

The Charge-Density Study of the Laves Phases, MgZn_2 and MgCu_2

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Abstract. MgZn_2 : $M_r = 155.05$, hexagonal, $P6_3/mmc$, $a = 5.223$ (1), $c = 8.566$ (3) Å, $V = 202.4$ Å³, $Z = 4$, $D_x = 5.09$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 24.1$ mm⁻¹, $F(000) = 288.0$, room temperature. $R = 0.0229$ for 199 independent reflections. MgCu_2 : $M_r = 151.39$, cubic, $Fd\bar{3}m$, $a = 7.034$ (2) Å, $V = 348.0$ Å³, $D_x = 5.78$ Mg m⁻³, $Z = 8$, $\mu(\text{Mo } K\alpha) = 25.1$ mm⁻¹, $F(000) = 560.0$, room temperature. $R = 0.0134$ for 57 independent reflections. Structure factors for the Laves phases MgZn_2 and MgCu_2 were measured by X-ray diffraction. The population analysis of valence electrons in MgZn_2 and MgCu_2 was performed in addition to the refinement of structural parameters using the full-matrix least-squares program. That the kagomé nets in MgZn_2 are deformed, in contrast to the case in MgCu_2 , is analyzed as being due to the different atomic radii for Zn atoms at different positions. Electron transfer from Mg to Zn in MgZn_2 and Cu to Mg in MgCu_2 was found. Difference Fourier synthesis shows that there are residual electrons at the center of the tetrahedra formed by small atoms, *i.e.* Zn or Cu.

Introduction. Recently, charge-density studies in metals have been performed extensively using the X-ray diffraction method. A charge asphericity in a pure V metal has been found by Ohba, Sato & Saito (1981). They measured integrated intensities of reflection pairs from a spherically shaped single crystal of V metal and discussed the asphericity of the *d*-orbital electrons. Ohba, Saito & Wakoh (1982) have also made a measurement on Cr metal. Bilderback & Colella (1975) measured the 222 forbidden reflection of α -Sn. They analyzed the data using the tetrahedral deformation parameter and found the effect of bonding electrons. Merisalo & Soininen (1979) investigated the bonding electrons in β -Sn with the measurement of the almost-forbidden structure factor of 202 from a flat crystal. The intermetallic compounds V_3Si and Cr_3Si were studied by Staudenmann, Coppens & Muller (1976) and Staudenmann (1977, 1978). They compared the electron density at room temperature with that in the superconducting state.

In the Laves-phase compounds, there are three fundamental structures – MgZn_2 (C14), MgCu_2 (C15)

and MgNi_2 (C36) – which were analyzed by Friauf (1927*a,b*) and Laves & Witte (1935). These structures are considered as size-factor compounds. The radius ratio r_A/r_B for them is about 1.23. Laves & Witte (1936) and Lieser & Witte (1952) studied the pseudobinary systems of these compounds and found a close relationship between the crystal structure and the electron concentration.

The pseudobinary systems of MgCu_2 – MgZn_2 , MgZn_2 – MgNi_2 , MgCu_2 – MgNi_2 , MgZn_2 – MgAg_2 and MgCu_2 – MgAl_2 were investigated in detail (Komura, 1962; Komura, Mitarai, Nakatani, Iba & Shimizu, 1970; Komura, Nakaue & Mitarai, 1972; Komura, Mitarai, Nakaue & Tsujimoto, 1972; Komura & Kitano, 1977). The authors ascertained that their crystal structures were strongly governed by the electron concentration. In the course of their investigations several stacking variants were found in addition to the three fundamental structures of C14, C15 and C36.

Komura & Tokunaga (1980) have refined the structures of MgZn_2 , MgNi_2 , MgZn_2 –0.03 MgAg_2 (8*H*), MgZn_2 –0.07 MgAg_2 (9*R*) and MgZn_2 –0.10 MgAg_2 (10*H*) using a full-matrix least-squares method.

