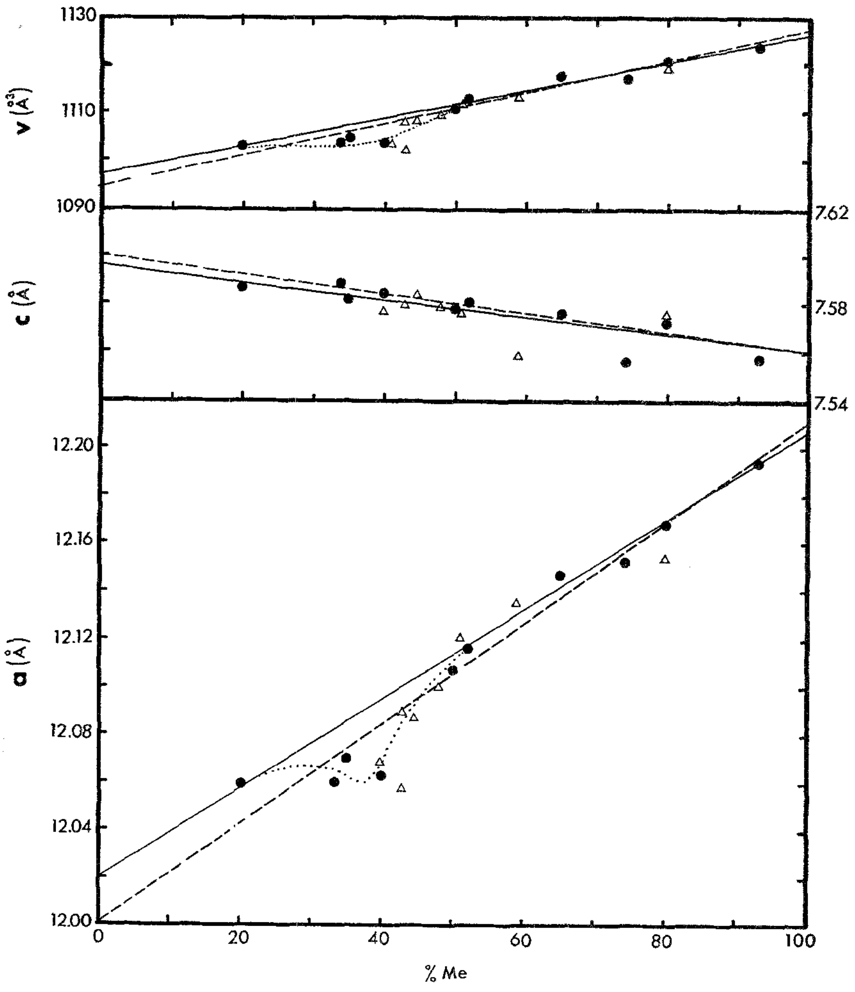

Fig. 2. The cell dimensions of scapolites as a function of the chemical composition (% Me). The dashed line represents the linear regression covering whole range of composition, while the full line, the linear regression excluding the tange of 25% Me ~ 45% Me. Dots are data from present study and triangles are data from *Haughton* (1967).

Discussion

Intensities of $h + k + l$ *odd* Reflections and Their Relationship to the Chemical Composition of Scapolite

The stoichiometric line (Fig. 3a) was derived by plotting Cl atoms against Ca + Sr atoms, on a basis of Si + Al = 24.0. Fig. 3b is a plot of the ratio (r) against the % Me (cf. Table 3) of the scapolites. The ratio increases to a maximum near 37% Me. This plotting has also been checked by visual comparison with the intensity of two other scapolites, M637 and ON6A. There is a relationship between this r-% Me curve and the stoichiometric line of scapolite (Figs. 3 a, b). It is known that the

