

Tabelle 6. Volumen der Elementarzelle V_E von isoelektronischen $A^{II}B^{IV}C_2^V$ - und $A^{III}B^V$ -Verbindungen

	$V_E = a^2c$ (Å ³)		$2V_E = 2a^3$ (Å ³)
ZnGeP ₂	320,5	GaP	323,9
ZnGeAs ₂	358,6	GaAs	361,4
CdSnAs ₂	442,4	InAs	444,8

nischen Verbindungen. In Tabelle 6 ist das Zellvolumen von ZnGeP₂, ZnGeAs₂ und CdSnAs₂ dem entsprechenden doppelten Zellvolumen der isoelektronischen $A^{III}B^V$ -Verbindungen gegenübergestellt. Die Volumenunterschiede betragen lediglich etwa 1%.

Bei den $A^{III}B^V$ -Verbindungen ist die Bindung neben einem geringen heteropolaren Anteil im wesentlichen homöopolar (Welker, 1952). Nach Pauling (1940) lässt sich der heteropolare Anteil einer intermediären Bindung aus der Differenz der Elektronegativitäten der an der Bindung beteiligten Atome abschätzen. Vergleichen wir daraufhin z. B. die Verbindung GaAs mit der dazu isoelektronischen Verbindung ZnGeAs₂, so finden wir als Differenz der Elektronegativitäten für eine Ga-As-Bindung den Wert 0,4 und für eine Zn-As-Bindung bzw. eine Ge-As-Bindung die Werte 0,5 bzw. 0,3. Nach der von Hannay & Smyth (1946) aufgestellten Beziehung zwischen der Differenz der Elektronegativitäten und dem heteropolaren Bindungsanteil einer A-B-Bindung ergibt sich für eine Ga-As-Bindung ein heteropolarer Bindungsanteil von 7% und für eine Zn-As-Bindung bzw. eine Ge-As-Bindung

ein Anteil von 9% bzw. 5%. Im Mittel ist also in ZnGeAs₂ der heteropolare Anteil einer Bindung ebenfalls 7%. Da eine solche Übereinstimmung auch bei den anderen Verbindungen besteht, ist anzunehmen, dass der heteropolare Bindungsanteil der $A^{II}B^{IV}C_2^V$ -Verbindungen etwa gleich gross ist wie bei den isoelektronischen $A^{III}B^V$ -Verbindungen.

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Literatur

- FOLBERTH, O. G. & PFISTER, H. (1956). Vortrag auf dem Internationalen Kolloquium über Halbleiter und Phosphore in Garmisch-Partenkirchen.
 HAHN, H., FRANK, G., KLINGLER, W., MEYER, A. & STÖRGER, G. (1953). *Z. anorg. Chem.* **271**, 153.
 HANNAY, N. B. & SMYTH, C. P. (1946). *J. Amer. Chem. Soc.* **68**, 171.
 PAULING, L. (1940). *The Nature of the Chemical Bond*, 2. Aufl. London: Oxford University Press.
 PAULING, L. & BROCKWAY, L. O. (1932). *Z. Kristallogr.* **82**, 188.
 PAULING, L. & HUGGINS, M. L. (1934). *Z. Kristallogr.* **87**, 205.
 TAYLOR, A. & FLOYD, R. W. (1950). *Acta Cryst.* **3**, 285.
 WELKER, H. (1952). *Z. Naturforsch.* **7a**, 744.

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The structure of the high-temperature modification of sodium lithium sulfate. By T. FÖRLAND, *Institutt for uorganisk kjemi, Norges Tekniske Högskole, Trondheim, Norway* and J. KROGH-MOE, *Svenska silikatforskningsinstitutet, Göteborg, Sweden*

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The cubic high-temperature modification of lithium sulfate will take a considerable amount of sodium sulfate in solid solution. Phase equilibria studies by Nacken (1907) suggest that this solid solution extends to about 60 mole% sodium sulfate.

The structure of cubic lithium sulfate reported by Förland & Krogh-Moe (1957) can account for a substantial solid solubility of sodium sulfate. The sulfate ions in this structure are arranged in a face-centered cubic lattice (c.f. the sodium perchlorate structure type). The lithium ions, however, are probably distributed over an excess number of available cation positions. At least some of these cation positions are large enough to accommodate sodium ions, leading to solid solubility.

X-ray powder patterns were recorded at elevated temperatures on a standard General Electric diffraction unit, fitted with a furnace. An argon-filled Geiger counter and Cu $K\alpha$ radiation were used. A sample, containing 30 mole% of sodium sulfate, showed a face-centered cubic arrangement, as in lithium sulfate. The lattice had expanded somewhat relative to that of pure cubic lithium sulfate. At 610° C. the unit-cell length of lithium sulfate is 7.07 Å, whereas for the solid solution containing 30 mole% sodium sulfate the unit-cell length is 7.34 Å.

X-ray patterns taken at 556° C. of a sample containing 50 mole% sodium sulfate showed that a change had taken place. Observed lines and their intensities for this composition are given in Table 1.