In order to study the characteristics of the electron-density distribution in the Mg-based Laves phase, we measured the structure factors of single crystals of MgZn_2 and MgCu_2 accurately and refined the structures by using population analysis and difference Fourier synthesis.

Experimental. Alloy specimens of MgZn_2 and MgCu_2 were prepared by melting together pure Mg and Zn or Cu in an argon-filled induction furnace. The ingot was crushed into small fragments. A tiny fragment was picked out for the intensity measurement for each compound. The fragment of MgZn_2 was shaped into a sphere, but that of MgCu_2 was not, since it was nearly spherical. Diameters of the fragments of MgZn_2 and MgCu_2 were approximately 60 and 40 μm , respectively. Both were confirmed to be single crystals from Laue and oscillation photographs.

Rigaku-automated four-circle diffractometer, graphite monochromator (AFC-5). Monitor counting method used to avoid the effect of the fluctuation of the

than the other principal axes. The thermal ellipsoid of Cu in MgCu_2 is almost a sphere.

Table 1 shows that in MgZn_2 the electron transfer takes place from Mg to Zn. This is consistent with the calculation performed by Rennert & Radwan (1977). They investigated the stability of the structure of MgZn_2 using Shaw's model potential and showed that the charge transfer from Mg to Zn plays an important role. Hafner (1979) calculated the charge-density distribution in CsK_2 which has a MgZn_2 -type structure. He reported that in CsK_2 the electronic charge around Cs is less than that of pure Cs ion-core and the charge around K is more than that of pure K ion-core and a few residual electrons are found in an interstitial region. Although the elements are different, the direction of the charge transfer is the same as in MgZn_2 . Haydock & Johannes (1975) calculated the electronic structure of a transition-metal Laves phase. However, they did not consider the effect of the charge transfer or of the charge-density distribution in the real space. On the other hand, Table 1 reveals that the electrons in Cu in MgCu_2 move to Mg. The direction of the electron transfer of MgCu_2 is opposite to that of MgZn_2 .

Table 2. *Interatomic distances (Å) for MgZn_2 and MgCu_2*

MgZn ₂			MgCu ₂				
Mg			Mg				
Mg	(×1)	3.2061 (20) Å	Mg	(×4)	3.0458 (5) Å		
Mg	(×3)	3.2021 (5)	Cu	(×12)	2.9161 (7)		
Zn(1)	(×3)	3.0632 (6)	Cu	Mg	(×6)		
Zn(2)	(×3)	3.0624 (13)					
Zn(2)	(×6)	3.0644 (6)	Cu			(×6)	2.4869 (5)
Zn(1)							
Mg	(×6)	3.0632 (6)					
Zn(2)	(×6)	2.6340 (7)					
Zn(2)							
Mg	(×2)	3.0624 (13)					
Mg	(×4)	3.0644 (8)					
Zn(1)	(×2)	2.6340 (7)					
Zn(2)	(×2)	2.6562 (5)					
Zn(2)	(×2)	2.5668 (8)					

The interatomic distances in MgZn_2 and MgCu_2 are shown in Table 2. Those in MgZn_2 are almost the same as those given in a previous paper (Komura & Tokunaga, 1980). On the basis of the spherical-atom model, we can understand that if the atomic radii of Zn(1) and Zn(2) were the same as those of Cu in MgCu_2 , the kagomé net would not be deformed. The fact that the kagomé net is deformed suggests that the atomic radii of Zn(1) are different from those of Zn(2). Table 1 shows that the Zn(1) atoms have more electrons than the Zn(2) atoms; therefore, it can be assumed the atomic radii of Zn(1) are larger than those of Zn(2). The larger atoms Zn(1) repel the sandwiched atoms Zn(2) which form the triangles in the kagomé net as seen in Fig. 1(b).

