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Studies on AB_2-type intermetallic compounds, I. Mg_2Ge and Mg_2Sn: single-crystal structure refinement and ab initio calculations

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Abstract

The crystal structures of the two Zintl phases Mg_2Ge and Mg_2Sn have been refined using single-crystal X-ray data (anti-CaF_2 type; Mg_2Ge: $a = 6.3849(4)$ Å, $R1 = 0.0149$, $wR2 = 0.0194$; Mg_2Sn: $a = 6.7594(4)$ Å, $R1 = 0.0066$, $wR2 = 0.0165$). Moreover we performed state-of-the-art ab initio calculations within the framework of density functional theory (DFT), in connection with the local density approximation (LDA) and scalar-relativistic, norm-conserving pseudopotentials. We calculated the structural and electronic properties of Mg_2Ge and Mg_2Sn, and obtained the valence charge transfer by applying the method of zero-flux surfaces. We found that a large charge transfer exists, but not as large as predicted by the Zintl–Klemm–Busmann concept.

Keywords: Zintl phases; Magnesium–germanium alloys; Magnesium–tin alloys; Ab initio calculations; Zero-flux surfaces; Valence charge transfer

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1. Introduction

The intermetallic compounds Mg_2Ge and Mg_2Sn belong to the class of Zintl phases. Zintl phases are compounds which consist of two or more (main group) metals or semimetals with a relatively large electronegativity difference, which obey the concept of Zintl, Klemm and Busmann (ZKB). The ZKB concept states that the valence electrons of the less electronegative element (often an alkali or alkaline-earth metal) are completely transferred to the more electronegative one. The latter, with a new number of valence electrons, now builds up partial structures which are also built by main group elements with the corresponding number of valence electrons, or, more generally speaking, partial structures, which obey the $(8 - n)$ rule. For a detailed discussion of the ZBK concept, see the review article by Schäfer et al. [1].

In the case of Mg_2Ge and Mg_2Sn, four valence electrons are formally transferred from magnesium to germanium or tin, respectively. This leads to $4 + 4 = 8$ valence electrons at the germanium or tin atom and corresponds to the valence electron configuration of a noble gas (krypton or xenon, respectively). In accordance with the $(8 - n)$ rule, solids built up by noble gases are characterized by isolated noble-gas atoms. This phenomenon can also be found for Mg_2Ge and Mg_2Sn. Both compounds crystallize in the cubic anti-CaF_2 structure. The germanium or tin atoms are surrounded by eight magnesium atoms, forming a regular cube. Magnesium in turn is tetrahedrally coordinated by germanium or tin (Fig. 1).

The work published in this article had two aims:

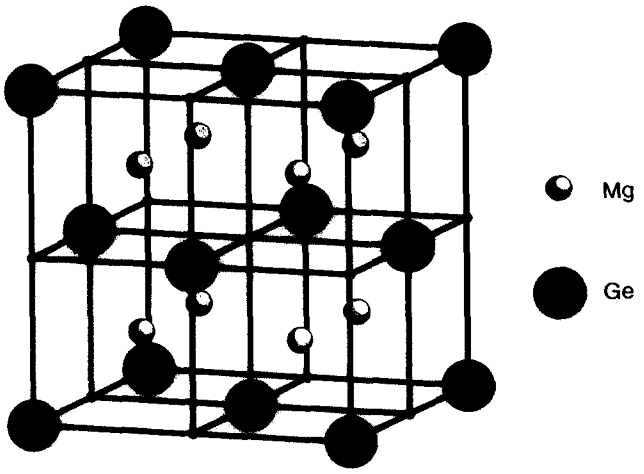

Fig. 1. Anti-CaF_2-type structure of Mg_2Ge (and Mg_2Sn).

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(i) Synthesis and single-crystal structure refinement of Mg_2Ge and Mg_2Sn. Although there can be no serious doubt about the structure type (i.e. anti-CaF_2 type) assignment [2–4] for Mg_2Ge and Mg_2Sn (but see Ref. [5] for a completely different view on the matter), it should be noted that there are no accurate single-crystal data available for these compounds up to now [6].

(ii) Determination of structural and electronic properties by performing state-of-the-art ab initio calculations [7–12]. With the ZKB concept, illustrated above, in mind, we calculated the valence charge transfer by applying the method of zero-flux surfaces [9–16]. This should allow us to compare the formal charge transfer of the valence electrons with the transfer predicted from ab initio calculations.

