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An X-ray Diffraction Study of Lattice Compression of the $L1_0$-type Intermetallic Phase PdZn

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Abstract

The pressure dependence of the lattice parameters of PdZn having an $L1_0$-type structure has been measured up to 24 GPa (240 kbar) with a diamond-anvil-type cell and sodium chloride as an internal-pressure marker. The axial ratio c/a, which was originally 0·814 (1) [between the two extreme values 1·00 and 0·707 $(=1/\sqrt{2})$ for this type of structure], does not decrease but increases with increasing pressure and after reaching 0·822 at 10 GPa it remains almost constant on further compression. The equation of state has been derived for the $L1_0$-type structure assuming pairwise interactions between like atoms and between unlike atoms and comparison is made between the calculated and observed compression curves of the a and c axes. The anisotropy in the lattice compressibility leads to a considerably larger interatomic potential for the unlike atom pair than for the like atom pair.

Introduction

The $L1_0$-type superlattice is one of the common types formed by binary alloys with equiatomic composition. It is based on a face-centered cubic lattice and, as shown in Fig. 1, alternate (002) planes are occupied exclusively by one kind of atom. Hence, each atom has eight nearest neighbors of opposite kind in the adjacent (002) planes and four of the same kind in its own (002) plane. The resulting structure is tetragonal with axial ratio c/a generally smaller than unity.* The layered arrangement of atoms in the $L1_0$-type structure suggests an anisotropy in the lattice compressibility which may be observed when the alloy is subjected to high pressures. The present author (Iwasaki, 1978) observed for MgIn, with c/a = 0·957, a larger compressibility in the **a** direction than in the **c** direction.

In the palladium–zinc alloy system, there exists a β_1 phase with the $L1_0$-type structure. The axial ratio is far from unity, being 0·817 at Pd–50 at.%Zn (Neumann, Ipser & Chang, 1978). If c/a is decreased to 0·707 $(=1/\sqrt{2})$, the structure becomes a $B2$ type, another common type for alloys with equiatomic composition. The structure of PdZn is therefore regarded as an intermediate between the ideal $L1_0$ ($c/a = 1{\cdot}00$) and $B2$ ($c/a = 0{\cdot}707$) types. It will be of interest to see what kind of anisotropy is observed in the compressibility for PdZn having a larger tetragonal distortion and, furthermore, to what extent c/a changes.

Any crystal shows a resistance against compression, most of which arises from interatomic interactions. If the interactions are expressed as a function of the interatomic distance, it is possible to calculate an equation of state for that crystal and compare it with the observed pressure dependence of the lattice parameters. For the crystal with an alternate layering of atoms such as the $L1_0$-type structure, the interaction between atoms lying on a layer is different from that between atoms on adjacent layers and the comparison can provide information on how these are different.

In the present paper, results of high-pressure X-ray diffraction experiments on PdZn using a diamond-anvil cell are described together with their interpretation in terms of the equation of state derived for the $L1_0$-type phase.

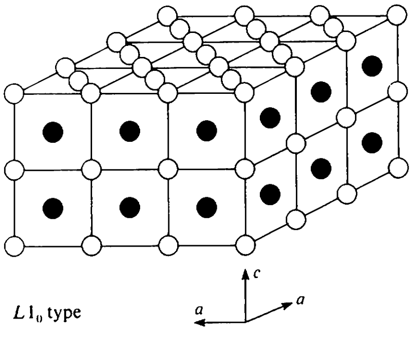

Fig. 1. Atomic arrangement on the $L1_0$-type superlattice.

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* Strictly speaking, the true crystallographic unit cell of the $L1_0$-type structure contains two atoms with $c/a > 1$, but in the present paper we prefer the conventional unit cell containing four atoms with $c/a < 1$ often used in the literature.

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Experimental procedures

The alloy was prepared by melting palladium (99·99% pure) and zinc (99·999% pure) in an evacuated quartz tube placed in a high-frequency induction furnace. A large difference in the melting points of the two constituent metals made it difficult to obtain a homogeneous alloy ingot, but several attempts showed that if the zinc content was slightly decreased from 50 at.%, the high-concentration limit of the β_1 phase, the alloy formation proceeded satisfactorily. The ingot thus prepared and subjected to homogenizing heat treatment was silvery yellow in colour. Its composition was determined by chemical analysis to be Pd–47·3 ± 0·5 at.%Zn. The lattice parameters were measured using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5405$ Å) to give $a = 4{\cdot}101 \pm 0{\cdot}002$ and $c = 3{\cdot}338 \pm 0{\cdot}002$ Å with $c/a = 0{\cdot}814 \pm 0{\cdot}001$. These values are in fair agreement with those reported by Neumann, Ipser & Chang (1978).

