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Structure of $ZnGa_2S_4$, a Defect Sphalerite Derivative

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Abstract. Digallium zinc tetrasulfide, $ZnGa_2S_4$, M_r = 333·07, tetragonal, $I\bar{4}2m$, a = 5·2744 (7), c = 10·407 (1) Å, V = 289·51 (9) Å^3, Z = 2, D_x = 3·82 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 146·78 cm^{-1}, $F(000)$ = 312, T = 292 K. $ZnGa_2S_4$ crystallizes in the defect stannite structure which is related to sphalerite. Refinement of different models of cation distribution gave R values of 0·041 to 0·043 for 360 independent reflections with $|F_o| > 3\sigma(F)$. Of the models considered, the ordered model with Zn only at point set 2(a) and Ga only at point set 4(d) was found to be worse, statistically, than models with some degree of cation disorder. Models with cation disorder are consistent with a previous review in which it was suggested that the displacement of the anion from the ideal ($\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{8}$) was insufficient in $ZnGa_2S_4$ to indicate cation ordering. Disorder amongst the cation sites is also consistent with reported Raman and photoluminescence results. The slight difference observed between the metal–sulfur bond lengths for the two crystallographic cation sites is attributed to the differing effect of the vacancy on these sites rather than to cation ordering.

Introduction. Non-oxide inorganic compounds such as ternary sulfides and phosphides are of interest as possible infrared-transmitting window materials. $ZnGa_2S_4$ is of interest in second-phase toughening studies of ZnS (Zhang, Chen, Dunn & Ardell, 1988) and exhibits long-wavelength infrared transparency comparable to that of ZnS (Wu, He, Dwight & Wold, 1988; Gao, Wu, Kershaw, Dwight & Wold, 1989).

The title compound was first reported by Hahn, Frank, Klingler, Stoerger & Stoerger (1955). Hahn *et al.* (1955) postulated that the structure of $ZnGa_2S_4$ was that of an ordered defect sphalerite, the ordering of the vacancy and the two different cations giving rise to two possible structural arrangements, A and B, Fig. 1. These two arrangements cannot be distinguished by X-ray powder diffraction since the scattering factors for Zn and Ga are nearly identical. In the parent AX sphalerite structure each cation is tetrahedrally bonded to four anions and each anion is tetrahedrally bonded to four cations. The relationship between the sphalerite structure and the possible zinc thiogallate structures can be seen in Fig. 1. The (cubic) sphalerite cell has been doubled in one direction for ease of comparison to the thiogallate cell. In the thiogallate structure, one-quarter of the cations have been removed from the sphalerite structure in an ordered fashion, lowering the symmetry to tetragonal. This results in equivalent anion sites, each coordinated by one vacancy and three cations, while pseudo-tetrahedral coordination about each of the metal sites is preserved. The thiogallate structure has been considered as an ABX_2 defect chalcopyrite or defect stannite structure; the chalcopyrite and stannite structures are themselves ordered (tetragonal) versions of sphalerite but without vacancies. In the parent 'ideal' sphalerite the anion would be at (x,y,z) coordinates ($\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$) or at ($\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{8}$) in a cell doubled in c. In these sphalerite derivatives the cations and vacancies occupy special positions; the anion position is specified by two or three coordinates x,x,z or x,y,z, that determine all of the metal–sulfur and vacancy–sulfur distances.

Despite the ease of growing crystals of $ZnGa_2S_4$ by iodine transport (Nitsche, Boelsterli & Lichtensteiger, 1961) a full single-crystal structure deter-

