Ga(1)–4 Pu	3·23 ± 0·03 Å	–4 Ga(2)	3·06 ± 0·02
–1 Ga(1)	2·54 ± 0·13	–1 Ga(2)	3·15 ± 0·07
–4 Ga(2)	2·58 ± 0·05	–2 Ga(2)	3·19 ± 0·10

The mean value Pu–12 Ga = 3·18 Å is considerably larger than the distance Pu–13 Ga = 3·08 Å observed in $PuGa_4$, and suggests that the effective valence of plutonium is four in $PuGa_6$ and closer to five in $PuGa_4$.

In gallium metal each atom forms seven bonds, one of length 2·44 Å and six in the range 2·71–2·80 Å. Short Ga–Ga bonds of 2·45 Å also occur in $PuGa_2$ (Ellinger, Land & Struebing, 1965).

The authors are grateful to V. O. Struebing for preparation of the alloys, to M. Gibbs and P. Vigil for aid in obtaining the X-ray data, and to D. T. Cromer for the $PuGa_4$ intensity and interatomic distance calculations.

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Hybrid solid solution.

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The purpose of this note is to draw the attention of crystallographers to the existence of an unusual kind of solid solution, which was discovered by Kushiro & Schairer (1963). Forsterite, Mg_2SiO_4, an orthosilicate (isolated tetrahedra), forms a limited solid solution in diopside, $CaMg\,Si_2O_6$, a metasilicate (chains of tetrahedra). Such a solid solution, which not only involves the usual topological rearrangements of the crystal structure of the solvent, but also requires changes in the anionic building blocks themselves, is here called a *hybrid solid solution*. In the three common types of solid solution, substitution, addition and omission, minor structural rearrangements accompany the variations in composition; no strong linkages, such as Si–O bonds, are broken. In the present case the ratio of tetrahedrally coordinated cation to oxygen changes from 1:3 in diopside towards 1:4 in forsterite. Drastic structural rearrangements must take place, which will be shown to involve more than one type of solid solution. The three most likely hypotheses will be discussed in turn. A fourth one, involving cation vacancies at the centers of oxygen tetrahedra will be presented by Kushiro & Schairer in the forthcoming publication of their phase-diagram study.

Above 1300°C and up to the melting point, forsterite can amount to about 5 weight per cent of the solid solution in diopside, so that the composition can be written in moles per cent: $Di_{93}Fo_7$. For reference in the subsequent discussion we write:

$$CaMgSi_2O_6 + 0{\cdot}08\ Mg_2SiO_4 = CaMg_{1.16}Si_{2.08}O_{6.32}\ .$$

1. If *the number of silicon atoms is considered constant*, the formula becomes $Ca_{0.96}Mg_{1.12}Si_{2.00}O_{6.08}$ or, for x moles of forsterite to one mole of diopside, $(Ca_{1-y}Mg_y)\ Mg_{1+2y}\ Si_2\ O_{6+2y}$, where $y = x/(2+x)$.

The Si/O ratio is now less than $\frac{1}{3}$ and some of the silicon tetrahedra must share only one corner instead of two. This would result from breaking one Si–O bond in the $Si_2O_6^{4-}$ chain, and adding one oxygen atom to the depleted tetrahedron. The broken ends of the chain must move apart and one of the added magnesium ions would fit between them. Moreover, for every two such magnesium ions, one more magnesium ion is added, which substitutes for calcium. The cells where the breaks occur must be randomly distributed. Since there are four diopside formula units per cell, the maximum number of chain-breaks is 4 × 0·08 = 0·32, or about one in every three unit cells.

2. If *the number of oxygen atoms is considered constant*, the formula becomes $Ca_{0.95}Mg_{1.10}Si_{1.97}O_{6.00}$.

Table 1. *Calculated densities of diopside-forsterite solid solution in the three structural interpretations*

	Type	Formula	Formula weight	Density, calc.
End member	Diopside	$CaMgSi_2O_6$	216·56	3·275* g.cm⁻³
Hybrid solid solution	Substitution and double addition: broken chains	$(Ca_{0{\cdot}96}Mg_{0{\cdot}04})Mg_{1{\cdot}08}\ Si_2O_{6{\cdot}08}$	219·18	3·315
	Double substitution and addition: Si-Mg chains	$(Ca_{0{\cdot}95}Mg_{0{\cdot}05})Mg_{1{\cdot}02}\ (Si_{1{\cdot}97}Mg_{0{\cdot}03})O_6$	216·145	3·269
	Double substitution and omission: crosslinked Si–Mg chains	$(Ca_{0{\cdot}94}Mg_{0{\cdot}06})Mg\ (Si_{1{\cdot}96}Mg_{0{\cdot}04})O_{5{\cdot}96}$	214·88	3·250

* Observed densities for diopside, quoted from the literature by Deer, Howie & Zussman (1963), range from 3·22 to 3·38 g.cm⁻³. No densities have been determined for the solid solutions.

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

$$(Ca_{1-2z}Mg_{2z})\ Mg_{1+z}\ (Si_{2-z}Mg_z)\ O_6,\ \text{where}\ z=2x/(6+4x).$$

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 $Ca_{0\cdot94_3}Mg_{1\cdot09_4}Si_{1\cdot96_3}O_{5\cdot96}$ or, for x moles of forsterite to one mole of diopside,

$$(Ca_{1-3u}Mg_{3u})Mg(Si_{2-2u}Mg_{2u})O_{6-2u},\ \text{where}\ u=x/(4+3x).$$

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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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 ($a=5\cdot402$, $b=6\cdot372$, $c=5\cdot007$ 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:

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

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 $\delta_{Li}=0$, 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:

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

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