The high-pressure equipment used was of the diamond-anvil type used in a previous study (Iwasaki, 1978). The anvils were a pair of gem-quality diamonds on which the culet faces were ground, one to a diameter of 0·3 (or 0·5 mm) and the other to 0·7 mm. Fine-grained powder of PdZn was squeezed between the anvils using an Inconnel disc 0·3 mm thick as a gasket. Filtered Mo $K\alpha$ radiation from a sealed-off tube with fine focus (45 kV and 14 mA) as well as that from a high-power tube with rotatory anode (60 kV, 500 mA) were used to take X-ray diffraction photographs of the compressed alloy. A fine collimated X-ray beam, 0·1 mm in diameter, was incident upon the alloy sample intimately mixed with fine-grained powder of NaCl, which served as a pressure-transmitting medium and simultaneously as an internal-pressure marker. The diffraction pattern was recorded on a flat film placed at a distance of 62 mm from the sample. Five diffraction lines, 111, 200, 002, 220 and 202, were used for the determination of the lattice parameters of PdZn. Error arising from a shrinkage of the film was corrected for by measuring the distance between the shadow edges of the film cassette. An attempt to correct the error arising from sample displacement was made by adopting the method proposed by Singh (1972), but its magnitude was very small with no serious effect on the lattice-parameter determination. The accuracy of the a and c values was estimated to be ±0·1–0·2% at lower pressures, but with increasing pressure it became progressively difficult to read correct positions on the film of the diffraction lines with higher indices owing to their broadening and the increased background, resulting in a lower accuracy of 0·4% at pressures in excess of 15 GPa. The diffraction lines 200, 220 and 222 of NaCl were used for the determination of pressure generated within the cell, adopting Decker's (1971) scale. The error of the pressure values which arises from that in the lattice-parameter measurement of NaCl was estimated to be about ±3% at low pressures and it increased to ±4% at pressures higher than 15 GPa.

Recent work (Sato, Akimoto & Inoue, 1973; Yamamoto, Nomura & Fujiwara, 1977) has shown that there are some difficulties in high-pressure X-ray diffraction experiments using solids as the pressure-transmitting medium. The difficulties are, for example, the effect of pressure intensification and that of stress inhomogeneity and anisotropy. The best way to avoid these difficulties is to use a liquid medium, but there is no substance which remains in a liquid state beyond 10 GPa. However, the relatively low shear strength of both the metallic specimens and NaCl is thought to reduce the effects and here no allowance was made for them.

Experimental results

Fig. 2 shows the pressure dependence of the a and c parameters of PdZn, where they are normalized to their respective values at atmospheric pressure. Vertical bars attached to each data point represent a measure of the accuracy. At lower pressures, a is seen to decrease faster than c: for instance, at 4·8 GPa $a = 4{\cdot}056 \pm 0{\cdot}007$ Å with $a/a_0 = 0{\cdot}989$, while $c = 3{\cdot}330 \pm 0{\cdot}007$ Å with $c/c_0 = 0{\cdot}998$. The anisotropy in the lattice compressibility is not much marked compared with other layered compounds, but it suggests that the nearest-neighbor interaction between unlike atoms gives rise to a stronger resistance against compression than that between like atoms. It, however, becomes gradually less clear with increasing pressure. The axial ratio c/a is shown as a function of pressure in the lower part of Fig. 2. As a result of the anisotropy it first increases from the initial value of 0·814 to 0·822 ± 0·003 at 10 GPa and then has an almost constant value on further compression. The larger compressibility of a has already been observed for MgIn and this suggests that the $L1_0$-type superlattices are deformed in a similar way under pressure, but the form of the compression

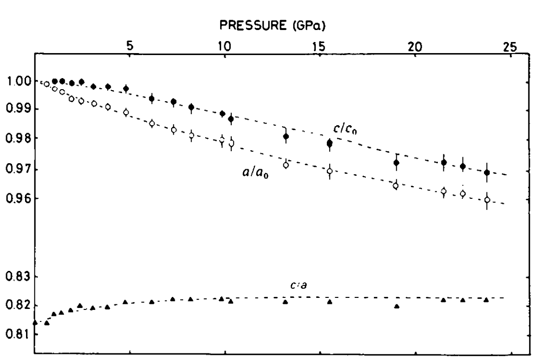

Fig. 2. Pressure dependence of the lattice parameters and axial ratio of PdZn. $a_0 = 4{\cdot}101$ and $c_0 = 3{\cdot}338$ Å. Broken lines drawn through the data points represent the compression curves calculated on the basis of the pairwise interaction model.

curve of c of MgIn is somewhat different from that of PdZn. The curve of MgIn is always concave upwards, showing that the compressibility decreases continuously with increasing pressure. The difference in the pressure dependence of the lattice parameters of PdZn and MgIn may be due to a difference in the mechanism of crystal cohesion.

