Lattice Modulation in the Hexagonal-Type Antiphase Domain Structure of Au–33at.% Cd Alloy

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Abstract
The crystal structure of an ordered Au–33at.% Cd alloy has been reinvestigated by X-ray diffraction. Least-squares refinement using single-crystal intensity data collected by photographic methods has shown that mixed occupation by the two kinds of atoms preferentially occurs in the atomic sites located near the boundaries of the hexagonal antiphase domains, confirming the results obtained by electron diffraction [Hirabayashi, Yamaguchi, Hiraga, Ino, Sato & Toth (1970). J. Phys. Chem. Solids, 31, 77-94]. The refinement has also shown that many of the atoms are periodically displaced from the normal positions of the fundamental h.c.p. lattice. The physical significance of the occupancy and displacement modulations is discussed. The latter bears a resemblance to the motion of cations in the transition-metal dichalcogenides and the direction of the displacements in the alloy can be explained if charge-density waves synchronizing with the occupancy waves are assumed.

1. Introduction
There exist many binary alloys crystallizing in the so-called long-period superlattice (LPS) structure (Sato & Toth, 1965; Ogawa, 1973). The fundamental lattice of these alloys is f.c.c. and periodic out-of-step shifts occur in one, or simultaneously in two, principal crystallographic direction(s). Burkhardt, Schubert, Toth & Sato (1968) found that a LPS is also formed in the alloys whose fundamental lattice is h.c.p. Later, Hirabayashi, Yamaguchi, Hiraga, Ino, Sato & Toth (1970) made a structural study of the hexagonal Au–Cd alloys. Electron diffraction patterns of the alloys containing 29–33%Cd exhibit clear splitting of superlattice reflections and an analysis of the intensity distribution in reciprocal space led to the ordered structure in which hexagonal antiphase domains derived from the \( D_{019} \)-type ordered lattice are arranged in a regular fashion. Formation of the hexagonal-type LPS was also observed in Cu–Sb alloys (Yamaguchi & Hirabayashi, 1972).

During the structure refinement of Au–33°, Cd alloy by X-ray diffraction, we have found that there is an asymmetry in intensity between a pair of split superlattice reflections and it becomes more conspicuous for the reflections with higher indices. Another remarkable feature of the intensity distribution is the non-existence of the higher-order components of the split reflections, and the other reflections allowed by the crystal symmetry are not detected. These observations remind us that the LPS formed in f.c.c. alloys is always accompanied by some kind of lattice modulation (Iwasaki, Hirabayashi & Ogawa, 1965; Jehanno & Perio, 1966; Okamura, Iwasaki & Ogawa, 1968; Okamura, 1970; Iwasaki, Okamura & Ogawa, 1971). On the basis of an electron theory, Kataoka (1979) showed that the excess atoms in LPS alloys with off-stoichiometric composition can preferentially occupy the sites near the antiphase domain boundaries, thus producing a concentration or an occupancy wave with the wavelength commensurable with that of the long period. Furthermore, conduction electrons are shown to induce periodic displacements of atoms from the normal lattice positions of the LPS (Kataoka & Iwasaki, 1981), which can be represented by a displacement wave (Iwasaki & Watanabe, 1979). Since the LPS formed in h.c.p. alloys also has the origin of its structural stability in the conduction-electron energy, lattice-modulation waves similar to those found in the LPS of the f.c.c. alloys are expected to exist. The present paper reports the results of an X-ray diffraction study on the ordered Au 33°, Cd alloy. The feature of the concentration and displacement waves found in the hexagonal LPS is described.

2. Experimental procedures
(a) Specimen preparation
The alloy was prepared by melting appropriate amounts of Au (99.99°, pure) and Cd (99.9°, pure) in quartz capsules filled with argon gas. Small tips were cut from the ingot, remelted at 1073 K and slowly cooled. Single crystals thus grown were annealed at
473 K for two months to attain an ordered state. Chemical analysis indicated the content to be 33.4\%.

The specimens used for X-ray diffraction examination were thinned in aqua regia and one of them has a final shape of an ellipsoid with diameters of 0.05, 0.06 and 0.03 mm in the x, y and z directions, x being parallel to the [11.0] direction.