For that reason the present paper is organized as follows. In Sections 2 and 3 the synthesis and details of the structure refinement for Mg_2Ge and Mg_2Sn are presented. Section 4 deals with the theoretical results. The paper is closed by a conclusion.

2. Experimental details

During the preparation of Mg_2Ge and Mg_2Sn, difficulties arise from the relatively high vapour pressure of magnesium compared to those of germanium or tin. Two different strategies have been used to overcome this problem. The first is synthesis in a closed high-pressure system. This method avoids the vaporization losses inevitably found in normal-pressure experiments and allows for a relatively exact control of composition even at the very high temperatures which are needed for a complete reaction and for single-crystal growth. The method — used here for the synthesis of Mg_2Ge — has been successfully applied before for the synthesis of intermetallic phases in other systems with highly volatile components ([17] and references cited therein).

Another strategy has been followed in the case of Mg_2Sn. From the phase diagram of the Mg–Sn system [18] it follows that the solubility of tin in Mg_2Sn is close to zero. We therefore used a starting mixture with an excess of tin. This reduces the necessary reaction temperatures considerably. The disadvantage of the method is, of course, that the products obtained are inhomogeneous. For the attempted growth of single crystals, however, the presence of excess tin is even favourable, because it acts as a flux material.

The synthesis of Mg_2Ge was carried out in a modified Belt-type high-pressure apparatus [19]. A 2:1 mixture of the reactants magnesium (99.99%; Alfa) and germanium (99.999%; Alfa) was loaded into a tantalum crucible. The reaction conditions were 1.0 GPa, 1400 °C and 20 min. After that, the mixture was slowly cooled down to 900 °C while maintaining the pressure, and then quenched to ambient conditions. The product contained grey metallic, brittle crystals of Mg_2Ge which were not very sensitive to air and moisture. A crystal fragment of approximate dimensions $0.03 \times 0.04 \times 0.06$ mm^3, checked by X-ray film methods, was used for data collection on an Enraf–Nonius CAD-4 diffractometer (Mo Kα radiation, graphite monochromator in incident beam).

For the synthesis of Mg_2Sn a 1:1 mixture of magnesium (99.99%; Alfa) and tin (99.999%; Alfa) was loaded into a corundum ampoule in an atmosphere of dry argon. The corundum ampoule was placed in a quartz ampoule, which was sealed under vacuum. The reaction was carried out in a gradient furnace. The temperature of the reaction zone was 700 °C, and was held for 60 h. After slow cooling down to room temperature it was found that the quartz ampoule was corroded by magnesium vapour during the reaction time. The product in the corundum ampoule, however, did not contain any silicon, as was proved by an EDX analysis. From the grey metallic, brittle ingot a crystal fragment with approximate dimensions $0.02 \times 0.02 \times 0.04$ mm^3 was isolated, checked by X-ray film methods and used for data collection on the CAD-4 diffractometer.

Details of the data collection for Mg_2Ge and Mg_2Sn can be taken from Table 1.

3. Structure analysis

The structures of Mg_2Ge and Mg_2Sn were solved by routine direct methods (SIR 92). In the least-squares refinement (program system SHELXL-93), F^2 magnitudes were used to refine occupation factors and displacement parameters. A numerical correction for absorption was applied to the original data set using the program DIFABS. Convergence was obtained after a few cycles with site occupancy factors (SOFs) corresponding to a 2:1 stoichiometry within one to two standard deviations. Consequently, the SOFs were fixed again at 100% before performing the final refinement. The results are (see also Table 1):

Mg_2Ge: Absorption correction, $T_{min} = 0.688$, $T_{max} = 1.00$; final $wR2 = 0.0194$, $R1 = 0.0149$, $GooF(S) = 0.892$ for all 48 unique reflections; $w^{-1} = \sigma(F^2) + (0.0106P)^2$, $P = [2\max(F_o) + F_c]/3$; four parameters, max shift/esd = 0.000; $\Delta\rho_{min,\ max} = -0.38$, $+0.36$ e Å^{-3}.

Mg_2Sn: Absorption correction $T_{min} = 0.803$, $T_{max} = 1.00$; final $wR2 = 0.0165$, $R1 = 0.0066$, $GooF(S) = 0.973$ for all 51 unique reflections; $w^{-1} = \sigma(F^2) + (0.0094P)^2$, $p = (2\max(F_o) + F_c)/3$; four parameters, max. shift/esd = 0.000; $\Delta\rho_{min,\ max} = -0.26$, $+0.29$ e Å^{-3}.

