For x moles of forsterite to one mole of diopside, we can write the structural formula,

$$(\mathrm{Ca}_{1-2z}\mathrm{Mg}_{2z})\ \mathrm{Mg}_{1+z}\ (\mathrm{Si}_{2-z}\mathrm{Mg}_z)\ \mathrm{O}_6,\ \text{where } z=2x/(6+4x).$$

Magnesium must substitute not only for calcium but also for silicon. In addition magnesium must occur interstitially. Random replacement of silicon by magnesium has not been reported in silicates. Magnesium has been found in tetrahedral oxygen coordination, in structures such as spinel (Bacon, 1952) and melilite (Smith, 1953), but the Mg–O distance (1·87 Å) in melilite exceeds that of Si–O (1·63 Å) by 15%. It is also difficult to see where in the structure interstitial magnesium could be placed.

3. If *the sum of the metal ions is considered constant*, the formula becomes $\mathrm{Ca}_{0.94_3}\mathrm{Mg}_{1.09_4}\mathrm{Si}_{1.96_3}\mathrm{O}_{5.96}$ or, for x moles of forsterite to one mole of diopside,

$$(\mathrm{Ca}_{1-3u}\mathrm{Mg}_{3u})\mathrm{Mg}(\mathrm{Si}_{2-2u}\mathrm{Mg}_{2u})\mathrm{O}_{6-2u},\quad \text{where}\quad u=x/(4+3x).$$

In this interpretation magnesium must again substitute for calcium and for silicon, but it is not necessary to postulate interstitial magnesium. Instead there is a deficiency of oxygen atoms, so that we are dealing with an omission solid solution. Structurally this means that some oxygen tetrahedra share more than two corners, so we must expect adjacent single chains occasionally to cross-link by sharing one oxygen atom. These amphibole-type cross-linkages would have to occur, on the average, once in every six cells for maximum solid solution. (One formula contains 5·96 oxygen atoms, which is 0·04 short of the 6 oxygen atoms in diopside. Per cell the number of deficient oxygen atoms is 0·16).

Table 1 summarizes the three interpretations and shows how very difficult it will be to find the correct one from density determinations, even if good single crystals should become available. Powder data of the maximum solid solution lead to a cell volume (439·03 Å)^3 (Kushiro, private communication) equal to that of pure diopside (439·08 Å)^3, which was determined by Clark, Schairer, & de Neufville (1962). These values were used in the density calculations (Table 1).

It is a pleasure to thank Dr J. F. Schairer, who drew my attention to the phenomenon, and also Professor J. D. H. Donnay and Dr Hatten S. Yoder, Jr., who critically read the manuscript and made many pertinent suggestions.

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Anomalous dispersion in LiGaO$_2$

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(*Received* 17 *November* 1964 *and in revised form* 25 *January* 1965)

The anomalous scattering of Cu $K\alpha$ radiation by a single crystal of lithium metagallate, LiGaO$_2$, is reported in this note. The structure of this compound has been determined recently by the writer (1965*a*). It is orthorhombic ($a=5{\cdot}402$, $b=6{\cdot}372$, $c=5{\cdot}007$ Å) with space group symmetry $Pna2_1$ and four molecules per unit cell.

The atomic scattering factor is a complex quantity $f'=f_0+\Delta f'+i\Delta f''=f+i\Delta f''$[*], so that in general in acentric structures I_{hkl} is different from $I_{\bar{h}\bar{k}\bar{l}}$. This effect, known as the anomalous dispersion effect, has been used increasingly in the last few years for determining absolute configurations. In a recent paper Zachariasen (1965) has shown that this effect can be conveniently expressed by the dimensionless quantity X_H defined by:

$$X_H=\frac{I_H-I_{\bar{H}}}{\frac{1}{2}(I_H+I_{\bar{H}})}$$

$$=\frac{4}{|F|^2+|\Psi|^2}\sum_{j>k}\sum|F_j||F_k|\ (\delta_j-\delta_k)\sin(\alpha_k-\alpha_j)$$

where:

I_H = intensity of the hkl reflection

$I_{\bar{H}}$ = intensity of the $\bar{h}\bar{k}\bar{l}$ reflection

F = structure factor corresponding to the f's

Ψ = structure factor corresponding to the $\Delta f''$'s

α = phase of F

δ = $\Delta f''/f$, where $f=f_0+\Delta f'$

F_j (or F_k) = contribution to the scattering amplitude due to the atoms of the jth (or kth) chemical species.