Pressure dependence of the unit-cell volume of PdZn calculated from the a and c parameters and normalized to its value at atmospheric pressure is shown in Fig. 3 by solid circles. A least-squares fitting of a Birch–Murnaghan equation, originally derived on the basis of a finite-strain theory and customarily used in high-pressure research, to the observed pressure–volume relation gives a bulk modulus K_0 (at 0 GPa) of 160 GPa for PdZn. This value is a little smaller than that of palladium metal, but appreciably larger than that of zinc metal.

Equation of state for a $L1_0$-type structure and analysis of the compression curves of PdZn

In order to derive an equation of state for a crystal, it is necessary to know the total crystal energy as a function of volume or lattice parameters. This is available for ionic crystals in which Coulombic and core-repulsive interactions make the main contributions to the cohesion and they are described as pairwise interactions between atoms. For metallic crystals, the interaction arising from conduction electrons takes part in the cohesion mechanism and some intuitive treatments are required to obtain a volume dependence of the crystal energy. Though successful calculation of an equation of state has been carried out for simple metals (for example, Senoo, Mii & Fujishiro, 1976), lack of information on the electronic structure of intermetallic phases does not permit one to perform such a calculation. It has been shown (Heine & Weaire, 1970), however, that the energy of a metal crystal can be expressed to a first approximation as a sum of the pairwise interaction energies of atoms. The same situation is here assumed to exist for PdZn, and in what follows an attempt is made to calculate the compression curves and to see how the observed curves can be reproduced.

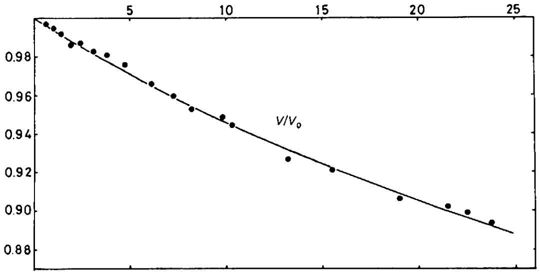

Fig. 3. Pressure dependence of the volume of PdZn.

Gibbs free energy consists of the three terms

$$G = U_0 + F_{\text{vib}} + PV, \qquad (1)$$

where U_0 is the energy of a crystal at 0 K, F_{vib} the free energy due to the thermal vibration of the atoms and V the volume of the crystal. In binary intermetallic phases there are three kinds of interaction, *i.e.* those between A and A, between A and B and between B and B atoms, which are described respectively as $v_{AA}(r)$, $v_{AB}(r)$ and $v_{BB}(r)$. Then, U_0 in (1) can be written as

$$U_0 = \frac{N}{2}\left\{\sum_i m_i[v_{AA}(r_i) + v_{BB}(r_i)]/2 + \sum_j n_j v_{AB}(r_j)\right\}, \quad (2)$$

N being the total number of atoms, m_i multiplicity of the like atom pair with separation r_i and n_j a similar quantity for the unlike atom pair with separation r_j.

For a tetragonal crystal such as the $L1_0$ type, the interatomic distances and the crystal volume are a function of a and c and their equilibrium values at a given pressure and temperature are obtained by differentiating (1) with respect to a and c as follows,

$$\left(\frac{\partial G}{\partial a}\right)_{P,T} = 0 \quad \text{and} \quad \left(\frac{\partial G}{\partial c}\right)_{P,T} = 0. \qquad (3)$$

