

Fig. 2 represents charge density in contours at intervals of  $\sigma(0.074 \text{ e } \text{\AA}^{-3})$  on the plane  $z = 0.75$ . The interatomic axes  $\text{Be}'\text{-F}(1')$ ,  $\text{Be}'\text{-F}(2')$ ,  $\text{Li}(1')\text{-F}(4')$ ,  $\text{Li}(1')\text{-F}(2')$ ,  $\text{Li}(2')\text{-F}(2')$ , and  $\text{Li}(2')\text{-F}(3')$  lie approximately on this plane. The deformation density features associated with the  $\text{Be}\text{-F}(1)$  and  $\text{Be}\text{-F}(2)$  bonds have maxima of about  $0.42 \text{ e } \text{\AA}^{-3}$  and features similar to those seen in Fig. 1. As in Fig. 1, there appears to be little or no localization of charge deformation density on the  $\text{Li}\text{-F}$  bond axes.

McGinney (1972) has suggested the  $\text{Li}\text{-F}$  bonding interactions may have covalent character. In the figures which display the deformation density along the (approximate) axis of each type of interaction, only  $\text{Li}(1)\text{-F}(4)$  has substantial density symmetrically disposed about its axis. Because the density pattern has its maximum less than  $0.5 \text{ \AA}$  from F, and in any case does not rise as high as  $3\sigma$ , this feature cannot be considered significant. By the pattern of no significant charge accumulation or localization in the  $\text{Li}\text{-F}$  bonds, the diffraction data fail to support the suggestion that covalent character associated with the  $\text{Li}\text{-F}$  bond is significant.

### Conclusion

Charge deformation density provides direct experimental support of McGinney's (1972) prediction of

covalent character for the  $\text{Be}\text{-F}$  bonds. The corresponding deformation density features are significant point-by-point at better than  $3\sigma$  and the overall patterns are unambiguously recognizable as typical of covalent bonding between the lighter elements with orbitals of  $s$  and  $p$  character. On the other hand, we have not been able to evince clear indications of the suggested covalency in  $\text{Li}\text{-F}$  bonds.

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## Lattice Modulation in the Long-Period Superstructure of $\text{Cu}_3\text{Sn}$

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### Abstract

An X-ray diffraction investigation has been made on single crystals of  $\text{Cu}_3\text{Sn}$  having a periodic antiphase domain structure based on the  $\text{Cu}_3\text{Ti}$ -type ordered lattice. Refinement of the structure has shown that most of atoms are not located exactly on the sites of the basic lattice but are displaced with a largest magnitude of  $0.126 \text{ \AA}$ . The displacements of the atoms consist of two parts having different characteristics. One has its component in the direction of the long period and is opposite in sense for Cu and Sn atoms. This character-

istic is the same as that of the displacements of atoms found in the periodic antiphase domain structures based on the  $L1_2$ - and  $L1_0$ -type ordered lattices and this identity suggests that electron charge density waves are responsible for its production. The other part has its components in both the long-period direction and the direction perpendicular to it and is observed only for Cu atoms; the origin for this can be found in the marked disparity in sizes between the two sorts of atoms. [Crystal data:  $\text{Cu}_{75.5}\text{Sn}_{24.5}$ , orthorhombic, *Cmcm*,  $a = 5.529(8)$ ,  $b = 47.75(6)$ ,  $c = 4.323(5) \text{ \AA}$ ,  $V = 1141(5) \text{ \AA}^3$ , 80 atoms/cell,  $D_x = 8.97(4) \text{ g cm}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 390.4 \text{ cm}^{-1}$ .]