(b) X-ray diffraction intensity measurements

Intensity of the split superlattice reflections of Au–33\%Cd alloy is generally weak and a high-power X-ray source was necessary to observe the intensity with accuracy. An X-ray generator of RU-500 with a rotatory molybdenum target operated at 50 kV and 500 mA was employed and the intensity was photographically recorded using a Buerger-type precession camera. The primary beam was monochromated by crystal reflection from pyrolytic graphite. Since the unit cell of the ordered structure is known to be short in the [00.1] direction and the long-period direction lies in the plane perpendicular to this direction, intensity measurement of the \( hk0 \) -type reflections is sufficient to obtain information on the lattice modulation. Photographs of the intensity distribution were made mainly for this type of reflection and supplementarily for the \( hh1 \) and \( ho1 \) types. Multiple exposures were made in order to bring the photographic density of the diffraction spots into the linearity range. Use was made of a microphotometer to measure the photographic density and an integrated intensity was obtained by measuring planimetrically the area under each diffraction peak. Correction of the measured intensity was made for Lorentz–polarization and absorption effects. For the calculation of the absorption factor, the method given by Wuensch & Prewitt (1965) was used; the averaged \( \mu R = 8 \). Correction was also made for the secondary-extinction effect, a brief description of which is given below. Measured intensities, after correction, were averaged over equivalent reflections.

3. Characteristics of the intensity distribution

Fig. 1(a, b) shows X-ray precession photographs of an ordered Au–33\%Cd alloy. Fig. 1(a) represents a (00.1) section and (b) a (10.0) section of the reciprocal lattice. Diffraction spots with stronger intensity are the fundamental reflections, from which the lattice constants of the fundamental h.c.p. structure were determined to be \( a_f = 2.919 \pm 0.004 \), \( c_f = 4.818 \pm 0.007 \) Å and \( c_f/a_f = 1.651 \).

A number of superlattice reflections can be seen to split in the characteristic manner, indicating the formation of a LPS in the alloy. From the separation of the pair of split superlattice reflections, it is possible to determine the long period of the ordered structure. For the Au–Cd alloy the long period, expressed in units of the fundamental h.c.p. cell, was found in general to be non-integral (Hirabayashi et al., 1970) and to change with changing alloy composition. However, for the Au–33\%Cd alloy, the long period is measured to be 7.0 ± 0.1, so that a large hexagonal unit cell with \( a = 7 a_f \) and \( c = c_f \) can be defined. This is why attention is focused on this alloy in the present

![Fig. 1. X-ray precession photographs of an ordered Au–33\%Cd alloy: (a) a (00.1) section and (b) a (10.0) section of the reciprocal lattice. Monochromated Mo K\alpha radiation was used. Arrows show the spurious reflections arising from the (λ/2) contamination and simultaneous reflection.](image-url)
study. Indices of the reflections shown in Fig. 1(a, b) are given in terms of the large unit cell. Besides the fundamental and superlattice reflections, there are additional spots in the precession photographs as indicated by the arrows. An inspection made with a change in the wavelength of the X-rays has shown that these are due to the \( \lambda/2 \) contamination and simultaneous reflection. After exclusion of the spurious reflections, it is possible to deduce a systematic-extinction rule for the reflections which is compatible with the space group \( P6_3/mmc \) assigned by the previous researchers.

The asymmetry in intensity for the pair of split superlattice reflections is clearly seen for the \( 10.10.0 \) and \( 11.11.0 \) reflections, indicated A and B in Fig. 2, or for the \( 10.20.0 \) (A) and \( 11.22.0 \) (B) reflections, with larger intensity for the split component on the higher diffraction-angle side. The asymmetry is not remarkable for pairs of reflections such as \( 6.18.0 \) (C) and \( 8.17.0 \) (D), \( 6.24.0 \) (C) and \( 8.25.0 \) (D) and \( 1.10.0 \) (E) and \( 1.11.0 \) (E), split in a direction nearly perpendicular to the radial lines, even though they have high indices. This dependence of the asymmetry on the indices of the reflections gives a clue to the determination of the polarization of the displacement wave existing in the alloy.

The hexagonal LPS structure is constructed by introducing periodic out-of-step shifts into the \( D0_{19} \)-type ordered lattice, as originally suggested. If the Au–33% Cd alloy had this ideal ordered atomic arrangement, many more superlattice reflections allowed by the space-group symmetry should be observed in addition to those seen in Fig. 1(a, b). The fact that appreciable intensities are detected only for the ‘first-order pair’ of the split superlattice reflections, for example \( 10.10.0 \) and \( 11.11.0 \), and not for the ‘higher-order pair’, \( 99.0 \) and \( 12.12.0 \), can be regarded as an indication of the existence of an occupancy modulation of the two kinds of atoms in the ordered lattice.

Refinement of the structure has been made with these facts taken into consideration.