For LiGaO$_2$ we have:

$$X_H=\frac{4}{|F|^2+|\Psi|^2}\{(\delta_{\mathrm{Ga}}-\delta_{\mathrm{O}})|F_{\mathrm{Ga}}||F_{\mathrm{O}}|\sin(\alpha_{\mathrm{O}}-\alpha_{\mathrm{Ga}})$$
$$+(\delta_{\mathrm{Ga}}-\delta_{\mathrm{Li}})|F_{\mathrm{Ga}}||F_{\mathrm{Li}}|\sin(\alpha_{\mathrm{Li}}-\alpha_{\mathrm{Ga}})$$
$$+(\delta_{\mathrm{O}}-\delta_{\mathrm{Li}})|F_{\mathrm{O}}||F_{\mathrm{Li}}|\sin(\alpha_{\mathrm{Li}}-\alpha_{\mathrm{O}})\}\ .$$

X_H is a function of the difference $\delta_j-\delta_k$, but for this compound δ_{Ga} and δ_{O} can be obtained independently if one sets $\delta_{\mathrm{Li}}=0$, since the latter is negligible with respect to δ_{Ga} and δ_{O}. Furthermore, $|\Psi|$ is small with respect to $|F|$ and therefore one can neglect $|\Psi|^2$ with respect to $|F|^2$. The above equation then becomes:

$$X_H=\frac{4}{|F|^2}\delta_{\mathrm{Ga}}(A_{\mathrm{Ga}}B-B_{\mathrm{Ga}}A)+\delta_{\mathrm{O}}(A_{\mathrm{O}}B-B_{\mathrm{O}}A)$$

where $A=|F|\cos\alpha$, $B=|F|\sin\alpha$, $A_{\mathrm{Ga}}=|F_{\mathrm{Ga}}|\cos\alpha_{\mathrm{Ga}}$, *etc.*

The observation of this effect does not require the use of special apparatus for measuring X-ray intensity or the use of unusual wave lengths. For instance, values of $|X_H|$ up to 50% can be observed for some reflection pairs in quartz

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[*] $f_0=\int_0^\infty U(r)\,\frac{\sin sr}{sr}\,dr$, namely the atomic scattering factor as ordinarily tabulated. $\Delta f'$ and $\Delta f''$ are the real and imaginary dispersion corrections.

(Zachariasen, 1965), and in $LiAlO_2$ (Marezio, 1965*b*). In both cases the Cu $K\alpha$ wavelength is less than one fourth that of the nearest critical absorption edge.

During the determination of the structure of $LiGaO_2$, the intensities of all $0kl$, $1kl$, $h0l$, $h1l$, $hk0$ and $hk1$ reflections were measured with Cu $K\alpha$ radiation and a General Electric XRD-3 spectrometer rebuilt for single-crystal work and equipped with a proportional counter. The dispersion effect was observed for the $0kl$, $1kl$, $h0l$ and $h1l$ reflections. It was not observed for the $hk0$ and $hk1$ reflections, in the first case because $X_H=0$ by symmetry, and in the second case because the intensities corresponding to $\bar{\mathrm{H}}$ were not measured. The half width of the distribution function for the $|X_H|$ values is 2·9 %, which is not much greater than the accuracy of the intensity measurements. It was estimated that the standard deviation for each measurement varied from 1 % for strong reflections to 3 % for the weakest reflections.