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mination had not been reported, to our knowledge, when we initiated this structure determination. We have become aware of the single-crystal structural work of Krämer, Hirth, Hofherr & Trah (1987) and Solans, Font-Altaba, Moreiras, Trobajo-Fernandez & Otero-Arean (1988) in which $I\bar{4}$ was proposed as the space group for $ZnGa_2S_4$. Garbato, Ledda & Rucci (1987) point out that the crystallographic data for AB_2X_4 compounds is somewhat confused, in many cases due to similarity in atomic scattering factors, and that the correct symmetries have not always been unequivocally determined. In $I\bar{4}$ the four possible cation/vacancy sites all have the same site symmetry, $\bar{4}$; hence, regardless of the position of the vacancy an origin transformation will give an equivalent structure. In addition, owing to the nearly equivalent scattering of Zn and Ga, in space group $I\bar{4}$ there will be nearly equivalent atoms at point sets 2(*c*) and 2(*d*) which, if combined, are point set 4(*d*) in $I\bar{4}2m$. The differences in intensities between the space groups $I\bar{4}$ (Laue symmetry $4/m$) and $I\bar{4}2m$ (Laue symmetry $4/mmm$) will be due only to slight differences in the nearly equal scattering between Zn and Ga and by movement of the sulfur away from *x*,*x*,*z* in $I\bar{4}2m$ to *x*,*y*,*z* in $I\bar{4}$, reducing the site symmetry about the vacancy and one cation site from $\bar{4}2m$ to $\bar{4}$. The position of the vacancy is not the Laue-symmetry-determining factor. If Zn and Ga are completely disordered on the cation sites, then movement of the S atoms away from *x*,*x*,*z* to *x*,*y*,*z* would be the only Laue-symmetry-determining factor. Since our preliminary report (Kipp, Lowe-Ma & Vanderah, 1989), Carpenter, Wu, Gao & Wold (1989), hereafter abbreviated CWGW, provided us with the results of their recent structure determination of $ZnGa_2S_4$. In contrast to the earlier reports, the work of CWGW and that reported here indicate space group $I\bar{4}2m$ for $ZnGa_2S_4$.

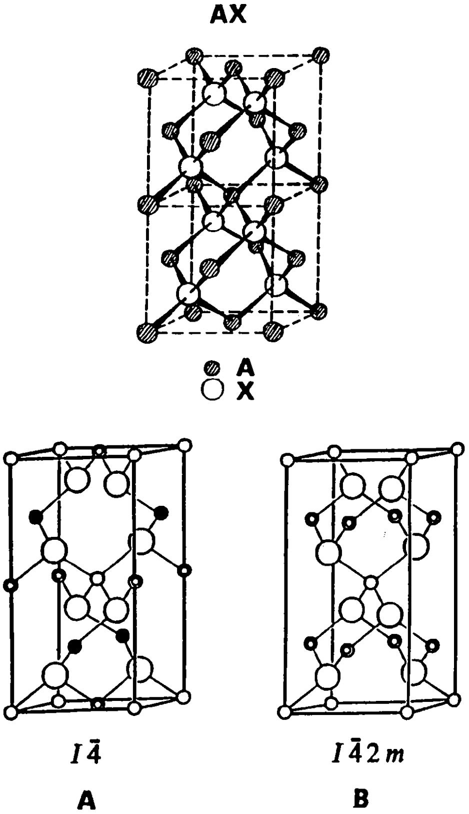

Fig. 1. Comparison of the cubic *AX* sphalerite structure (two cells shown) with the possible ordering arrangements *A* and *B*. Large open circles represent anions and each set of small circles represents a crystallographic point set for the cation sites.

Experimental. A modified version of the procedure of Nitsche *et al.* (1961) was used to grow transparent colorless $ZnGa_2S_4$ crystals with tetrahedron-like morphology from polycrystalline $ZnGa_2S_4$ using iodine as the transport agent. 0·33 g $ZnGa_2S_4$ and 5–8 mg I_2 were placed in one end of an evacuated silica ampule (1·0 cm internal diameter × 19 cm long). For the first 16 h, the temperature of the deposition end of the ampule (T_d) was held at 1233 K, 50–75 K higher than that (T_s) of the charged end. The gradient was then reversed and T_s was held at 1233 K for 4 d followed by air quenching of the ampule. Fused masses of colorless tetrahedra, some 2–3 mm on an edge, were obtained as well as smaller seperate crystals suitable for X-ray diffraction studies. The metal stoichiometry of the crystals as found by ICP (inductively-coupled plasma) emission analysis, 1·00 Zn:2·00 Ga (± 0·05), was consistent with the expected composition. From a preliminary investigation of the $ZnS–Ga_2S_3$ phase diagram, White (1980) concluded that there was no evidence for a solid solution (variation of the Zn:Ga ratio) and that $ZnGa_2S_4$ exists as a line compound between 1173 and 1373 K. Zhang *et al.* (1988) also reported seeing only one phase at 1173 K for 1:1 $ZnS:Ga_2S_3$. This is in agreement with the elemental analyses of our crystals which indicated no appreciable non-stoichiometry. The X-ray powder diffraction pattern of our crystals matched that reported for tetragonal $ZnGa_2S_4$ (Gates, 1976; Hahn *et al.*, 1955).