These are just the equations of state for the anisotropic crystal. $(\partial U_0/\partial a)$ and $(\partial U_0/\partial c)$ are easily obtained from (2), while in order to obtain an explicit form of $(\partial F_{\text{vib}}/\partial a)$ and $(\partial F_{\text{vib}}/\partial c)$, it is necessary to evaluate the following quantities

$$\sum_{j=1}^{3N} \frac{\mathrm{d}\ln\omega_j}{\mathrm{d}\ln a} \quad \text{and} \quad \sum_{j=1}^{3N} \frac{\mathrm{d}\ln\omega_j}{\mathrm{d}\ln c},$$

where ω_j is the frequency of the jth vibrational mode. Leibfried & Ludwig (1961) suggested that the average over the vibrational modes of the logarithmic derivative can be approximated by one-half of the logarithmic derivative of the average squared frequency. We use this approximation here. Then,

$$\frac{1}{3N}\sum_{j=1}^{3N} \frac{\mathrm{d}\ln\omega_j}{\mathrm{d}\ln a} = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}\ln a}\left[\ln\left(\frac{1}{3N}\sum_{j=1}^{3N}\omega_j^2\right)\right]$$

$$= \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}\ln a}(\ln \overline{\omega^2}), \qquad (4)$$

with a similar equation for c. $\overline{\omega^2}$ can be calculated, following a method given by Roy, Manna & Sen Gupta (1974), as a sum over the derivatives of the interatomic potential $v(r)$.

The equation of state for a is then written in the following form:

$$\sum_i m_i \frac{\mathrm{d}v_l}{\mathrm{d}r_i}\frac{\partial r_i}{\partial a} + \sum_j n_j \frac{\mathrm{d}v_u}{\mathrm{d}r_j}\frac{\partial r_j}{\partial a}$$

$$+ \frac{3}{2}kT\left[\sum_i m_i (r_i^2 v_l''' + 2r_i v_l'' - 2v_l')\frac{\partial r_i}{\partial a}\right.$$

$$\left. + \sum_j n_j (r_j^2 v_u''' + 2r_j v_u'' - 2v_u')\frac{\partial r_j}{\partial a}\right]$$

$$\times\left[\sum_i m_i (r_i^2 v_i'' + 2r_i v_l') + \sum_j n_j (r_j^2 v_u'' + 2r_j v_u')\right]^{-1}$$

$$+ acP = 0, \tag{5}$$

where v_l is $(v_{AA} + v_{BB})/2$ and v_u is v_{AB}. v''', v'' and v' represent respectively the third, second and first derivative of $v(r)$. The equation for c has the same form as (5), except that $(\partial r_i/\partial a)$ and $(\partial r_j/\partial a)$ are replaced respectively by $(\partial r_i/\partial c)$ and $(\partial r_j/\partial c)$ and acP is replaced by $a^2 P/2$.

As the form of $v(r)$, we choose the Morse potential function

$$v(r) = D\{\exp[-2\alpha(r - r_o)] - 2\exp[-\alpha(r - r_o)]\}, \tag{6}$$

which has been widely used for describing interatomic potentials in metals (for example, Milstein, 1971) and alloys (for example, Kuwano, Ogata & Eguchi, 1977). The function contains three parameters, D, α and r_o to be determined by comparing the calculated equation-of-state curves with the observed compression curves. In principle, v_{AA} is different from v_{BB}, but the symmetry of the $L1_0$-type structure does not allow one to distinguish one from the other as far as volume dependence of the free energy of the crystal is concerned. The equation of state of PdZn is calculated using v_l for like atom pairs and v_u for unlike atom pairs as defined above.

The anisotropy in the initial compressibilities of the a and c axes suggests that $\alpha_l^2 D_l$ is appreciably smaller than $\alpha_u^2 D_u$ and its gradual decrease with increasing pressure suggests that $\alpha_l > \alpha_u$, while approximate values of $r_{o,l}$ and $r_{o,u}$ are determined from the observed a and c values at atmospheric pressure. An iterative calculation has been carried out, with the aid of a computer, to obtain the parameter values which can reproduce the observed compression curves through (5) for the a axis and through the corresponding equation for the c axis. In doing the calculation, the interaction out to the fiftieth neighbor was taken into account. Broken lines drawn through the data points in Fig. 2 represent the calculated equation-of-state curves and the six parameters* used in this calculation are listed in Table 1. For PdZn, pressure arising from the term F_{vib} in (1), the so-called thermal pressure, has been shown to be small compared with that arising from the term U_0.

Table 1. *Parameter values of interatomic potentials of* PdZn *and* MgIn *determined from the lattice compression curves*

The potential has the form

$$v(r) = D\{\exp[-2\alpha(r - r_o)] - 2\exp[-\alpha(r - r_o)]\}.$$

		D (10^{-22} J)	α (Å^{-1})	r_o (Å)
PdZn	like	530 ± 2	1·422 ± 0·005	3·052 ± 0·002
	unlike	952 ± 4	1·338 ± 0·001	2·911 ± 0·0005
MgIn*	like	132 ± 2	2·234 ± 0·01	3·230 ± 0·001
	unlike	222 ± 3	2·046 ± 0·005	3·166 ± 0·0005

* Based on the data of Iwasaki (1978).