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### Introduction

A series of X-ray diffraction studies (Iwasaki, 1962; Iwasaki, Hirabayashi & Ogawa, 1965; Okamura, Iwasaki & Ogawa, 1968; Okamura, 1970; Iwasaki, Okamura & Ogawa, 1971) have shown that the formation of the periodic antiphase domain structure in such binary intermetallic phases as  $Au_{3+x}Zn$ ,\*  $Au_3Cd$ ,  $CuAu$  II,  $Cu_3Pd$  and  $Pd_3Mn$  is always accompanied by small displacements of atoms from the sites of the basic  $L1_2$ - or  $L1_0$ -type ordered lattice, one kind of atom thereby being displaced towards the antiphase domain boundary while the other kind of atom is displaced away from the boundary. Kataoka & Iwasaki (1981) derived, laying emphasis upon the role of conduction electrons, an expression for the crystal energy of the antiphase ordered alloys and showed that the interaction between electron charge density waves and the potential field of the atoms makes the alloy structure unstable against atomic displacements. The theory can give correctly (when they are described as displacement waves) the polarization, wavelength and phase of the waves, although it is not accurate enough to calculate exactly their amplitude. Since the existence of electron charge density waves is possible whenever the periodic antiphase domain structure forms in alloys (Sato, 1979), similar displacement-type lattice modulation is expected to exist in other alloys having long-period superstructures.

In the Cu–Sn system, the  $\epsilon$  phase forming at the composition Cu–25 at.% Sn is known to crystallize in a long-period superstructure (Bernal, 1928; Schubert, Kiefer, Wilkens & Haufler, 1955). The basic lattice is of the orthorhombic  $Cu_3Ti$  type, shown in Fig. 1, and antiphase shifts occur at every five unit cells along the  $b_0$ -axis direction, the resultant superstructure also being orthorhombic with the lattice constants  $a = a_0$ ,  $b = 10b_0$  and  $c = c_0$ , where  $a_0$ ,  $b_0$  and  $c_0$  are those of the basic  $Cu_3Ti$ -type structure. Since this is regarded as an ordered structure formed in the hexagonal close-packed

\* The notation  $Au_{3+x}Zn$  indicates that the structure is based on the composition  $Au/Zn = 3/1$  but that the phase actually exists in the composition rich in Au.

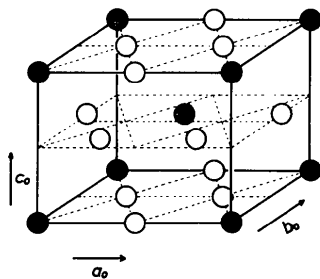


Fig. 1.  $Cu_3Ti$ -type ordered lattice as a basic structure of the long-period superstructure of  $Cu_3Sn$ .

lattice, the long-period superstructure of  $Cu_3Sn$  is considered to belong to a family of the h.c.p.-lattice-based antiphase structures. When monovalent Cu atoms are replaced by divalent Zn atoms on forming  $Cu_{3-x}Zn_xSn$  ternary alloys, the long period has been observed to decrease from  $10b_0$  for  $x = 0$  to  $8b_0$  for  $x = 0.07$  and to  $6b_0$  for  $x = 0.14$  (van Sande, de Ridder, van Tendeloo, van Landuyt & Amelinckx, 1978). This variation of the long period with the electron-atom ratio suggests that the idea of Fermi surface–Brillouin zone boundary construction introduced by Sato & Toth (1965) is applicable to the case of  $Cu_3Sn$ , and its long-period superstructure is stabilized by the energy of the conduction electrons. It is therefore highly likely that the electron charge density waves induce displacements of atoms in  $Cu_3Sn$  just as they do in the family of the f.c.c.-lattice-based antiphase structures.

In an X-ray diffraction study of the superstructure of  $Cu_3Sn$ , Schubert *et al.* (1955) showed that observed intensities recorded on single-crystal rotation photographs could be accounted for if every atom in the structure were assumed to be displaced in the direction of the long period. The number of reflections they used for the structure determination was, however, not so large that a feature of the atomic displacements could not be determined unambiguously.

We present in this paper the results of a structural investigation in which X-ray intensity data collected from a much wider region of reciprocal space have been used. New aspects of the periodic displacements of atoms in  $Cu_3Sn$  have been found and physical significance has been given to them taking into account the electron theory of displacement waves in alloys and the large difference in size between Cu and Sn atoms.