A crystal of 0·22 mm on an edge was used for data collection. The unit-cell parameters were determined by a least-squares fit of 25 computer-centered reflections. The parameters for $2\theta/\theta$ data collection on a Nicolet *R*3 diffractometer were as follows: 2θ range 4 to 70°; all *hkl* with minimum–maximum *hkl* values of *h* 0 to +9, *k* 0 to +9, *l* −17 to +17 collected; 2θ scan range of $2\theta(\alpha_1) - 1{\cdot}0$ to $2\theta(\alpha_2) + 1{\cdot}0°$; ratio of total background counting time to scan time of 1·0; variable 2θ scan speeds of 4 to 12°; three check reflections (112, 008 and 440) collected every 93 reflections with check-reflection variation of about ±5% during data collection. The only observed systematic absences were $h+k+l=2n+1$ indicating a body-centered tetragonal cell without any additional elements of translational symmetry. Data reduction included Lorentz and polarization corrections as well as numerical absorption corrections from *SHELXTL* (Sheldrick, 1984) for a tetragonal dispenoid with faces $\{\bar{1}12\}$. Minimum and maximum transmission values were 0·161 and 0·282, respectively. The location of mirror planes on preliminary X-ray precession alignment photographs relative to the external morphology of three tetrahedron-like crystals of $ZnGa_2S_4$ clearly showed that the crystals were, indeed, tetragonal dispenoids (tetragonal tetrahedrons). Laue photographs exhibited Laue symmetry $4/mmm$. After corrections the 1600 observations were merged in $I\bar{4}2m$ ($R_{\rm int}=0{\cdot}042$) to give 363 unique reflections, 360 with $|F_o|>3\sigma(F)$. Data were also merged in $I\bar{4}$ ($R_{\rm int}=0{\cdot}063$) and reflections that would be equivalent in $I\bar{4}2m$ were checked for true equivalence, which they appeared to be. A sharpened Patterson map exhibited peaks at (u,v,w) coordinates of $(0,0,0)$, $(\frac{1}{2},0,\frac{1}{4})$, $(\frac{1}{2},\frac{1}{2},0)$ and $(0{\cdot}2567, 0{\cdot}2567, 0{\cdot}1275)$. Refinement was initiated with the following atomic (x,y,z) coordinates: Zn $(0,0,0)$, point set $2(a)$; Ga $(0,\frac{1}{2},\frac{1}{4})$, point set $4(d)$; S $(x=y=0{\cdot}2567, 0{\cdot}1275)$, point set $8(i)$. In our preliminary communication (Kipp, Lowe-Ma & Vanderah, 1989) we reported a model ($R=0{\cdot}043$) with Ga fully occupying point set $4(d)$, S fully occupying point set $8(i)$, variable Zn occupancy at $(0,0,0)$ with 5·6% more 'Zn' than expected and 1·8% 'Zn' at the vacancy site $(0,0,\frac{1}{2})$ [point set $2(b)$]. However, 1·8% 'Zn' at $(0,0,\frac{1}{2})$ is an amount only twice that of the e.s.d. for the site occupancy factor of that position. As suggested to us by R. E. Marsh, equally reasonable models might be with the 'Zn' at $(0,0,\frac{1}{2})$ eliminated and mixing between the Zn and Ga sites allowed.