Table 1
Crystallographic data and details of the structure analysis for Mg_2Ge and Mg_2Sn

	Mg_2Ge	Mg_2Sn
Space group	$Fm\bar{3}m$	
a (Å)	6.3849(4)	6.7594(4)
V (Å^3)	260.30(3)	308.84(4)
Z	4	
$F(000)$	224	296
Density (calc.) (g cm^{-3})	3.092	3.597
Crystal size (mm^3)	$0.03 \times 0.04 \times 0.06$	$0.02 \times 0.02 \times 0.04$
Diffractometer	Enraf–Nonius CAD-4	
Radiation	Mo Kα ($\lambda = 0.71073$ Å)	
Monochromator	Graphite	
Scan mode	$\omega/2\theta$	
Scan width (°)	$0.5 + 0.4 \tan\theta$	$0.55 + 0.45 \tan\theta$
$(\sin\theta/\lambda)_{max}$	0.81	
hkl limits	$-10 \leq h \leq +10$ $0 \leq k \leq +10$ $-10 \leq l \leq +6$	$0 \leq h \leq 9$ $-9 \leq k \leq 9$ $-9 \leq l \leq 9$
Loss of intensity	2.3%	0.3%
Intensities measured	545	680
Unique reflections, R_{int}	48, 0.05	51, 0.04
Absorption correction	DIFABS	
Refined parameters	4	
Mean shift/esd, max. shift	0.000, 0.000	
Final R_1, wR_2, S for all data	0.0149, 0.0194, 0.892	0.0066, 0.0165, 0.973
$(\Delta\rho)_{max, min}$ (e Å^{-3})	+0.38, −0.34	+0.29, −0.26
Extinction factor	0.0035(11)	0.0023(5)

Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the depository number CSD-59093.

4. Ab initio calculations

We performed ab initio calculations within the framework of density functional theory (DFT) [7,8,10,11,13], which is usually evaluated in the local density approximation (LDA). We used scalar-relativistic and norm-conserving pseudopotentials for Ge ($4s^24p^2$), Sn ($5s^25p^2$) and Mg ($2p^63s^2$), which were generated in a scheme proposed by Troullier and Martins [20]. The considered valence electron configurations for Ge, Sn and Mg are given in parentheses. For k-space summation, a set of 19 weighted Monkhorst–Pack points [21,22] was used. The self-consistent calculations were performed with a plane-wave basis set with a kinetic energy cut-off $(\mathbf{k} + \mathbf{G})^2$ of 40 Rydberg (Mg_2Ge) and 45 Rydberg (Mg_2Sn), respectively.

First we calculated the structural properties of Mg_2Ge and Mg_2Sn, assuming for both the anti-CaF_2-type structure, found by experiment. In these calculations the unit-cell volume was allowed to vary. The equilibrium volumes (and hence, the lattice parameters, because the systems considered are cubic) as well as the bulk moduli were determined by fitting the total energy vs. volume curves against Vinet's equation of state [23,24].

The obtained lattice constants, given in Table 3, are in excellent agreement with the experimental data. For comparison purposes, the results of a very recent ab initio calculation for Mg_2Ge and Mg_2Sn [25] are also given. As can be seen from Table 3, our values for the

Table 2
Atomic parameters, displacement factors (Å^2) and selected interatomic distances (Å) for Mg_2Ge and Mg_2Sn

Atom	Position	x	y	z	U_{11}[a]
Ge	4a ($m\bar{3}m$)	0	0	0	0.0072(2)
Mg	8c ($\bar{4}3m$)	1/4	1/4	1/4	0.0109(2)
Sn	4a ($m\bar{3}m$)	0	0	0	0.0098(1)
Mg	8c ($43m$)	1/4	1.4	1/4	0.0138(3)
Ge–Mg	2.7647(3) (8×)		Sn–Mg	2.9269(3) (8×)	
Mg–Ge	2.7647(3) (4×)		Mg–Sn	2.9269(3) (4×)	

[a] $U_{11} = U_{22} = U_{33}$; $U_{12} = U_{13} = U_{23} = 0$.