### Experimental

The alloy was prepared from 99.99% pure Cu and 99.999% pure Sn by melting them in quartz capsules filled with argon gas. Small tips were cut from the ingot and remelted at 1073 K. The melt was quickly cooled to 903 K across the intermediate  $\gamma$ -phase region and annealed at 723 K for about one month. By this heat treatment, growth of the  $\gamma$  phase was suppressed and single crystals of the low-temperature  $\epsilon$  phase were obtained. Chemical analysis of the ingot showed the composition of the alloy to be Cu–24.5 at.% Sn, showing that loss in the content upon melting was very small. This value was adopted hereafter as the composition of the single crystals. The sample for X-ray diffraction study was selected from them and thinned in a mixed solution of hydrofluoric acid and nitric acid.

Precession photographs indicated Laue class  $mmm$  for the long-period superstructure of  $Cu_3Sn$ . All

reflexions could be indexed with integral numbers in conformity with the results of the earlier studies that the superperiod was just ten times the period of the basic  $\text{Cu}_3\text{Ti}$ -type lattice. Systematic absences for  $hkl$  reflexions with  $h+k$  odd and for  $h0l$  reflexions with  $l$  odd lead to the possible space group  $Cmcm$ . Crystal data including the measured lattice constants are summarized in the *Abstract*.

Intensity data were collected on a Rigaku four-circle diffractometer equipped with a scintillation counter and pulse-height analyzer with a  $\theta-2\theta$  scan. The incident beam from a rotatory molybdenum target, operated at 50 kV and 100 mA, was monochromated by reflexion from a pyrolytic-graphite plate. The single-crystal sample used was an irregular tetrahedron, 0.23 mm on one edge. Reflexions in a hemisphere ( $h > 0$ ) of reciprocal space were measured and intensities were averaged for crystallographically equivalent reflexions. 1779 independent reflexions remained, of which 811 had values of structure factors larger than  $3\sigma$ ,  $\sigma$  being obtained from counting statistics.

The measured intensities were corrected for Lorentz and polarization effects, and also for absorption assuming the sample shape to be spherical with  $\mu R = 2.7$ .

### Structure refinement

Fig. 2 shows a zero-layer precession photograph of  $\text{Cu}_3\text{Sn}$  taken with monochromated  $\text{Mo } K\alpha$  radiation, in which an array of  $hk0$ -type reflexions is seen. Closely spaced vertical rows of spots along the  $k$  axis are the

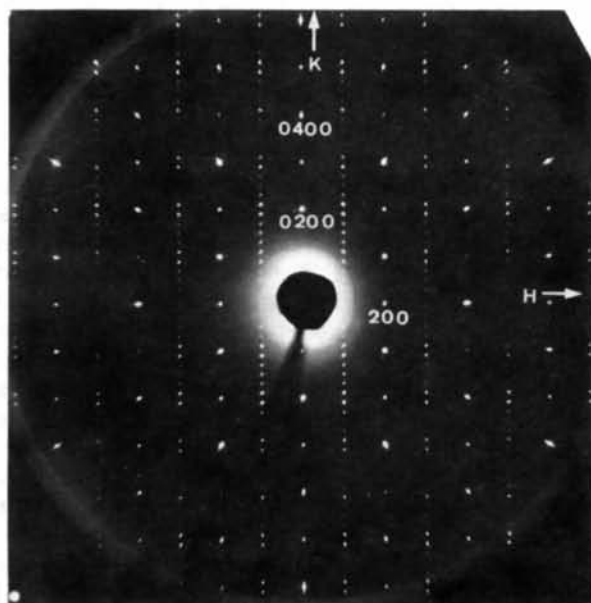


Fig. 2. X-ray precession photograph of  $\text{Cu-24.5 at.}\%$  Sn alloy, showing a section parallel to the (001) plane of the reciprocal lattice. Monochromated  $\text{Mo } K\alpha$  radiation was used.