After completion of refinement of a model with mixing of Zn and Ga at the two cation sites, the structure determination of CWGW became available to us. They reported in their structure determination a model with Ga at $(0,0,0)$, point set $2(a)$; 0·5Ga + 0·5Zn at $(0,\frac{1}{2},\frac{1}{4})$, point set $4(d)$; and S in point set $8(i)$. For stoichiometric $ZnGa_2S_4$ in $I\bar{4}2m$, the cation distribution could be modelled in four ways: (I) Zn at point set $2(a)$ and Ga at point set $4(d)$ with no disorder; (II) that of CWGW with Ga at point set $2(a)$ and 0·5Zn + 0·5Ga disordered on point set $4(d)$; (III) complete disorder with $\frac{1}{3}$Zn + $\frac{2}{3}$Ga at point set $2(a)$ as well as at point set $4(d)$; (IV) a disordered model intermediate and variable between (II) and (III). Least-squares refinements of the four models was by minimization of $[\sum w(|F_o|-k|F_c|)^2]$ with $w=1/[\sigma^2(F)+0{\cdot}0008F^2]$ from *SHELXTL* (Sheldrick, 1984) using neutral-atom scattering factors (*International Tables for X-ray Crystallography,* 1974, Vol. IV). A single temperature factor was used for each site including those with disordered occupancy. A parameter for extinction was included in the refinement. Refinement of model (I) converged for 12 parameters (max. shift/e.s.d. of 0·001) with $R=0{\cdot}043$, $wR=0{\cdot}045$, $S=1{\cdot}35$, slope of normal probability plot = 1·20. Refinement of model (II) converged for 12 parameters (max. shift/e.s.d. of 0·000) with $R=0{\cdot}041$, $wR=0{\cdot}041$, $S=1{\cdot}24$, slope of normal probability plot = 1·03. Refinement of model (III) converged for 12 parameters (max. shift/e.s.d. of 0·000) with $R=0{\cdot}041$, $wR=0{\cdot}042$, $S=1{\cdot}26$, slope of normal probability plot = 1·06. For model (IV), the amount of Zn (and Ga) at each site was allowed to vary with the total occupancy constrained to be 1 although the total Zn:Ga stoichiometry could not be constrained to be 1:2. From $\frac{1}{3}$Zn + $\frac{2}{3}$Ga at both point set $2(a)$ and point set $4(d)$ model (IV) with 14 parameters refined to $R=0{\cdot}041$, $wR=0{\cdot}041$, $S=1{\cdot}24$ and slope of normal probability plot = 1·04. However, the resulting occupancies, 34% Zn + 66% Ga (±12%) at point set $2(a)$ and 24% Zn + 76% Ga (±12%) at point set $4(d)$, did not truly converge (max. shift/e.s.d. of 0·4); the large e.s.d.'s on the occupancy indicate that a true minimum may not exist due to the similarity in Zn and Ga scattering.

Refinement of the X-ray diffraction data indicates that an unambiguous choice between models (II), (III) and (IV) is not possible although the statistically worse refinement of model (I) suggests that a structure with completely ordered cations can be ruled out. In the absence of neutron diffraction studies of $ZnGa_2S_4$, the choice of the most chemically reasonable of the remaining models depends on consideration of crystal-chemical arguments and the results of other types of experiments. Accordingly, as discussed below, we conclude that the most chemically reasonable model is (III), with essentially complete, or nearly complete, cation disorder between the $2(a)$ and $4(d)$ point sets. The atomic coordinates, thermal parameters, and bond lengths and angles for model (III) are given in Table 1.*

Discussion. In the study by CWGW the choice of model (II) with Ga in point set $2(a)$ and $\frac{1}{2}$Ga + $\frac{1}{2}$Zn disordered in point set $4(d)$ was largely predicted on the observation of a slightly shorter metal–sulfur bond length about point set $2(a)$, 2·281 (1) *vs* 2·315 (1) Å about point set $4(d)$. Our interest in the reasonableness of this assumption was piqued by

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* Lists of structure factors for model (III) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53628 (2 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates, thermal parameters* (Å^2), *and bond lengths* (Å) *and angles* (°) *for model* (III)

	x	y	z	Occupancy	U_{11}	U_{33}	U_{23}	U_{12}	U_{eq}
Zn(1)/Ga(2)	0·0	0·0	0·0	0·333/0·667	0·0114 (3)	0·0081 (4)	0·0	0·0	0·0103 (2)
Zn(2)/Ga(1)	0·0	0·50	0·25	0·333/0·667	0·0110 (3)	0·0110 (4)	0·0	0·0	0·0110 (2)
S	0·25761 (14)	x	0·11902 (9)	1·0	0·0112 (4)	0·0094 (5)	−0·0009 (2)	0·0007 (2)	0·0106 (2)

Bond lengths		Bond angles		
Point set 2(*a*) to sulfur	2·288 (1)	About point set 2(*a*)	4 × 107·1 (1),	2 × 114·4 (1)
Point set 4(*d*) to sulfur	2·312 (1)	About point set 4(*d*)	4 × 110·4 (1),	2 × 107·7 (1)
		About sulfur	2 × 107·4 (1),	107·6 (1)

* The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots + 2hka^*b^*U_{12})]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Representative* Ga—S *bond lengths*