Interatomic distances in Table 2 show that those between Zn(1) and Zn(2) are larger than the average distance 2.6115 (5) Å between Zn(2) and Zn(2). In a previous paper, Komura & Tokunaga (1980) reported that, in MgNi_2 and other long-period structures, the kagomé nets which are in the mode of connection of the MgZn_2 structure are also deformed, whereas those in the mode of connection of the MgCu_2 structure are not deformed. Therefore, the deformation of the kagomé net may probably be caused by the difference in the atomic radii mentioned above.

Difference Fourier maps of MgZn_2 synthesized with the coefficients ($F_o - F_c$) after the population analysis are shown in Fig. 2. They are shown in sections every $c/16$ parallel to (001). In this figure, there are residual electrons at the corner of the unit cell on the section $z = \frac{3}{16}$. Their positions are at the centers of the tetrahedra formed by Zn atoms. Above the Mg atom on the plane $z = \frac{1}{16}$, there are also residual electrons at $z = \frac{2}{16}$. The section at $z = \frac{4}{16}$ shows the steepest hills and valleys; this may be related to the fact that the Zn(2) atoms on this plane are shifted from the positions which form the regular hexagons. The difference Fourier section through the kagomé net in the cubic MgCu_2 corresponding to the plane $z = \frac{4}{16}$ in Fig. 2 is shown in Fig. 3(a). The map shows a smoother feature than that

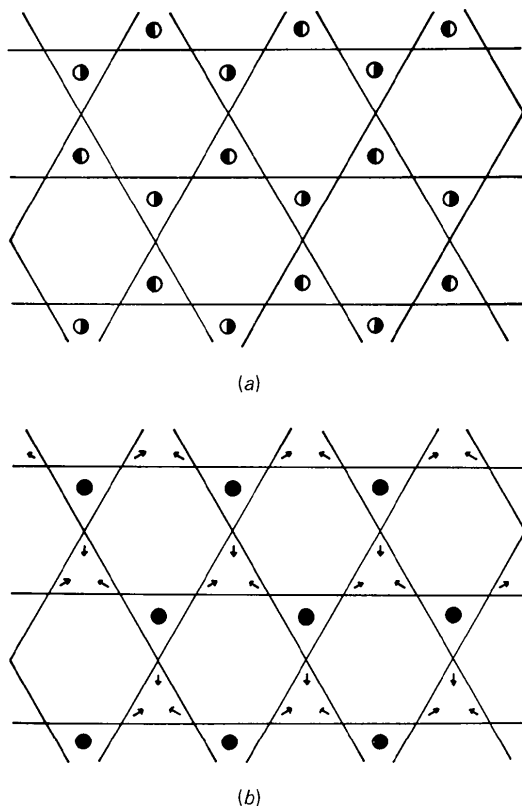


Fig. 1. (a) Kagomé net in MgCu_2 . (b) Kagomé net in MgZn_2 . Atoms Cu or Zn are placed at every cross point of the lines. \bullet atoms placed below the net; \circ atoms above the net; \bullet atoms placed above and below the kagomé net. Arrows indicate the directions of atom shifts.

of MgZn₂. In Fig. 3(b) the section parallel to (001) of MgCu₂ is shown. The positions $\frac{1}{8}, \frac{5}{8}, \frac{1}{8}$ and $\frac{5}{8}, \frac{1}{8}, \frac{1}{8}$ on the plane $z = \frac{1}{8}$ are the centers of the tetrahedra formed by Cu atoms at $z = 0$ and $z = \frac{1}{4}$. Residual electrons are found at these positions just as in the case of MgZn₂ in Fig. 2. Although the directions of charge transfer are opposite, the residual electrons in both MgZn₂ and MgCu₂ are found at the centers of the tetrahedra formed by small atoms. In the Laves-phase structure, there are many kinds of tetrahedra formed by large (*A*) and small (*B*) atoms; that is, AB_3 , A_2B_2 and B_4 aggregate for the AB_2 -type Laves phase. The residual electrons, however, are not found at the centers of tetrahedra except for B_4 tetrahedra formed by major small component atoms. Edward (1972) noted a qualitative relationship between the structure of the element of major small atoms and the occurrence of C14 or C15 in the Laves phase. In the present study, the residual electrons are found at the centers of the tetrahedra which are formed by major small atoms.