superlattice reflexions split due to the formation of a periodic antiphase domain structure. If there were no displacement-type lattice modulation, the superlattice reflexions with  $k = 10 \pm 1, 20 \pm 1, 40 \pm 1$  and  $50 \pm 1$  would have strong intensities, while those with  $k = \pm 1, 30 \pm 1$  and  $60 \pm 1$  would have negligibly weak intensities. What is actually observed is strong intensities for the reflexions with  $k = 30 \pm 1$  and  $60 \pm 1$ , as seen in Fig. 2; there is also another systematic deviation. It is to be noted that the intensity variation along the vertical row of the superlattice reflexions depends on the index of  $h$ , suggesting that the lattice modulation exists not only along the  $b$  axis but also along the  $a$  axis in the superstructure.

Within the framework of the space group  $Cmcm$ , Cu atoms are allocated to five sets of 8( $g$ ) sites with the positional parameters  $(x, y, \frac{1}{2})$  and five sets of 4( $c$ ) sites with  $(0, y, \frac{1}{2})$ , while Sn atoms are allocated to another five sets of 4( $c$ ) sites in the superstructure of the stoichiometric composition. The  $x$  and  $y$  values for the structure in which all the atoms are exactly located on the positions of the basic  $\text{Cu}_3\text{Ti}$ -type lattice are given in Table 1 under the column heading 'Ideal parameters'.

Starting from the ideal structure model, structure refinement was carried out using the programs UNICS-III (Sakurai & Kobayashi, 1979) and LS1 on the Tohoku University ACOS computer. The parameters to be refined were 36 in all, *i.e.* one scale factor, twenty atomic positional parameters and fifteen isotropic temperature factors. Also included were two isotropic parameters based on the method proposed by Becker & Coppens (1974). The function minimized in the refinement was

$$\sum_{\mathbf{h}} w_{\mathbf{h}} \{ [F_o(\mathbf{h})]^2 - [KF_c(\mathbf{h})]^2 \}^2, \quad (1)$$

where  $K$  is the scale factor and  $w_{\mathbf{h}}$  is a weight given by

$$w_{\mathbf{h}}^{-1} = [\sigma^2(F_o) + (0.09F_o)^2] 4F_o^2. \quad (2)$$

Table 1. Structural parameters for  $\text{Cu}_3\text{Sn}$

Atomic sites	$A^*$	Ideal parameters		$x$	$y$	$B (\text{\AA}^2)$	
		$x_0$	$y_0$				
4( $c$ ) (0, $y$ , $\frac{1}{2}$ )	(1)	i	0	$-\frac{1}{30}$	-0.03373 (8)	0.76 (9)	
	(2)		0	$-\frac{1}{30}$	-0.13388 (8)	0.70 (9)	
	(3)		0	$-\frac{1}{30}$	-0.23383 (8)	0.73 (9)	
	(4)		0	$-\frac{1}{30}$	-0.33370 (8)	0.70 (9)	
	(5)		0	$-\frac{1}{30}$	-0.43340 (8)	0.78 (9)	
4( $c$ ) (0, $y$ , $\frac{1}{2}$ )	(1)	ii	0	$\frac{2}{30}$	0.06821 (16)	1.02 (13)	
	(2)		0	$\frac{1}{30}$	0.16903 (18)	1.04 (13)	
	(3)		0	$\frac{2}{30}$	0.26900 (16)	0.92 (12)	
	(4)		0	$\frac{1}{30}$	0.36930 (17)	0.94 (13)	
	(5)		0	$\frac{2}{30}$	0.46879 (17)	0.97 (14)	
8( $g$ ) ( $x$ , $y$ , $\frac{1}{2}$ )	(1)	ii	$\frac{1}{20}$	$\frac{1}{20}$	0.2607 (11)	0.01577 (13)	0.94 (10)
	(2)		$\frac{1}{20}$	$\frac{2}{20}$	0.2514 (10)	0.11574 (13)	0.97 (10)
	(3)		$\frac{1}{20}$	$\frac{13}{20}$	0.2508 (11)	0.21594 (12)	0.98 (10)
	(4)		$\frac{1}{20}$	$\frac{14}{20}$	0.2525 (11)	0.31594 (12)	0.97 (10)
	(5)		$\frac{1}{20}$	$\frac{21}{20}$	0.2528 (10)	0.41585 (12)	0.95 (9)