Compound	Range (Å)	Reference
$CaGa_2S_4$*	2·252 (4)–2·297 (4)	Eisenmann, Jakowski, Klee & Schäfer (1983)
$SrGa_2S_4$*	2·424 (6)–2·335 (6)	Eisenmann *et al.* (1983)
$YbGa_2S_4$*	2·241 (1)–2·292 (7)	Guseinov, Mamedov, Amiraslanov & Mamedov (1983)
$EuGa_2S_4$*	2·237 (4)–2·311 (4)	Roques, Rimet, Declercq & Germain (1979)
$Ga_{1·33}Cr_4S_8$†	2·292 (4), 2·242 (4)	Ben Yaich, Jegaden, Potel, Sergent, Huguet & Alquier (1983)
$GaMo_4S_8$†	2·275	Ben Yaich *et al.* (1983)
$Ca_2La_2Ga_6S_4$	2·196 (4)–2·285 (4)	Mazurier, Jaulmes & Guittard (1987)
α-Ga_2S_3		
Monoclinic	2·18 (3)–2·32 (4)	Goodyear & Steigmann (1963)
Hexagonal‡	2·07 (2)–2·38 (5)	Tomas, Pardo, Guittard, Guymont & Famery (1987)
β-Ga_2S_3	2·251 (2)–2·269 (6)	Tomas *et al.* (1987)

* Isostructural compounds, space group *Fddd*.
† Isostructural compounds, spinel structure, space group *Fd*3*m*.
‡ For cation sites with partial Ga occupancy.

considering the possible reasons for cation disorder on only one of the tetrahedral cation sites. Unlike the spinel system, in which the well known 'normal' and 'inverse' forms involve cation exchange and order–disorder across tetrahedral and octahedral sites, the two cation sites in $ZnGa_2S_4$ are coordinatively very similar. The Ga—S bond length calculated from the defect sphalerite form of Ga_2S_3 is 2·24 Å and the Zn—S bond length in sphalerite is 2·342 Å. These bond lengths suggest that in $ZnGa_2S_4$, with cation–sulfur bond lengths observed in the present study of 2·288 (1) and 2·312 (1) Å [for the distances from point set 2(*a*) to S and from point set 4(*d*) to S, respectively], there is mixing of Zn and Ga on both of the cation sites which favors a model with at least some disorder across point sets 2(*a*) and 4(*d*). If Ga—S and Zn—S bond lengths were well known and constant in similar structures, then the difference in bond lengths in $ZnGa_2S_4$ might indicate the relative populations of Zn and Ga on the two sites. However, this is not the case; observed variations in Zn—S and Ga—S distances in tetrahedral coordination are as large as the differences observed in $ZnGa_2S_4$. A summary of Ga—S distances in compounds containing GaS_4 tetrahedra is presented in Table 2. For a Zn—S bond length Shannon's ionic radii would predict 2·34 Å, the same bond length as observed in sphalerite. However, Shannon (1981) noted large deviations (up to 0·04 Å) for mean Zn—S bond lengths. From quantum-mechanical considerations rather than a hard-sphere model, Van Vechten & Phillips (1970) developed a table of additive covalent radii for tetrahedrally bonded (diamond, sphalerite, wurtzite) structures and concluded that Zn and Ga have the same covalent radii (1·225 Å) and, hence, identical bond lengths (2·352 Å) in tetrahedrally bonded structures.

For model (II), the occupation of point set 2(*a*) solely by the higher-valent Ga atoms is not consistent with the observed bond angles about the two cation sites in $ZnGa_2S_4$. As noted by Shay & Wernick (1975) structural distortions in chalcopyrite-type compounds are driven by a tendency to form more ideal tetrahedra about the higher-valent cation with accommodating distortions of the tetrahedra about the lower-valent species. In $ZnGa_2S_4$ the anion tetrahedron about site 2(*a*) is significantly more distorted [with four angles of 107·1 (1) and two of 114·4 (1)°] than the anion tetrahedron about site 4(*d*) [with four angles of 110·4 (1) and two angles of 107·7 (1)°]. This would suggest that Zn is predominantly at the 2(*a*) site (0,0,0), since it displays the more distorted tetrahedral coordination, in apparent contradiction to the shorter cation—anion bond length observed for this site.

