

## NOTIZEN

**Single-Crystal Structure Refinement of LiZnAs**

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Ternary Arsenide

The crystal structure of LiZnAs has been verified with single crystal X-ray methods. LiZnAs crystallizes in a filled-up zinc blende type of structure ( $F\bar{4}3m$ ,  $a = 593.9(1)$  pm, As at site  $4a$  (000); Zn at site  $4d$  ( $3/4$   $3/4$   $3/4$ ); Li at site  $4c$  ( $1/4$   $1/4$   $1/4$ );  $25 hkl$ ;  $R = 0.018$ ). As is coordinated by 4 Li and 4 Zn atoms with identical distances of  $257.2(1)$  pm. Li and Zn atoms are tetrahedrally coordinated by As. No indications for a disorder between Li and Zn have been found.

**Introduction**

The ternary compound LiZnAs has been characterized as a half ionically (Li to As) and half covalently bonded (Zn to As) semiconductor by the aid of electronic structure calculations [1]. It has also been shown by X-ray powder investigations, that LiZnAs crystallizes in the antiferrotype of structure [2] with an ordered or statistical distribution of Li and Zn. Other authors report a disordered distribution of Li and Zn atoms [3]. However, no further details how the reported intensities have been recorded were given. Preliminary calculations of the intensities disagree with the reported ones. Therefore, a single crystal study seems to be meaningful, which allows to check the proposed structural models of a filled-up zinc blende type of structure [1] as well as of the antiferrotype of structure [2, 3].

**Synthesis and X-Ray Investigation**

Small single crystals, suitable for X-ray crystallographic studies, were synthesized from the elements in stoichiometric amounts in niobium tubes. Approximately 4.45 g As, 3.88 g Zn and 0.41 g Li were filled under inert conditions into an arc-welded niobium crucible (15 mm outer diameter,

80 mm in length), which was closed by crimping and subsequent arc-welding. This ampoule was heated for 3 d at  $520^\circ\text{C}$  in an evacuated quartz jacket and then cooled to room temperature within one day. LiZnAs crystallizes as grey lumps with sometimes metallic lustre. Well crystallized samples are not very sensitive to air and humidity, but excess Li may lead to a remarkable sensitivity [3].

A small single crystal was chosen under the microscope in a glove box and fixed with baked-out silicone grease in a thin capillary. Conventional precession photographs reveal the Laue symmetry  $m\bar{3}m$  with the Bravais lattice  $F$ . The lattice constant was determined from the refined  $2\theta$  angles of  $22 hkl$  in the range  $11^\circ \leq 2\theta \leq 31^\circ$  to be  $593.9(1)$  pm. Intensities were collected on an automated four-circle diffractometer SYNTEX P3 with  $\text{MoK}_\alpha$  radiation and a scintillation counter. In the range  $3^\circ \leq 2\theta \leq 60^\circ$  the intensities of  $85 hkl$  were measured, averaging leads to 25 unique  $hkl$ . Standard polarization and Lorentz factor corrections were performed. Absorption was corrected for by a  $\psi$  scan measurement of 10 reflections  $hkl$ . The crystal structure was refined straightforward with the SHELX programme system [4]. The final reliability factors were found to be  $R = 0.018$  and  $R_w = 0.019$  with  $w = \sigma^{-2}$ . Table I gives the atomic parameters together with their refined Debye Waller factors (e. s. d.)\*.

Table I. LiZnAs; positional and displacement parameters U [ $\text{pm}^2$ ].

Atom	Site	$x$	$y$	$z$	U
Li	$4c$	$1/4$	$1/4$	$1/4$	169(150)
Zn	$4d$	$3/4$	$3/4$	$3/4$	187(15)
As	$4a$	0	0	0	118(12)

**Results and Discussion**

The determined structure agrees completely with the so-called  $\alpha$ -LiZnAs type proposed by Wei and Zunger [1] at the most stable one. It disagrees

\* Further crystal structure data may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2, by quoting the Registry No. CSD 57010, the name of the author, and the journal citation.

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with the antiferrotype as given by Kuriyama and Nakamura [3]. Furthermore, we find no agreement with the intensity values as given by the latter authors [3]. As they gave no space group for their calculations, we assume, that they have overlooked weak reflections (*cf.* deposited data\*). Other possible arrangements have also been checked, but could be ruled out. They yield  $R = 0.021$  [As at  $4a$ , Li at  $4b$ , Zn at  $4d$ , (anomalous dispersion effect)] and  $R = 0.023$  [As at  $4a$ , Li at  $4b$ , Zn at  $4c$ ].

The ionic bonding between Li and As and the covalent bonding between Zn and As can be explained with Zintl's concept [5], the Mooser-Pearson [6] rule, and Parthé's tetrahedral concept [8]. Following these concepts, the valence electron of lithium is transferred to the ZnAs partial structure, thus leading to the formulation  $\text{Li}^+(\text{ZnAs})^-$ , with the partial structure (ZnAs) having 4 valence electrons per atom. One possible arrangement is a zinc blende type of structure, in which the octahedral holes are filled by tetrahedrally coordinated Li ions.

Table II gives the observed bond lengths  $d_{\text{obs}}$  together with the sum of the covalent radii  $\Sigma r_{\text{cov}}$  as well as of the ionic radii  $\Sigma r_{\text{ion}}$ . Pauling's values for electronegativity  $\chi$  and  $\Delta\chi$  have also been included.

Atom	$\chi$	$r_{\text{cov}}$	$r_{\text{ion}}$
Li	0.98	125	60
Zn	1.65	125	74
As	2.18	122	222

Table II. LiZnAs; electronegativity values  $\chi$ , covalent and ionic radii (pm), observed bond lengths ( $d_{\text{obs}}$ ), in pm, multiplicity of bonds, differences in electronegativity ( $\Delta\chi$ ), percentage of ionic character, sum of covalent radii ( $\Sigma r_{\text{cov}}$ ) in pm, and sum of ionic radii ( $\Sigma r_{\text{ion}}$ ) in pm.

Atom-atom	$d_{\text{obs}}$	mult.	$\Delta\chi$	%ion char.	$\Sigma r_{\text{cov}}$	$\Sigma r_{\text{ion}}$
Li-As	257.2(1)	4×	1.20	30%	247	282
Li-Zn	297.0(1)	6×	0.67	11%	250	134
Zn-As	257.2(1)	4×	0.53	7%	242	296

According to Pauling [8], the ionic character of a bond can be estimated from the difference of  $\chi$ . The Li-As bond therefore is much more ionic than the Zn-As bond. As can be seen from the values in Table II, neither the sum of the covalent radii, nor of the ionic radii reflect the experimental values.

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