\* Allocation of atoms: (i) 0.98 Sn + 0.02 Cu; (ii) Cu.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974), the relativistic Hartree-Fock wavefunction values being used for Cu and Sn. Corrections for anomalous scattering with Mo  $K\alpha$  radiation were also taken from *International Tables* (1974).

During the refinement, appreciable correlation was found for the two extinction parameters  $\rho$  and  $g$ , and these were determined separately, first by fixing one and varying the other and subsequently *vice versa*. Finally, the agreement factor  $R$  decreased to 0.087, where  $R = \sum_{\mathbf{h}} |F_o(\mathbf{h}) - |F_c(\mathbf{h})|| / \sum_{\mathbf{h}} F_o(\mathbf{h})$  and the reflexions with  $F_o(\mathbf{h}) < 3\sigma$  were excluded. If the summation was extended to include all reflexions, it yielded the  $R$  value 0.135. The real composition of our alloy was not stoichiometric but slightly rich in Cu, as was described above, and an attempt was made to determine whether the excess Cu atoms were distributed randomly among the Sn sites by introducing five occupancy parameters in the refinement calculation. We found that no improvement in the  $R$  value was obtained when the excess Cu atoms were assumed to enter in particular Sn sites. Hence, the occupancy parameters were fixed to be 0.98 Sn + 0.02 Cu for all the Sn sites.

The final, refined atomic positional parameters and temperature factors are given in Table 1.\* The parameters  $K$ ,  $\rho$  and  $g$  are respectively 1.33,  $1.7 \times 10^4$

and  $5.0 \times 10^3$ . With these last two parameters, the extinction factors  $y$  of the five most affected reflexions have values smaller than 0.5, and the minimum is 0.33.

The calculated interatomic distances are listed in Table 2.

### Displacements of atoms in the superstructure of $\text{Cu}_3\text{Sn}$

The refined atomic positional parameters listed in Table 1 show significant deviations from the values listed under the column heading 'Ideal parameters'; this is particularly notable for the  $y$  parameters of Cu atoms on the  $4(c)(i)$  sites with  $i = 1-5$ . The magnitudes of the displacements are 0.074, 0.113, 0.112, 0.126 and 0.102 Å for  $i = 1, 2, 3, 4$  and 5, respectively. For Sn atoms (strictly 0.98 Sn + 0.02 Cu atoms) on the  $4(c)(j)$  sites with  $j = 1-5$ , the sense of the displacements is opposite to that of the Cu atoms and their magnitudes are smaller by a factor of 4-7. The Cu atoms on the  $8(g)$  sites have displacement components not only in the  $b$ -axis direction, of magnitude ranging from 0.035 to 0.044 Å, but also in the  $a$ -axis direction. Those on the  $8(g)(1)$  sites have a component in this direction as large as 0.059 Å, while the others have a component of very small magnitude. In Fig. 3, the

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38286 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Interatomic distances (Å) in  $\text{Cu}_3\text{Sn}$