The crystal-chemical effects of the vacancy [at point set 2(*b*)] upon the cation sites 2(*a*) and 4(*d*) are different, however, and could reasonably cause the observed differences in bond lengths and bond angles even in the complete absence of cation ordering. Two unit cells for the $ZnGa_2S_4$ structure ($I\bar{4}2m$) are illustrated in Fig. 2. The structure can be viewed as alternating planes of metals/vacancies and S atoms along the *c* axis. The vacancies [point set 2(*b*)] are co-planar with metals at point set 2(*a*); in contrast, all of the cation sites are fully occupied in the plane of metals at point set 4(*d*). Thus, the crystal-chemical effects of the vacancy should be most pronounced in the sulfur–metal/vacancy[2(*a*),2(*b*)]–sulfur slab of the structure. The z coordinates of the sulfur planes are given in Fig. 2 along with the ideal values in parentheses. Relative to the ideal z coordinates, the sulfur layers shift slightly toward the 2(*a*),2(*b*) metal/vacancy plane, decreasing the metal—sulfur and vacancy—sulfur distances and leading to more highly distorted coordination polyhedra within this structural slab. As a consequence, the sulfur planes on either side of the 4(*d*)-metal layer are pulled slightly apart, increasing the metal–sulfur bond lengths while the tetrahedra remain more nearly ideal. The shortest distance in the structure is the distance from sulfur to the 2(*b*) vacancy site, 2·191 (1) Å. The slight shifts in S atom positions from the ideal values of $(\frac{1}{4},\frac{1}{4},\frac{1}{8})$ decrease the S–vacancy distance, which would be 2·274 Å if the S atom were at the ideal coordinates. The apparent tendency of the structure to collapse around the vacancy site might be attributable to incipient S—S interactions that predominate over any lone-pair effects (even though $ZnGa_2S_4$ is colorless). The closest observed S—S contacts in the structure range from 3·560 (1) to 3·843 (1) Å. The shortest S—S distances, two at 3·560 (1) and two at 3·616 (1) Å, do indeed occur in the pseudo-tetrahedron about the vacancy. These S—S distances are shorter than those observed in ZnS (3·82 Å) and completely randomized sphalerite-type Ga_2S_3 (3·66 Å). In monoclinic α-Ga_2S_3, with ordered vacancies, shrinkage about vacancies was also noted by Goodyear & Steigmann (1963). Thus, collapse of the structure about the cation vacancy causes slightly shorter bond lengths to, and a more distorted tetrahedron about, the cation 2(*a*) site. Assumption of higher Ga content at this site is, therefore, unnecessary.

Garbato, Ledda & Rucci (1987) have recently reviewed structural distortions in ABX_2 and AB_2X_4 tetrahedrally bonded compounds and, based on the available crystallographic information, suggest that the axial c/a ratio as well as the internal distortion of anion displacement away from the ideal $(\frac{1}{4},\frac{1}{4},\frac{1}{8})$ can be used to predict cation and/or vacancy disorder. A c/a ratio near 2·0 indicates little internal distortion and, if not at room temperature, probable cation disorder at higher temperatures. The observed c/a ratio for $ZnGa_2S_4$ is 1·97 suggesting cation disorder. As defined by Garbato *et al.* (1987), the anion distortion is $\sigma_0 = [(x-0{\cdot}25)^2 + (y-0{\cdot}25)^2 + (z-0{\cdot}125)^2]^{1/2}$. Based on their review of known structures a σ_0 value of 0·0145 (5) defines a critical value dividing structures into two classes, those that are ordered ($\sigma_0 > 0{\cdot}0145$) and those that are disordered ($\sigma_0 < 0{\cdot}0145$). Our refinement results for $ZnGa_2S_4$ yield a σ_0 value of 0·0123 which suggests cation disorder. These predictors, as well as a statistically worse least-squares refinement of an ordered cation distribution, are in complete agreement with the prediction by Garbato *et al.* (1987) that $ZnGa_2S_4$ should be disordered. The related compound $CdGa_2S_4$ has been found to be ordered in space group $I\bar{4}$ with Ga in the same layer as the vacancy; in the other layer the Cd and Ga are ordered in different sites (Krämer, Frick & Siebert, 1983). From the structural data given by Krämer *et al.* (1983) the σ_0 value for $CdGa_2S_4$ is 0·0146. The larger size of Cd and the differences in its bonding relative to that of Zn apparently force distortion of the anion array and ordering of the cations.