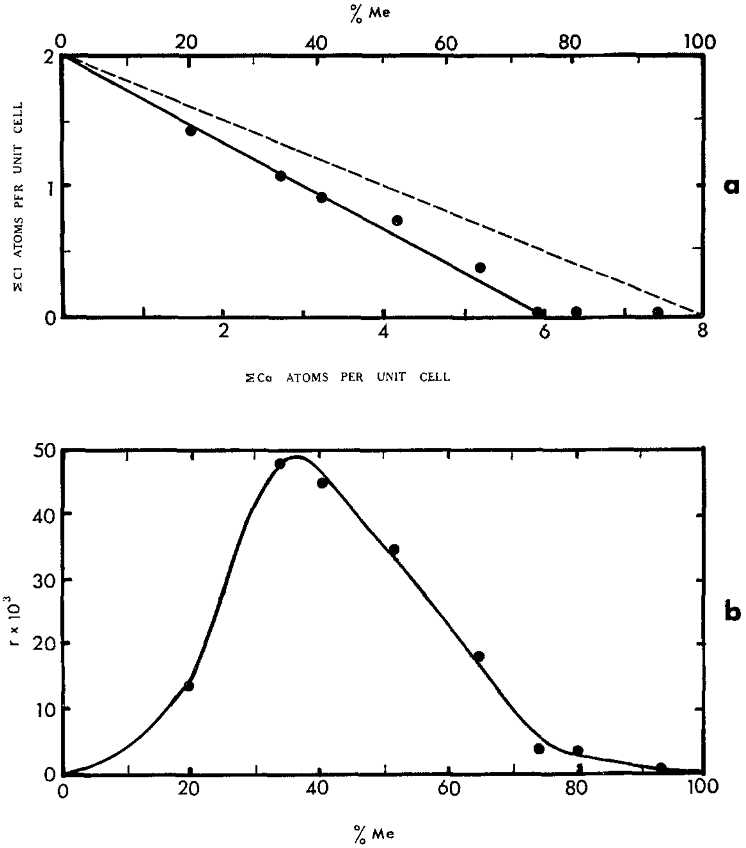

Fig. 3. (a) The stoichiometry of scapolites. The full line represents the real stoichiometry and the dashed line represents the ideal stoichiometry. (b) The relationship derived by plotting the ratio r ($r = \Sigma I_{h+k+l=odd} / \Sigma I_{h+k+l=even}$) vs. % Me of scapolites.

substitutions Na $\rightleftharpoons$ Ca and Si $\rightleftharpoons$ Al can take place without introducing a profound change of crystal structure in many minerals. However, the replacement of Cl^- by CO_3^{2-} or the minor SO_4^{2-} in scapolites is likely to introduce a certain change in the crystal structure of scapolites because Cl^- and CO_3^{2-} (or SO_4^{2-}) are more physically and chemically different. The departure from the structure of pure marialite or meionite caused by the strain due to the difference between Cl^- and ($CO_3^{2-} + SO_4^{2-}$) will be likely to reach a maximum with both Cl^- and ($CO_3^{2-} + SO_4^{2-}$) are present in equal amount in the crystal.

Considering chlorine in Fig. 3 a, the number of Cl atoms falls linearly to less than 0.1 at about Ca + Sr = 6.0. That is, from about 75% to 100% Me scapolite contain almost only CO_3^{2-}, probably plus the small amount of SO_4^{2-} (*Evans* et al., 1969). At about 37% Me, scapolites have an equal amount of Cl^- and ($CO_3^{2-} + SO_4^{2-}$), i.e., the anion sites are occupied half by Cl^- and ($CO_3^{2-} + SO_4^{2-}$). Consequently, a scapolite at this composition would have a maximum structural departure from both the chlorine end-member (i.e., pure marialite $Na_4Al_3Si_9O_{24}Cl$) and the carbonate end-member (i.e., carbonate-meionite $Na_{1-0}Ca_{3-4}Al_{5-6}Si_{7-6}O_{24}CO_3$) if the very minor SO_4^{2-} is ignored. This corresponds to the apex of the r-% Me curve (Fig. 3 b) which also occurs at about 37% Me. At 0% Me, scapolite is free of CO_3^{2-} and presumably has by extrapolation no $h + k + l$ *odd* reflections. Hence the pure marialite probably is body-centered. Similarly from 75% Me to 100% Me, scapolite is virtually free from Cl^- anion and should also be body-centered. Nevertheless, the natural scapolites with composition from 75% Me to 100% Me, usually contain not only a small amount of chlorine, but also a minor amount of sulfur, and this may be the reason why specimens M730 and ON47 still show very weak reflections of $h + k + l$ *odd*.

Superlattice Reflections and Pseudosymmetric Structure of Scapolites

The superlattice reflections which are systematically much weaker than the remainder are ascribed to the pseudosymmetric structure of the crystal (*Mackay*, 1953). A pseudosymmetric structure is one in which the atoms are only slightly displaced from positions corresponding to higher symmetry structure, usually termed the ideal structure. It can also be regarded as a slight distortion of the ideal structure and its space group is a subgroup of that of the ideal structure. If the number of formula units in the unit cells of the two structures is the same, then the difference in cell dimensions will be quite small. Otherwise the cell dimensions of these two structures will be integral multiples of one another. In this case, the pseudosymmetric structure is also referred to as a superstructure, and the weak superlattice reflections thereby induced are also called "superstructure reflections" (*Vousden*, 1954). Taking into account the experimental results mentioned previously, the crystal structure of scapolite with the $P4_2/n$ space group is obviously a pseudo-symmetric structure as a result of distortion of the ideal structure with space group $I4/m$. The superlattice reflections thereby induced are the $h + k + l$ *odd* reflections.