Sn*-Cu		Cu-Cu	
4(c)(1)-4(c)(1)	2.717 (6)	8(g)(1)-4(c)(1)	2.889 (10)
-4(c)(5)	2.767 (4)	-4(c)(5)	2.604 (10)
-8(g)(1)	2.736 (5)	-8(c)(1)	2.639 (5)
	2.769 (8)		2.634 (6)
-8(g)(5)	2.769 (8)		2.883 (10)
4(c)(2)-4(c)(2)	2.737 (6)	8(g)(2)-4(c)(1)	2.663 (10)
-4(c)(4)	2.769 (4)	-4(c)(2)	2.900 (10)
-8(g)(2)	2.711 (4)	-4(c)(4)	2.659 (5)
-8(g)(4)	2.759 (7)	-8(g)(2)	2.780 (9)
-8(g)(5)	2.740 (7)	-8(g)(5)	2.637 (5)
4(c)(3)-4(c)(3)	2.737 (6)	8(g)(3)-4(c)(2)	2.634 (10)
	2.768 (4)	-4(c)(3)	2.662 (5)
-8(g)(3)	2.706 (4)		2.888 (9)
	2.766 (7)	-8(g)(3)	2.773 (10)
-8(g)(4)	2.742 (7)	-8(g)(4)	2.644 (5)
4(c)(4)-4(c)(2)	2.768 (4)	8(g)(4)-4(c)(2)	2.657 (5)
-4(c)(4)	2.750 (6)	-4(c)(3)	2.641 (9)
-8(g)(2)	2.777 (8)	-4(c)(4)	2.905 (10)
-8(g)(3)	2.742 (7)	-8(g)(4)	2.792 (10)
-8(g)(4)	2.709 (4)		
4(c)(5)-4(c)(1)	2.766 (4)	8(g)(5)-4(c)(1)	2.668 (5)
-4(c)(5)	2.744 (6)	-4(c)(4)	2.626 (9)
-8(g)(1)	2.764 (8)	-4(c)(5)	2.889 (10)
-8(g)(2)	2.721 (7)	-8(g)(5)	2.796 (9)
-8(g)(5)	2.707 (4)		

\* 0.98 Sn + 0.02 Cu.

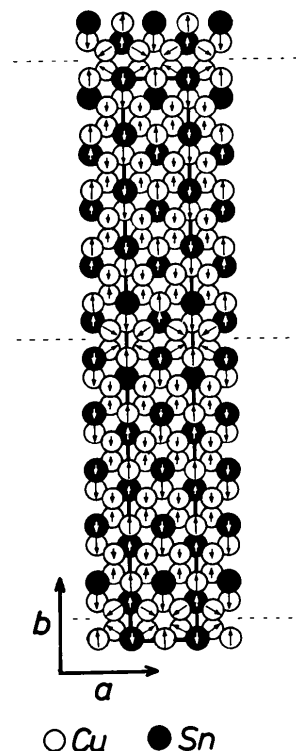


Fig. 3. Long-period superstructure of  $\text{Cu}_3\text{Sn}$  projected onto the (001) plane. Arrows indicate the direction and magnitude (though not to scale) of the displacements of atoms. Broken lines show where antiphase domain boundaries exist.

displacements of atoms in the long-period superstructure of  $\text{Cu}_3\text{Sn}$  are shown by the arrows, the structure thereby being depicted as a projection onto the (001) plane and the length of the arrows being approximately proportional (though not to scale) to the magnitudes of the displacements. It can be seen that the Cu atoms having displacement components both parallel to and perpendicular to the long-period direction are located near the antiphase domain boundaries, indicated by broken lines.

In the earlier investigation by Schubert *et al.* (1955), the magnitudes of the displacements were determined to be 0.04 Å for Cu atoms on the 4(c) sites, 0.08 Å for those on the 8(g) sites and 0.03 Å for Sn atoms, which are not in agreement with the values determined by the present work. The specific feature of the displacements of the atoms located near the antiphase domain boundaries was not disclosed.

If the atoms in  $\text{Cu}_3\text{Sn}$  were positioned exactly on the sites of the basic lattice, there would be only two kinds of nearest-neighbor distances: those of 2.765 Å between atoms lying on the same (001) plane, and those of 2.687 Å between atoms lying on adjacent planes, irrespective of the kind of atom pairs. The size of the larger Sn atom suggests that the latter distance would be too small for the Cu–Sn atom pair. As is seen from Table 2, the displacements in  $\text{Cu}_3\text{Sn}$  do occur so that they relax this unreasonably short interatomic distance and the shortest one between Cu and Sn atoms is increased to 2.706 Å. This point will be discussed below.