The results of spectroscopic studies provide additional support for our conclusion that the most chemically reasonable structural model for $ZnGa_2S_4$ is (III) with complete, or nearly complete, cation disorder across the 2(*a*) and 4(*d*) sites. Raman spectral studies of $ZnGa_2S_4$ (White, 1980; Razzetti, Lottici & Antonioli, 1987) revealed broad bands indicative of structural disorder. These results are consistent with similar studies of $Cd_{1-x}Zn_xGa_2S_4$ (Razzetti, Lottici & Antonioli, 1987) in which it was observed that ordering decreased with increasing Zn content. Recently, photoluminescence spectra of $ZnGa_2S_4$ have been interpreted as indicating cation disorder (Derid, Kozhachenko, Radautsan & Tiginyanu, 1989).

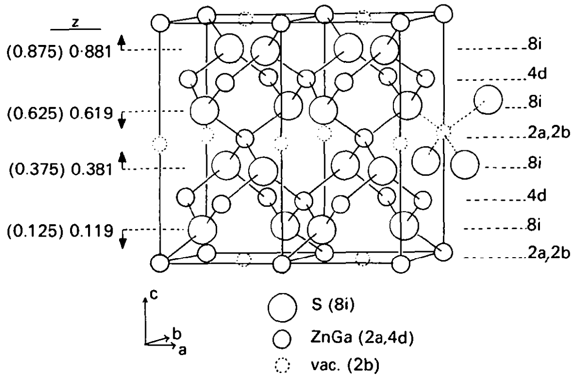

Fig. 2. Two unit cells of the $ZnGa_2S_4$ ($I\bar{4}2m$) structure with (ideal) and observed z coordinates of the S atoms.

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Structures of the Misfit Layer Compounds $(LaS)_{1.13}TaS_2$, 'LaTaS$_3$' and $(CeS)_{1.15}TaS_2$, 'CeTaS$_3$'

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Abstract. $(LaS)_{1.13}TaS_2$ and the isostructural compound $(CeS)_{1.15}TaS_2$ are misfit layer compounds built of alternate double layers of *MS* (*M* = La, Ce), each approximately a {100} slice of NaCl-type *MS*, and sandwiches of TaS$_2$ with Ta surrounded by distorted trigonal prisms of S. Both structural units are described in centered orthorhombic space groups, *Cm*2*a* for the *MS* part ($Z = 4$) and *Fm*2*m* for the TaS$_2$ part ($Z = 4$) of the structure. $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å. For $(LaS)_{1.13}TaS_2$, $M_r = 438{\cdot}3$, $D_x = 6{\cdot}63\ \text{g cm}^{-3}$, $\mu = 367{\cdot}3\ \text{cm}^{-1}$; the LaS part: $a = 5{\cdot}813\ (1)$, $b = 5{\cdot}773\ (1)$, $c = 11{\cdot}526\ (1)$ Å, $V = 386{\cdot}8\ (1)$ Å^3, $F(000) = 292$, $T = 295$ K, $R_F = 0{\cdot}038$ for 255 unique reflections; the TaS$_2$ part: $a = 3{\cdot}295\ (1)$, $b = 5{\cdot}778\ (1)$, $c = 23{\cdot}057\ (1)$ Å, $V = 439{\cdot}0\ (2)$ Å^3, $F(000) = 420$, $T = 295$ K, $R_F = 0{\cdot}034$ for 312 unique reflections; the layer stacking direction is **c**. For $(CeS)_{1.15}TaS_2$, $M_r = 443{\cdot}1$, $D_x = 6{\cdot}78\ \text{g cm}^{-3}$, $\mu = 328{\cdot}8\ \text{cm}^{-1}$; the CeS part: $a = 5{\cdot}737\ (1)$, $b = 5{\cdot}749\ (1)$, $c = 11{\cdot}444\ (2)$ Å, $V = 377{\cdot}5\ (1)$ Å^3, $F(000) = 296$, $T = 295$ K, $R_F = 0{\cdot}062$ for 427 unique reflections; the TaS$_2$ part: $a = 3{\cdot}293\ (1)$, $b = 5{\cdot}752\ (1)$, $c = 22{\cdot}892\ (2)$ Å, $V = 433{\cdot}6\ (2)$ Å^3, $F(000) = 420$, $T = 295$ K, $R_F = 0{\cdot}035$ for 310 unique reflections. The composition is determined by the misfit along the *a* axes (the ratio $a(MS)/a(TaS_2)$].

Introduction. Recent investigations (Wiegers, Meetsma, Haange & de Boer, 1988; Guemas, Rabu,

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