The superlattice reflections could have two possible origins, viz. (a) a change in atomic distribution as a result of the ordering of a disordered structure. This phenomenon is common in alloy systems and may be a function of thermal history (*Bragg* and *Williams*, 1934; *Henry* et al., 1961). (b) A change in atomic coordinates as a result of the distortion of an ideal structure. In this case these reflections have intensities directly related to the atomic displacements from the ideal positions. These two types are not mutually exclusive, but are often coexistent and interrelated in crystal structure. The type (b) often implies type (a) for a crystal containing crystallochemically similar atoms.

A pure case of the (a) type can be recognized by the constancy of the ratio of the mean intensity of the main reflections to that of the superlattice reflections for all ranges of θ (*Mackay*, 1953). The intensity data of the $(0kl)$ layer of scapolites were used to test the nature of the scapolite superlattice reflections. The results indicate that the superlattice reflections are of type (b) but with a possible component of type (a) because of the presence of crystallochemically similar atoms such as Al and Si. The regularity of the curve in Fig. 3 b implies that the intensity of the superlattice reflections of scapolites appears to be essentially dependent on chemical composition because the scapolites represented are from various geological environments.

The general features of the atomic displacement from the ideal positions can be understood by comparing the space groups $I4/m$ and $P4_2/n$. $I4/m$ will be transformed into $P4_2/n$ through the loss of the mirror plane and one other symmetry element, concomitantly the number of general equivalent sites is reduced from 16 for $I4/m$ to 8 for $P4_2/n$. The scapolite unit cell contains two formula units, and both the marialite and meionite end-members have space group $I4/m$ (Fig. 3), so that the 8 Na atoms in marialite and the 8 Ca atoms in meionite are on the mirror plane. So are some (Si, Al) atoms and some oxygen atoms (cf. any previous structure reports, e.g. *Schiebold* and *Seumel*, 1932). However, as one end-member is mixed with the other end member, atoms such as Na or Ca, originally located on the mirror plane become displaced along the c-axis direction in addition to the horizontal directions and thus come off the mirror plane. The original set of general equivalent atoms (e.g. Si, Al, O) consistent with $I4/m$ segregate into two sets which are then displaced independently from their original ideal positions. The atomic displacement along c is one of the essential factors causing the superlattice reflections. Moreover, their intensities are found proportional to this displacement (*Lin*, 1971; *Lin* and *Burley*, 1973).

Another factor causing the superlattice reflections is the related ordering of Al and Si in the tetrahedral framework of scapolite. The general equivalent set of (Al, Si) sites in the scapolite structure consistent with $I4/m$, must separate into two different sets in that with $P4_2/n$. The greater the difference in Al occupancy between these two sets of sites, the higher the degree of ordering of Al and hence the lower the degree of the symmetry. The intensity of the superlattice reflection violating the body-centered symmetry is therefore proportional to the degree of ordering (*Lin*, 1971; *Lin* and *Burley*, 1973).

The Nature of Disorder in the Solid Solutions of Scapolites

Unlike many rock-forming minerals, no microscopic twinning or exsolution has been yet found in the scapolite group. Generally speaking, a crystal which can have submicroscopic twinning will also display microscopic twinning. In addition to the optical homogeneity, the results of X-ray diffraction also indicate that scapolite solid solution has no inhomogeneities. Further the nearly linear variation of the cell dimensions (Fig. 2) suggests no sharp discontinuity of the structure. The X-ray photos of all scapolites are similar in general appearance and only differ slightly in the intensity of reflections. Moreover, the reflection spots and layer lines are very well-defined. There are no reflection streaks, satellites or split reflections, diffuseness, composite superlattice lines etc. (*Chao* and *Taylor*, 1940; *Laves*, 1950; *Morimoto* and *Tokonami*, 1969; *Papike* and *Zoltai*, 1967). Further, neither submicroscopic twinning nor domains with different symmetry explain the observed fact that the intensity of the $h + k + l$ *odd* reflections is a function of the chemical composition of scapolite (Fig. 3b).