Table 3
Calculated and experimental values of the equilibrium lattice constants and bulk moduli for Mg_2Ge and Mg_2Sn. The values calculated by Corkill and Cohen [25] are also given for comparison purposes. The experimental values for the bulk moduli are from Ref. [28]

Compound	$a_{o,calc}$ (Å)	$a_{o,exp}$ (Å)	$\frac{a_{o,exp} - a_{o,calc}}{a_{o,exp}}$	$b_{o,calc}$ (kbar)	$b_{o,exp}$ (kbar)
Mg_2Ge	6.309	6.3849(4)	0.012	529	440–547 [28]
Mg_2Ge [25]	6.12		0.042	576	
Mg_2Sn	6.728	6.7594(4)	0.005	445	412 [28]
Mg_2Sn [25]	6.52		0.035	474	

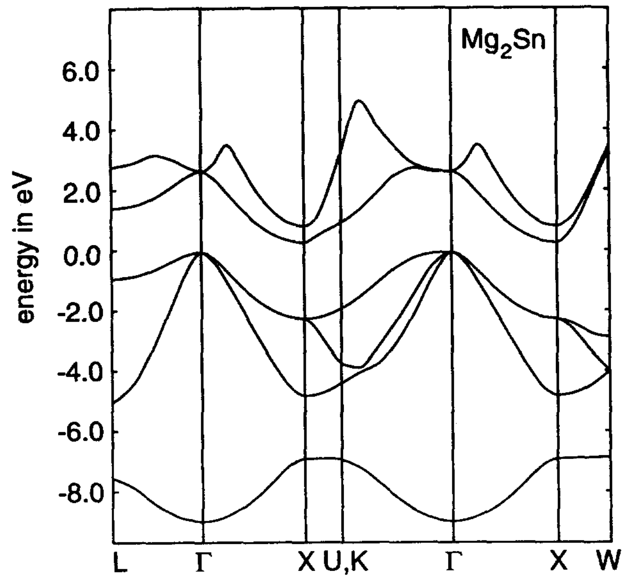

Fig. 2. Calculated band structure for Mg_2Sn.

bulk moduli are at the upper borders of the range of experimental values. This behaviour is even more pronounced with the calculated values of Corkill and Cohen [25].

In Fig. 2 the calculated band structure for Mg_2Sn is presented. Its general appearance agrees very well with that given by Corkill and Cohen. It should be noted, however, that we get a fundamental gap (from Γ to X) of 0.35 eV as compared with an experimental value of 0.23–0.36 eV. The calculated value reported by Corkill and Cohen is 0.026 eV.

Intersections through the valence charge density of Mg_2Ge along the (100) and (110) plane are shown in Fig. 3. The strong localization of the 2p states of magnesium can be seen, whereas the valence electrons of germanium are widely spread.

The main aim of the present investigation was to get a precise estimation of the valence charge transfer in Mg_2Ge and Mg_2Sn, i.e. an estimation of the amount of "ionicity" in these compounds. Some approaches for