4. Refinement of the structure

(a) Determination of occupancy modulation

There are 98 atomic sites in the large hexagonal unit cell defined above. Of these, 72 are for Au atoms and 26 for Cd atoms, if the alloy has an ideal hexagonal LPS structure.* The real cadmium content of our alloy is, however, 33.4%, containing 65 Au and 33 Cd atoms. The determination of the occupancy modulation must therefore reveal where the excess Cd atoms are accommodated and what kind of local disordering occurs in the structure. Hirabayashi et al. (1970) considered eight different types of occupancy models, including mixed occupation, and compared the calculated intensities for each type with the observed ones. Since their analysis was based on an electron diffraction observation with the intensities much affected by dynamical effects, a further investigation is necessary to deduce a more reliable occupancy model. We investigate here the distribution of Cd atoms through a different approach.

Let us define a function \( c(R_i) \) representing a con-

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* The composition corresponding to this structure is not Au–25% Cd but Au–26.5% Cd.
Table 1. Distribution of cadmium atoms in the atomic sites of the large hexagonal unit cell of Au–33% Cd alloy (space group $P6_3/mmc$)

<table>
<thead>
<tr>
<th>Atomic site</th>
<th>Allocation of the sites in the ideal structure</th>
<th>Positional parameters in the ideal structure</th>
<th>Occupancy parameters*</th>
</tr>
</thead>
<tbody>
<tr>
<td>12(j)(1)</td>
<td>Au</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>C[P1] C[P2] C[H2]</td>
</tr>
<tr>
<td>(2)</td>
<td>Au</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>0.22 0.08(1) 0</td>
</tr>
<tr>
<td>(3)</td>
<td>Au</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>0.07 0.00(1) 0</td>
</tr>
<tr>
<td>(4)</td>
<td>Au</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>0.03 0.00(1) 0</td>
</tr>
<tr>
<td>(5)</td>
<td>Cd</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>0.22 0.08(1) 0</td>
</tr>
<tr>
<td>6(h)(1)</td>
<td>Au</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>0.56 0.74(1) 1</td>
</tr>
<tr>
<td>(2)</td>
<td>Au</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>0.16 0.09(1) 0</td>
</tr>
<tr>
<td>(3)</td>
<td>Au</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>0.16 0.09(1) 0</td>
</tr>
<tr>
<td>(4)</td>
<td>Au</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>0.46 0.68(2) 1</td>
</tr>
<tr>
<td>(5)</td>
<td>Cd</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>0.46 0.68(2) 1</td>
</tr>
<tr>
<td>(6)</td>
<td>Cd</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>0.83 0.91(2) 1</td>
</tr>
<tr>
<td>2(c)</td>
<td>Cd</td>
<td>$x_0 \quad y_0 \quad z_0$</td>
<td>1.0 1.00(1) 1</td>
</tr>
</tbody>
</table>

* C[P1]: values from equation (3). C[P2]: refined values. C[H2]: values proposed by Hirabayashi et al. (1970).

The concentration of Cd atoms at the site $R_l$. This can be expanded into a Fourier series

$$c(R_l) - c_0 = \sum_k F(k) \exp(ik \cdot R_l),$$

where $c_0$ is the mean Cd concentration of the alloy and $F(k)$ the Fourier coefficient corresponding to the wavevector $k$. We consider the concentration wave projected onto the (00.1) plane so that $k$'s have components in the $(a^*_1, a^*_2)$ plane, $a^*_1$ and $a^*_2$ being the reciprocal vectors of the large unit cell. The minimum number of wavevectors specifying the distribution of the atoms is determined by the number of superlattice reflections observed in the first Brillouin zone. In Fig. 3 small solid circles represent the superlattice reflections and a hexagon indicated by the dotted lines the Brillouin zone. There are only six independent reflections, numbered 1, 1', 2, 2', 3 and 3', of which have the indices of 31.0 type. Using this limited number of reflections, the concentration map of Cd in the unit cell is synthesized. In performing the synthesis it is more convenient to use an alternative set of reflections, numbered 1', 1', 2', 2', 3' and 3', of the 33.0 type. These are equivalent to the first set of reflections, because their wavevectors can be produced from those corresponding to the first set simply by adding or subtracting the fundamental translation vector of the reciprocal lattice of the h.c.p. structure. We then have the wavevectors

$$k_1 = \pm 2\pi(3a^*_1 + 3a^*_2),$$
$$k_2 = \pm 2\pi(-6a^*_1 + 3a^*_2),$$
$$k_3 = \pm 2\pi(3a^*_1 - 6a^*_2).$$

The symmetry of the space group suggests that the structure factors of the 33.0-type reflections are all the same in their amplitude and sign. Equation (1) then becomes, putting $F(k) = F$ and $R_l = l_1 a_1 + l_2 a_2$, $c(l_1, l_2) = c_0 + 2F[\cos2\pi(l_1 + l_2) + \cos2\pi(-6l_1 + 3l_2) + \cos2\pi(3l_1 - 6l_2)]$. (3)