Variation of Cell Dimensions of Scapolites

The cell dimensions generally reflect the internal structure and chemical composition of crystals. In this paper, the variation of cell dimensions will be interpreted mainly by using the structural characteristic of scapolites instead of only using mathematical analysis without the proper knowledge of the scapolite structure. The a dimension of scapolite increases and the c dimension slightly decreases as % Me increases. The cell volume shows a nearly linear relationship with % Me (Fig. 2). These results generally agree with those found previously

(*Eugster* et al., 1962; *Papike*, 1964; *Haughton*, 1967), and can be explained by the following facts: (1) The aluminum content of the (Al, Si) tetrahedral framework increases as the % Me increases. The size of the framework increases because the Al—O bond is longer than Si—O bond. Thus the cell dimension a and the cell volume increase. (2) The Cl ion is replaced by the large planar CO_3^{2-} radical in the cavity of the scapolite structure as the % Me increases. The CO_3^{2-} radical lies mostly parallel to the (001) plane and distorts the crystal structure so that the a-axes are elongated whereas the c-axis is slightly shortened in spite of the expansion caused by the simultaneous increase of Al atoms in the framework. However, Fig. 2 also shows that points in the range 25% Me to 50% Me are scattered and show systematic deviations from the regression lines. The deviation can not be ascribed solely to the error of measurement. It is especially evident in the plotting of the a dimensions vs. % Me, and the cell volume V vs. % Me. Because $V = a^2 c$, it is also obvious that the three variables, V, a and c simultaneously can not be

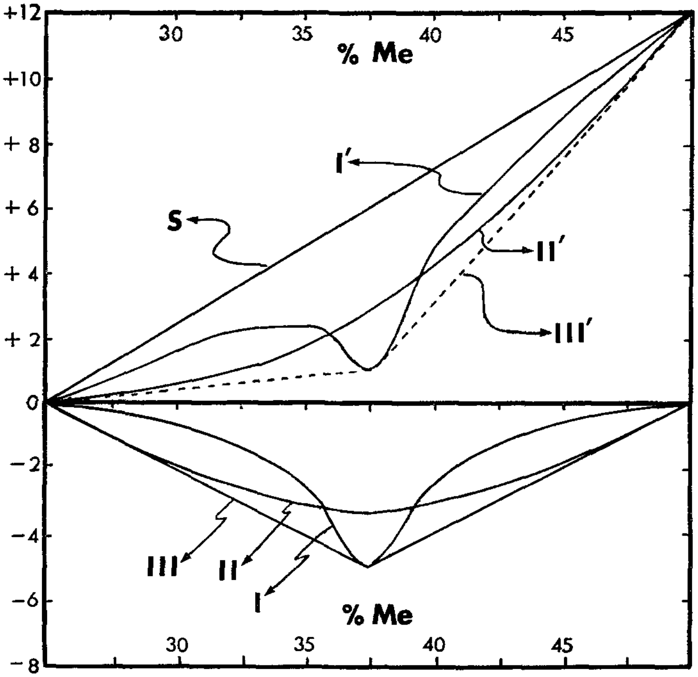

Fig. 4. Idealized illustration of the formation of the deviation from linearity on the plots of a vs. % Me and V vs. % Me by combining two kinds of curves representing two kinds of effects (see text). The length of the vertical unit is arbitrary but roughly 1 unit = 0.0033 Å.

linear functions of composition. The distortion of the ideal structure will in general result in a change in cell dimensions. In fact, in the structural analyses described in *Lin* (1971) and *Lin* and *Burley* (1973)