A comparison between observed and calculated X_H is given in Table 1 for those reflections which have $|X_H|$ greater than the accuracy of the intensity measurements. The X's were obtained using $\Delta f''_{Ga}=0{\cdot}903$ and $\Delta f''_{O}=0{\cdot}035$, which are the values calculated from the atomic absorption coefficients given in *International Tables for X-ray Crystallography* (1962). As was pointed out by Zachariasen (1965) fairly good values for $\Delta f''$ can be calculated from the atomic absorption coefficients, $\mu_a=(2e^2\lambda/mc^2)\Delta f''$, on the assumption that true absorption is the predominant process. During the refinement of the structure of $LiGaO_2$ the real part of the anomalous dispersion correction was applied to the scattering factor of gallium. The value used ($\Delta f'_{Ga}=-1{\cdot}5$) was taken from *International Tables for X-Ray Crystallography* (1962).

As can be seen, the dispersion effect is small as expected, but distinctly noticeable, even though the nearest critical absorption edge of the long wave side of Cu $K\alpha$ wave length is the L absorption edge of gallium (11·149 Å). Although the agreement obtained between $|X_c|$ and $|X_o|$ is satisfactory, it is not good enough for a calculation of $\Delta f''_{Ga}$ and $\Delta f''_{O}$ independently. In the fourth column of Table 1 the calculated $\Delta f''_{Ga}$ values are shown for those reflections for which $|X|\geq 0{\cdot}05$ when $\Delta f''_{O}$ is assumed to be 0·028, which was obtained experimentally in $LiAlO_2$ (Marezio, 1965*b*). The average of the $\Delta f''_{Ga}$ – values shown in Table 1 is 0·89 ± 0·03, which is in fairly good agreement with the value calculated from the atomic absorption coefficient (0·90) and with the value (0·9) given in the *International Tables for X-Ray Crystallography* (1962).

Table 1. *Anomalous dispersion data for* $LiGaO_2$

hkl	$X_o\,.\,10^2$	$X_c\,.\,10^2$	$\Delta f''_{Ga}$
002	−3·5	−4·2	
121	7·6	6·4	0·98
201	7·1	6·4	0·95
212	3·0	1·5	
203	5·1	2·5	
401	6·5	5·3	1·01
114	3·3	2·4	
214	2·5	2·3	
134	4·9	2·3	
403	4·5	2·6	
511	3·7	5·6	
413	−4·6	−4·9	
161	5·0	5·0	0·90
512	3·3	1·4	
414	3·6	2·7	
513	3·4	2·6	
071	6·3	5·5	0·96
601	6·6	9·1	0·73
163	4·1	3·0	
154	3·6	2·9	
602	−3·9	−5·6	
172	5·4	5·0	0·93
006	5·9	6·3	0·81
116	3·0	2·2	
064	−9·9	−10·0	0·85
073	4·8	2·9	
126	5·1	6·8	0·69
206	7·2	6·5	0·93

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Some new intermetallic compounds of holmium and erbium with Ag, Au, Pt, Al, In, Tl, and Ge.

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(*Received* 4 *January* 1965)

During an extensive investigation of the binary alloy systems of holmium and erbium in combination with twenty-one metallic elements a number of new intermediate phases were identified. The general approach and pattern of this study was suggested by results of earlier work described by Moriarty (1960). Structural data for compounds formed in similar systems with gadolinium and dysprosium can be found in reports by Baenziger & Moriarty (1961), also by McMasters & Gschneidner (1964).

Alloys were prepared by arc-melting stoichiometric proportions of the components on a water cooled copper hearth under an argon gas atmosphere. Each specimen was remelted repeatedly to improve homogeneity. Final weights differed from initial weights by less than 1·0 %. Purities of the metals used were: holmium and erbium, 99·8 %; all others were greater than 98·5 %.

In all cases the phases were identified by indexing the X-ray diffraction powder photographs. Diffraction equipment included a basic Norelco X-ray unit, using filtered copper radiation, 114·6 mm Debye–Scherrer cameras and Ansco Superay C film. The photographs were made of the

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