There are two kinds of coordination polyhedra in the Laves phase: CN12 icosahedron and CN16 Friauf polyhedron (Samson, 1958). There are no bonding

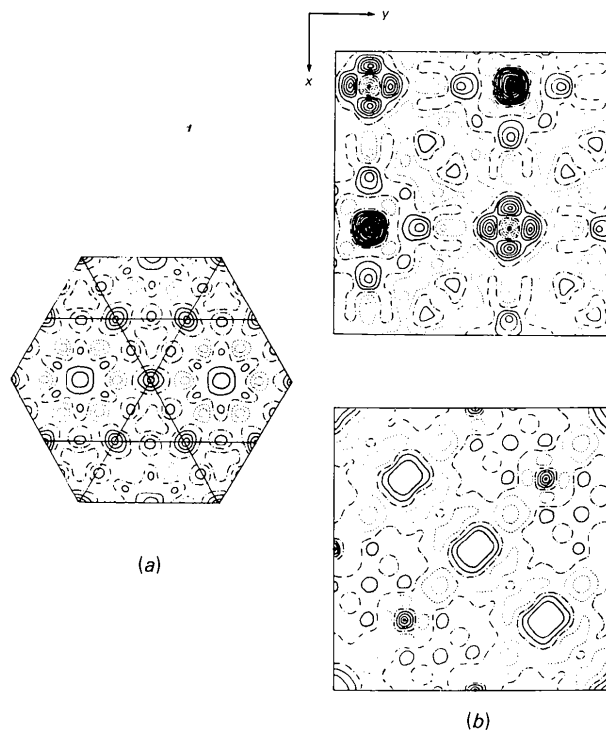


Fig. 3. Difference Fourier maps of MgCu₂. (a) (111) plane. Cu atoms are placed at every cross point of the lines and form the kagomé net. (b) Sections parallel to the (001) plane (upper, $z = \frac{1}{8}$; lower, $z = 0$). The contour interval is $0.1 \text{ e } \text{\AA}^{-3}$ and solid and dotted lines represent positive and negative contours, respectively. On the plane $z = 0$, small atoms Cu are placed at $\frac{1}{2}, 0, 0$; $\frac{1}{3}, \frac{1}{3}, 0$ and $0, \frac{1}{3}, \frac{1}{3}$ as indicated by black dots.