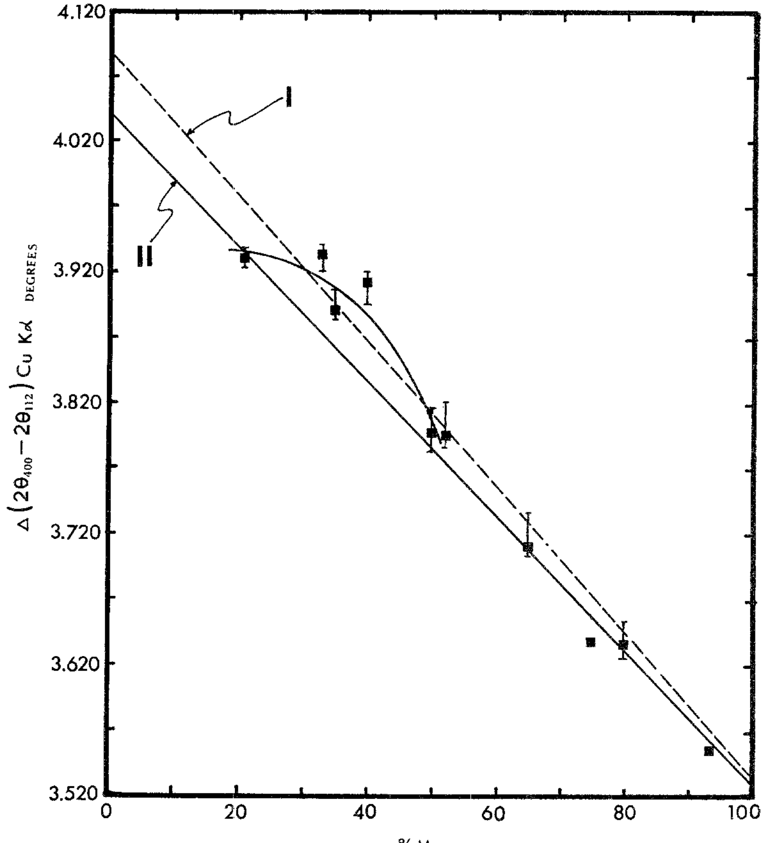

Fig. 5. Variation $\Delta\ (2\theta_{400} - 2\theta_{112})\mathrm{Cu}K\alpha$ with composition. The squares are the data calculated from the cell dimensions; the vertical bars indicate values measured from the powder diffractograms with its standard deviation. The dashed line represents the regression covering the whole range of composition, while the full line represents the regression excluding the range of 25% ~ 45% Me. The domed curve corresponds to the systematic deviation of cell dimensions from the linear regression in the range of 25% ~ 45% Me (Fig. 2).

the $CO_3{}^{2-}$ planar group in scapolite with 25 ~ 50% Me has been found to be considerably inclined to the (001) plane. This inclined orientation of the $CO_3{}^{2-}$ group will lessen the effect of increasing the *a*-axis as remarked above. Further the inclination of the $CO_3{}^{2-}$ planar group is proportional to the intensity of the $h + k + l$ *odd* reflections, so that the CO_3 group is most inclined to (001), at the composition around 37% Me (Fig. 3b). The depressed points systematically deviating from the linear regression line in Fig. 2, therefore, can be explained as a result of the combined effect of (1) the linear variation caused by increasing amounts of Al and CO_3^{2-} and (2) the variation due to the inclination of the CO_3 group from the (001) plane. The combined effect can be hypothetically illustrated by Fig. 4. The sloping line (S) represents the first kind of effect on the cell edge a and the curves (I, II, III) are supposed to be possible types of curve representing the second kind of effect. Then the idealized shape of the deviating curve can be simply formed by combining the slope line (S) and curve I or II or III to get the deviation curve I′ or II′ or III′, which looks quite similar to those in Fig. 2.

Because the deviation from linearity of a vs. % Me (Fig. 2) is systematic and considerable, it is appropriate to draw two regression lines: one icluding all the plotted points over the whole range and another one excluding the plotted points between 25% Me and 45% Me. The variation in cell dimensions will be probably further complicated by a considerable content of SO_4^{2-} or K^+ in scapolites. The regression line of cell volume vs. % Me can be used to estimate the % Me, because the precision of measurement of the cell volume is usually less than 1 Å^3 and the error in composition not more than 5% Me. The equation is $\% \text{Me} = 3.1192\, V - 3413.57$.

The variation of $(2\theta_{400}\text{–}2\theta_{112})\text{CuK}\alpha$ with composition (*Burley* et al. 1961) can also be used for roughly estimating the composition of scapolite. Both the averaged $(2\theta_{400}\text{–}2\theta_{112})\text{CuK}\alpha$ observed from powder diffractograms and the calculated $(2\theta_{400}\text{–}2\theta_{112})\text{CuK}\alpha$ from the cell dimensions for each specimen are plotted against the % Me in Fig. 5. The corresponding regression curves as a result of calculated based on the regression lines in the plots of cell dimensions vs. % Me (Fig. 2) are also shown in Fig. 5 and found to be practically straight. Line I is a regression including the range 25% to 45% Me. The deviation shown by the dome curve between 25% Me and 45% Me in Fig. 5 corresponds to the systematic deviation of the cell dimensions in the same chemical range discussed previously.

In summary, the fact that the maximum deviation of the cell dimensions from linearity coincides with the higher intensity of the $h + k + l$ *odd* reflections in the same composition range (Figs. 2 and 3) implies that scapolite does have a structural distortion as a function of composition. The further the structure deviates from the body-centred symmetry, the smaller the cell volume and the cell edge a become relative to the one expected from the linear regression. The variation of the cell dimensions may also be expected to affect the density, and the mean refractive index (n_m) of scapolites.

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