Discussion

The $L1_0$-type superlattice is one of the ideal structures in which an equal number of the two kinds of atoms are distributed on the face-centered cubic lattice so that each atom is surrounded by as many atoms of opposite kind as possible. It is not unreasonable to assume that this ordered arrangement is a result of attractive interaction between the nearest-neighboring unlike atoms and it gives rise to a shortening of the unit-cell edge in the **c** direction. The degree of the shortening depends on the strength of the interaction. For PdZn with large tetragonal distortion, the interaction may be so strong that Pd atoms with hard 4*d* core are almost in contact with Zn atoms and *vice versa*, whereas the like atoms are not close to each other. This is the origin of the initial lower compressibility of the c axis. At a pressure of about 10 GPa, both like and unlike nearest neighbors come into contact and on further compression all the atoms contract uniformly keeping the axial ratio nearly constant. The existence of the strong attractive interaction in PdZn is supported by the observed high stability and large heat of formation of the superlattice, as will be mentioned below. If the limiting value 0·822 of the axial ratio at higher pressures is regarded as that expected from the dense packing of Pd and Zn atoms in the $L1_0$-type superlattice, the ratio of atomic radii is calculated to be 0·812 from a simple geometrical consideration. This large difference in the atomic radii may be explained by Machlin's (1974) model, which assumes electron transfer from Zn to Pd atoms.

For MgIn, the attractive interaction is not strong compared with PdZn, giving small tetragonal distortion. Unlike PdZn, the small size of the atomic cores, especially that of magnesium, suggests that no effective contact occurs at atmospheric pressure and the a and c axes decrease in length monotonously with the application of pressure. The origin of the anisotropy in the

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* The parameter values were obtained neglecting a small deviation in the alloy composition from stoichiometry but, even if it were taken into account, only a minor change, of the order of several percent, would be introduced in the magnitudes.

compressibility may be found, as was discussed previously (Iwasaki, 1978), in the volume dependence of the two counteracting factors, the band-structure energy and the electrostatic energy.

Although the simplifying assumption for the crystal energy of PdZn was made, the calculated pressure dependence of the lattice parameters can well reproduce the observed anisotropy in the lattice compressibility as shown in Fig. 2. The interatomic potential, $v(r)$, has quite a large minimum for the unlike pairs and its steep rise with decreasing interatomic distance is a reflection of the initial low compressibility of the c axis, while the depth of the potential minimum for the like atom pairs is only half of that for the unlike atom pairs. Replacement of one like atom pair by one unlike atom pair at the nearest-neighbor distance will release an energy as large as 620×10^{-22} J, which is consistent with the fact that disordering of atoms in the PdZn superlattice does not occur up to a temperature of 1300 K. The potentials are rapidly damped with increasing interatomic distance, and at the tenth-neighbor distance they are only 1·8% of that at the nearest-neighbor distance. Roughly speaking, the resistance against compression comes from the interatomic interaction of the first- to sixth-neighbor pairs.

Similar analysis has been carried out for MgIn using the compression data obtained in a previous work (Iwasaki, 1978) and the parameter values are shown in Table 1 for comparison. The fact that the unlike atom pair has a deeper potential minimum is common to the two intermetallic phases, but the magnitude of $v(r)$ of PdZn is considerably larger than that of MgIn, indicating a much stronger interatomic interaction in the former. This is in agreement with the observations for these phases.

Once the interatomic potentials are known, it is possible to calculate physical quantities directly derivable from them. Energy of cohesion is defined as the energy required to decompose a PdZn crystal into separate atoms; it is 447 kJ/mol using the parameter values given in Table 1. This is approximately the same as the cohesive energy reported for the metals nickel, palladium and platinum. The corresponding value for MgIn is 74·1 kJ/mol. An approximate calculation of the heat of formation can be made by taking a difference between the calculated cohesive energy and the energy which is obtained assuming that all the interatomic interactions in the crystal are given by $v_l(r)$. The heat of formation thus calculated is 179 kJ/mol for PdZn. This value is larger than the reported value by a factor of two, but it can be said that the potentials obtained in the present work reproduce an abnormally large heat of formation of PdZn. The calculated heat of formation for MgIn is 23·1 kJ/mol.

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