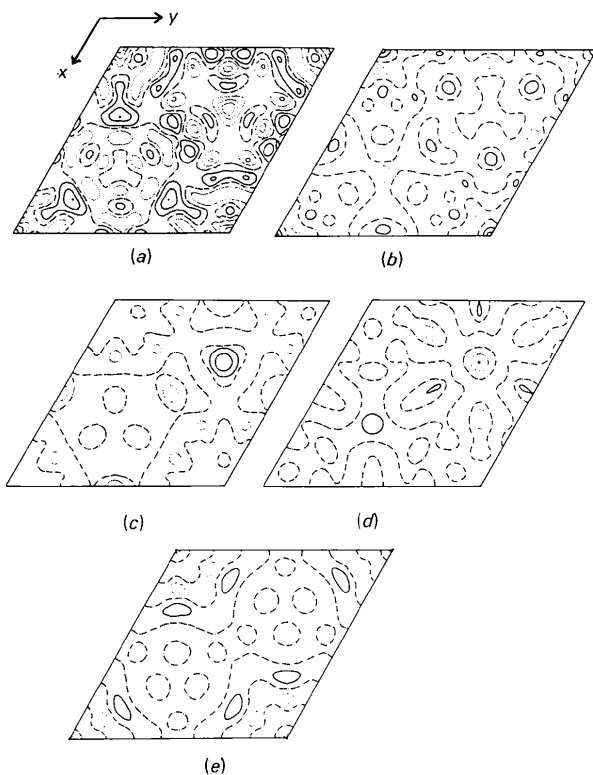


Fig. 2. Difference Fourier maps of MgZn₂, sections parallel to the (001) plane. The contour interval is $0.5 \text{ e } \text{\AA}^{-3}$ and solid and dotted lines represent positive and negative contours, respectively. Zn atoms are placed on the planes $z = 0$ and $z = \frac{1}{4}$ and are indicated by black dots. (a) $z = \frac{1}{16}$, (b) $z = \frac{3}{16}$, (c) $z = \frac{5}{16}$, (d) $z = \frac{7}{16}$, (e) $z = 0$.

electrons between the central atom and surrounding atoms in these polyhedra from inspection of difference Fourier maps. Charge asphericity around the atoms is observed in some cases; for example, there are residual electrons above the Mg atoms in MgZn₂ ($z = \frac{2}{16}$). However, a detailed analysis of the asphericity seems to be difficult with the present data.

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The Structure of Hexapotassium Disodium Hexatungstoplatinate(IV) Dodecahydrate, $K_6Na_2[PtW_6O_{24}]\cdot 12H_2O$

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Abstract. $M_r = 2178.77$, trigonal, $R\bar{3}m$, $a = 9.740(1) \text{ \AA}$, $\alpha = 84.81(1)^\circ$, $U = 913.3(1) \text{ \AA}^3$, $Z = 1$, $D_x = 3.961 \text{ g cm}^{-3}$, Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$), $\mu(\text{Mo } K\alpha) = 247.3 \text{ cm}^{-1}$, $F(000) = 970$, $T = 298 \text{ K}$. The structure was determined by the heavy-atom method and refined by the block-diagonal least-squares method. The final $R = 0.059$ for 859 independent reflections collected by diffractometry. The heteropolyanion has a structure with point symmetry $D_{3d}(\bar{3}m)$ of the ideal Anderson-type heteropolyanion. The Pt–W and W–W distances are $3.238(1) \text{ \AA}$. Three types of W–O (W–O_a, W–O_b and W–O_c) distances are $1.75(1)$, $1.97(2)$ and $2.16(2) \text{ \AA}$.

Introduction. Recently we reported the synthesis and crystal structure of $Na_5[H_3PtW_6O_{24}]\cdot 20H_2O$ (Lee, Kobayashi & Sasaki, 1983). Some heteropolytungstates containing platinum have been reported by Gibbs (Pt:W = 1:10, 1:20, 2:30 and 1:30) and Rosenheim (Pt:W = 2:7) (*Gmelin's Handbuch der Anorganischen Chemie*, 1933), but their syntheses could not be

reproduced in our laboratory. We report here the structure of the unprotonated heteropolyanion $[PtW_6O_{24}]^{8-}$ obtained at pH ca 7.5.

Experimental. 0.81 g of $K_2WO_4\cdot 2H_2O$ was dissolved in 40 ml of hot water. To this solution 40 ml of 0.16 g $K_2Pt(OH)_6$ solution (containing a small portion of Na^+ ion) was added dropwise and 3M HNO_3 was used to adjust the pH to ca 6.0. After the mixture was heated for half an hour on the water bath and cooled, the pH was adjusted to ca 7.5. Small pale-yellow hexagonal crystals were obtained after two days when the solution was concentrated to about 70 ml at room temperature. The crystals are stable in air and a TGA–DSC diagram showed that the water molecules (0.95 w%) were slowly lost from the crystals in the temperature range 356–411 K.

A single crystal of dimensions $0.13 \times 0.14 \times 0.08 \text{ mm}$, Rigaku automated four-circle diffractometer, graphite monochromator, cell parameters refined by least-squares method on the basis of 25 independent indices ($40 < 2\theta < 45^\circ$), Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$); intensity measurement performed to $2\theta = 60^\circ$ (the $+h$, $+k$, $+l$ set), ω – 2θ scan method, scan

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