### Discussion

The lattice modulation in the long-period superstructure of  $\text{Cu}_3\text{Sn}$  has some resemblance to that found in the f.c.c.-lattice-based antiphase structures, while there exist simultaneously some peculiarities. In order to obtain an insight into these, consider the superstructure to be composed of a sequence of two kinds of (010) planes, one consisting solely of Cu atoms (called hereafter unmixed plane) and the other consisting of equal numbers of Cu and Sn atoms (mixed planes). Then, the sequence of planes is (from top to bottom in Fig. 3) mixed, mixed, unmixed, unmixed, mixed, mixed,.... Fig. 4 shows the superstructure of  $\text{Au}_3\text{Cd}$  projected onto the (010) plane. In this structure, the direction of the long period lies along the *c* axis and the displacements of atoms occur on alternate (001) planes, which contain equal numbers of Au and Cd atoms and are mixed planes. The magnitudes of the displacements are larger for the lighter Cd atoms. No modulation exists in the unmixed planes. Although there is a difference in the structure of the basic ordered lattice between  $\text{Cu}_3\text{Sn}$  and  $\text{Au}_3\text{Cd}$ , it can be seen that the displacements of atoms located on the mixed planes

of the former are essentially of the same type as those of the latter. According to Kataoka & Iwasaki (1981), an interaction between the electron charge density waves existing in the superstructure of  $\text{Au}_3\text{Cd}$  and the potentials of atoms induces displacement waves. These consist of the waves of optical and acoustical modes and there are two optical waves with the wavevectors  $\mathbf{q} = (2\pi/a, 0, \pi/2a)$  and  $(0, 2\pi/a, \pi/2a)$ , where *a* is the lattice constant of the basic  $L1_2$ -type cell. Each of these waves gives displacements in the [001] direction that are opposite in sense for the different kinds of atoms on the plane parallel to the antiphase domain boundaries. However, the displacements from the two optical waves have signs such that they cancel out at the unmixed planes, while they add up at the mixed planes. The acoustical waves give displacements that are in the same sense for the two kinds of atoms and may produce periodic expansion and contraction of the lattice spacing. The atomic positions in  $\text{Au}_3\text{Cd}$  determined by X-ray diffraction investigation (Iwasaki *et al.*, 1965) are explained well by the two sets of optical waves, the amplitude of the acoustical waves thereby being small. It is not unreasonable to assume that a similar interaction between the charge density waves and the potentials of the atoms induces the displacements of atoms located on the mixed (010) planes of  $\text{Cu}_3\text{Sn}$ . That is, the Cu and Sn atoms on the 4(c) sites are displaced by the gradient of conduction electron charge density which has different signs at the different kinds of atoms on the same (010) plane.

There is such a general trend in the magnitudes of the displacements in the f.c.c.-lattice-based antiphase structures that the lighter atoms move by larger distances. As was mentioned above, the same is true for the structure of  $\text{Cu}_3\text{Sn}$ , but the ratio of the magnitude of the displacement of the Cu atoms to that of the Sn atoms is considerably larger as compared to that found in these antiphase structures. The origin of the anomalously large displacements of Cu atoms will be considered below.

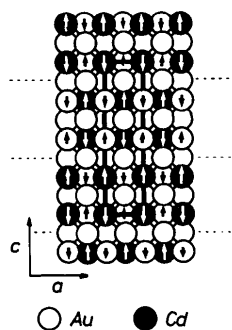


Fig. 4. Long-period superstructure of  $\text{Au}_3\text{Cd}$  projected onto the (010) plane.