Table 1. *X-ray pattern for NaLiSO₄ at 556° C.*

Cu K α radiation		
2θ (°)	$1/d^2$ (Å ⁻²)	Relative intensities
21.75	0.0601	10
31.0	0.1202	2
38.2	0.1804	1

These lines may be indexed by means of a cubic body-centered unit cell with an edge length of 5.77 Å. A density of 2.18 g.cm.⁻³ is calculated with two formula units of NaLiSO₄ in the cell. (By indexing the pattern as primitive cubic, the density would have been 3.08 g.cm.⁻³ with two formula units in the cell, or 1.54 g.cm.⁻³ with one formula unit in the cell. The former density is too high, and the latter too low.)

Space-group considerations are probably of limited value in determining the atomic positions in NaLiSO₄. Coupled rotation of the sulfate groups, together with translations of the cations, are likely to occur, as in cubic

lithium sulfate. The electrical conductivities of LiNaSO₄, as that of Li₂SO₄, were found to be of the same magnitude in the high-temperature modification and in the fused state (Förland & Krogh-Moe, unpublished). Thus it is not possible to assign definite single positions to the oxygens or the cations in the lattice. The sulfur remain fixed in the (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) positions.

The average volume per sulfate ion increases about 10% on adding 30 mole% sodium sulfate to cubic lithium sulfate. The sulfate ion volume is nearly the same with a sodium sulfate content of 30 mole% as with a content of 50 mole%. This demonstrates that the structural change from face centered to body centered results in a more efficient packing of the anions and the cations.

References

- FÖRLAND, T. & KROGH-MOE, J. (1957). *Acta Chem. Scand.* **11**, 565.
 NACKEN, R. (1907). *N. Jb. Min. Geol. A*, **24**, 1.

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The crystal structure of γ -glycine. By YOICHI IITAKA, *Mineralogical Institute, Science Department, University of Tokyo, Hongo, Tokyo, Japan*

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In a previous paper, the author reported on a new form of glycine. This new form, designated as γ -glycine, is strongly piezoelectric, and crystallizes with trigonal hemihedral symmetry. The space group is either $P3_1$ or $P3_2$, and the unit cell contains three molecules (Iitaka, 1954). The redetermination of the unit-cell dimensions gave

$$a = 7.037, \quad c = 5.483 \text{ \AA}.$$

In the following, a brief account of the structure determination of γ -glycine will be given. We shall describe the structure, comparing it with that of α -glycine (Albrecht & Corey, 1939; Marsh, 1957). Intensity data obtained from both oscillation and Weissenberg photographs were used.

The crystal shows a marked piezoelectric property along the c axis. The length of this axis is nearly equal to the c axis of α -glycine, the latter corresponding to the intermolecular distance arranged head-to-tail. These facts suggest that the dipolar molecules are arranged along the c axis. From the Harker section at $z = \frac{1}{3}$, it was possible to obtain approximate parameter values, x and y , for the oxygen, nitrogen and carbon atoms. Using conventional bond distances and bond angles for the molecule, and the hydrogen bond distance $\text{NH} \cdots \text{O}$ for nitrogen and oxygen atoms in neighbouring molecules, a satisfactory atomic arrangement was derived.

The refinement of the structure was carried out, using both ($hk0$) and ($0kl$) Fourier and difference Fourier projections, followed by three-dimensional structure-factor calculations. No further shifts of significance were indicated in the sixth ($0kl$) projection. At the present stage, the reliability indices are 0.14, 0.12 and 0.15 for ($0kl$), ($hk0$) and (hkl) reflexions, respectively, neglecting con-

tributions from hydrogen atoms. The Fourier projection along the a axis is shown in Fig. 1.

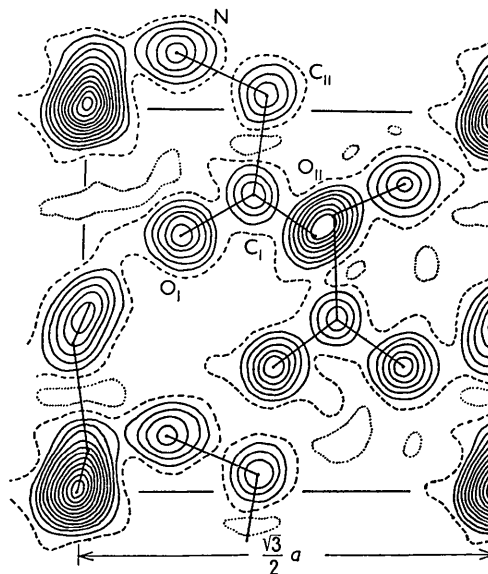


Fig. 1. The a -axis Fourier projection for γ -glycine. Contours at intervals of 2 e.Å⁻². Dotted lines indicate 0 e.Å⁻², and broken lines 2 e.Å⁻².

The shape of the molecule is found to be nearly the same as that of α -glycine. In Table 1, the bond distances and bond angles are given, together with the values