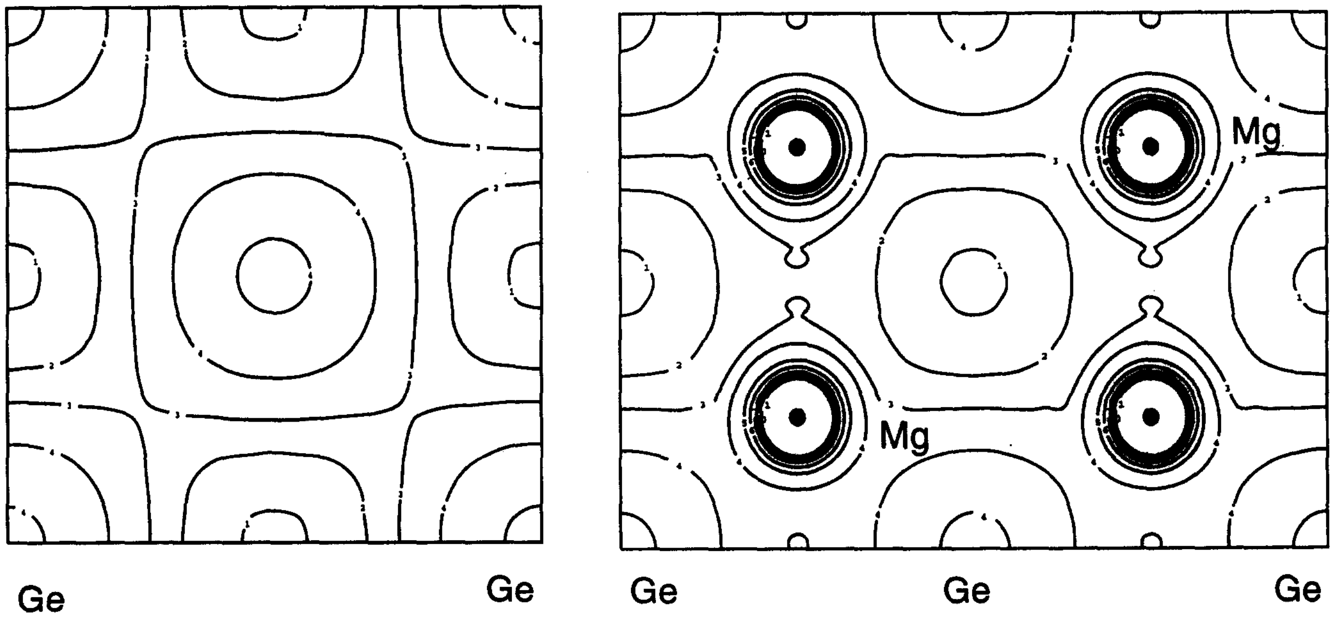

Fig. 3. Intersections through the valence charge density of Mg_2Ge along the (100) (left) and (110) (right) planes.

Table 4
Unit cell volume V_o, total valence charge ρ_o, atomic volumes V_i, atom ic valence charges ρ_i and valence charge transfer δ for Mg_2Ge and Mg_2Sn

	V_o (au^3)	ρ_o (e$^-$)	V_i (au^3)	ρ_i (e$^-$)	δ (e$^-$)
Mg_2Ge	424	20			2.98 ± 0.04
Mg			85 ± 7	6.51 ± 0.02	
Ge			254 ± 14	6.98 ± 0.04	
Mg_2Sn	514	20			2.68 ± 0.06
Mg			105 ± 9	6.66 ± 0.03	
Sn			304 ± 18	6.68 ± 0.06	

the calculation of the charge transfer and the ionicity in crystals are reviewed in Ref. [12]. The general principle behind all ionicity scales is to quantify the rearrangement of electronic charge when atoms are put together to form a solid. The most crucial point in doing this is the estimation of the atomic volumes. We used the quantum-mechanical concept of zero-flux surfaces which was introduced by Bader [13–16] for atoms and molecules and was applied by us to solids [10–12].

We have calculated the respective valence charges for Mg, Ge and Sn by integrating the self-consistent DFT (LDA) charge density over the volume included by the zero-flux surfaces in the anti-CaF_2-type structure for Mg_2Ge and Mg_2Sn. Using the valence charge of the isolated atoms, we easily obtain the valence charge transfer. The calculated atomic volumes and valence charges for Mg, Ge and Sn and the values for the valence charge transfer in Mg_2Ge and Mg_2Sn are given in Table 4. In accordance with experiments [26] and earlier calculations [27] we find that not all of the magnesium 2s electrons are transferred to the Group IV atom, as postulated by the ZKB concept (Mg_2^{2+} Sn^{4-}). The calculated valence transfer, however, gives evidence for the fact that Mg_2Ge and Mg_2Sn can be seen as predominantly ionic materials with a partial covalent bonding.

5. Conclusions

We have refined the crystal structures of the two Zintl phases Mg_2Ge and Mg_2Sn using single-crystal X-ray data, and could confirm the anti-CaF_2-type structure for both compounds. Moreover we performed ab initio calculations within the framework of density functional theory, evaluated in the local density approximation, using Troullier–Martins norm-conserving, scalar-relativistic pseudopotentials. The values obtained for the lattice constants and the fundamental band gaps are in excellent agreement with the experimental values. However, the agreement between the calculated and observed values for the bulk moduli is less satisfactory, bearing in mind the very good agreement between calculated and experimental lattice constants. A redetermination of the bulk moduli for Mg_2Ge and Mg_2Sn therefore seems desirable. An in situ high-pressure X-ray study is in progress in our laboratory.

Summarizing the facts illustrated above, it is clear that the formal valence charge transfer required by the ZKB concept overestimates the actual existing valence charge transfer. Nevertheless the predicting power of the ZKB concept is still large enough for it to be an useful tool to understand the structural behaviour of the Zintl-phase-type intermetallic compounds.

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