We next consider the displacements of Cu atoms on the 8(g) sites, which constitute the unmixed (010) planes. The origin of this part of the displacement can be found in the marked disparity in sizes between Cu and Sn atoms. Table 3 lists the ratio of atomic diameters for coordination number 12 (Pearson, 1972) of the intermetallic phases having long-period superstructures. The combination Cu–Sn gives a ratio significantly larger than unity. The same trend can be seen in the size factor of substitutional solid solutions (King, 1966) also listed in Table 3. This represents an expansion or a contraction of the f.c.c. solid solutions (the majority-atom component in each intermetallic phase is solvent atom) when 1 at.% of solute atoms (the minority-atom component) are dissolved. Hence, Sn atoms arranged in an ordered fashion in the superstructure of Cu<sub>3</sub>Sn push their immediate neighbors away, giving rise to the displacements of the Cu atoms on the 8(g) sites as shown in Fig. 3. Simultaneously, they push away the Cu atoms on the 4(c) sites, which have already been displaced by the charge density gradients. For the Cu atoms located in the interior of the antiphase domains, the symmetry of the Sn-atom arrangement around each of them allows them to move only in the direction of the *b* axis, whereas, for the Cu atoms located near the domain boundaries, the change in ordering scheme of the Sn atoms across the boundaries introduces a pushing force which has a component in the direction of the *a* axis. Cu<sub>3</sub>Sn is the first example in which two kinds of atomic displacements having different origins coexist. The fact that the atomic-size disparity influences the atomic positions is also found in the structure of ζ-bronze, Cu<sub>20</sub>Sn<sub>6</sub> (Brandon, Pearson & Tozer, 1975).

Au–33 at.% Cd (Au<sub>3</sub>Cd<sub>1+</sub>) alloy is also known to have a long-period superstructure which belongs to the family of h.c.p.-lattice-based antiphase structures. Unlike the case of Cu<sub>3</sub>Sn, the superstructure has hexagonal symmetry. A single-crystal X-ray diffraction investigation (Watanabe & Iwasaki, 1982)

Table 3. Ratio of atomic diameters for CN = 12 and size factor of the intermetallic phases in which a long-period superstructure forms

Intermetallic phase	$D_B/D_A^*$	Size factor† <i>B</i> in <i>A</i>
Cu <sub>3</sub> Sn	1.21	+0.8340
Au <sub>3</sub> Zn	0.97	–0.1382
Au <sub>3</sub> Cd	1.09	+0.1314
CuAuII	1.13	+0.4759
Cu <sub>3</sub> Pd	1.08	+0.2796
Pd <sub>3</sub> Mn	0.95	+0.0368
Au <sub>3</sub> Cd <sub>1+</sub>	1.09	+0.1314

\* *A* and *B* represent the majority- and minority-atom components, respectively (after Pearson, 1972).

† Taken from King (1966). It represents a percentage change in the lattice parameter when 1 at.% of *B* is dissolved in f.c.c. *A*.

revealed the existence of displacement-type lattice modulation which could be described as a superposition of three sets of sinusoidal, longitudinal displacement waves with their wavevectors making an angle of 120° with each other. This feature of the displacements was different from that of Cu<sub>3</sub>Sn, but the displacements were shown to be caused by an interaction with the electron charge density waves. Atomic-size disparity-induced displacements were not observed, because the size factor was small, as shown in Table 3.

Recently, Miida & Watanabe (1982) reported that a lattice modulation identical in type to that in Au<sub>3</sub>Cd exists in the intermetallic phase Al<sub>3</sub>Ti<sub>1+</sub>. Its origin may be found in the same interaction as that found in Au<sub>3</sub>Cd and other intermetallic phases. Judging from the small size factor, repulsive interaction between atoms will not be important in Al<sub>3</sub>Ti<sub>1+</sub>.

X-ray diffraction intensity measurements were carried out using the diffractometer at the Department of Applied Physics, Faculty of Engineering, Tohoku University. The authors express their thanks to Professors T. Ikeda and N. Yamada for providing an opportunity to use that diffractometer.

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