Since $c(l_1, l_2)$ is a concentration, it must not be a negative quantity and its value does not exceed unity at the atomic sites. The restriction imposed on $c(l_1, l_2)$ readily gives a possible range of values that $F$ can take. The strong observed intensity of the 33.0-type reflections suggests that atomic ordering has developed well in the alloy and, therefore, we choose the largest value of $\frac{1}{2}$ for $F$. $c(l_1, l_2)$ calculated according to equation (3) is shown in Table 1 under the column heading $C[P1]$, where 98 atomic sites are grouped into five 12(j) sites, six 6(h) sites and one 2(c) site of space group $P6_3/mmc$. The site 2(c) is exclusively occupied by Cd atoms and the sites 12(j)(2) and 12(j)(3) predominantly by Au atoms. On the other hand, an appreciable mixed occupation is observed in the 12(j)(5), 6(h)(3) and 6(h)(4) sites. For the sake of comparison, the allocation of the sites to the two kinds of atoms in the ideal structure is shown in the second column in the table.

Using the $c(l_1, l_2)$ values given by equation (3) as the initial values, the occupancy parameters of the atomic sites were refined by a least-squares method with the program LS1 on the Tohoku University ACOS computer. The intensities of 213 independent reflections, of which 53 were observed, were included. The function minimized is $M = \sum_w w_k[F_k^2(h) - |F_k(h)|^2]^2$, with the weight $w_k = F_m |F_k(h)|^2$. As $F_m$ we have taken the maximum $F_m$ value of the superlattice reflections. For the unobserved reflections, half of the minimum observable amplitude has been assigned as the $F_m$ value. For the calculation of the structure factor, atomic
scattering factors given in *International Tables for X-ray Crystallography* (1974) in an analytical form were used; these were corrected for the anomalous-dispersion effect using the values given therein. In this refinement process, the atomic positional parameters and temperature factors were kept fixed, since there was an abnormally strong correlation between the parameters and the refinement calculation did not converge rapidly. A scale factor and an isotropic dispersion effect using the values given therein. Under the column heading $C[P2]$ in Table 1, the occupancy parameters thus refined are shown. The positional parameters used in this refinement are shown as $x_0$, $y_0$, and $z_0$ in the table and the isotropic temperature factors are $B_0 = 1.0 \AA^2$ for the 12(j)(1), 12(j)(2), 12(j)(3), 12(j)(4), 6(h)(1) and 6(h)(2) sites, 1.3 $\AA^2$ for the 12(j)(5), 6(h)(3) and 6(h)(4) sites, and 1.5 $\AA^2$ for the 6(h)(5), 6(h)(6) and 2(c) sites. The $B_0$ values have been determined taking into account the results of the structural studies on Au–Cd alloys (Alasafi & Schubert, 1977, 1979). The final results indicate that the sites 12(j)(1), 12(j)(4), 6(h)(1) and 6(h)(2) can be assigned as the almost pure Au sites in addition to 12(j)(2) and 12(j)(3), and that the sites 6(h)(5) and 6(h)(6) turn out to be the almost pure Cd sites in addition to 2(c). The sites 12(j)(5), 6(h)(3) and 6(h)(4) still contain the two species of atoms approximately in the ratio of 1 to 2.

Fig. 4 shows schematically the distribution of Au and Cd atoms in the lattice sites of the large unit cell. Dashed lines represent the antiphase domain boundaries. This result is in essential agreement with the occupancy model proposed by Hirabayashi et al. (1970), which is shown in Table 1 under the column heading $C[H2]$. This model assumes that the excess Cd atoms are accommodated exclusively in the 6(h)(3) and 6(h)(4) sites and the other sites are assigned as pure Au or Cd. The real distribution of the atoms in the Au–33% Cd alloy is not in a state of ordering as represented by $C[H2]$.

### (b) Determination of displacements of atoms

The $R$ factor $\sum_h |F_o(h)| - |F_c(h)|$ calculated with the thus refined occupancy parameters and the ideal positional parameters is 0.098. Reduction of the $R$ factor is expected if periodic displacements of atoms from the fundamental h.c.p. lattice positions are taken into account that the observed asymmetry in intensity of the split superlattice reflections is reproduced. Refinement of the positional parameters was then carried out with the program *LS2*. The number of parameters refined included 16 positional parameters and 12 temperature factors in addition to the scale factor and the isotropic secondary-extinction factor.

Table 2 lists the final positional parameters and temperature factors along with their standard deviations and Table 3 the $F_o$ and $|F_c|$ values, which are normalized to express the structure factor with respect to one atom. Many atoms have positional parameters slightly different from the ideal ones. The final $R$ factor is 0.084. An attempt to refine again the occupancy parameters starting with the $x_i$, $y_i$, and $B_i$ values thus determined has not given any significant improvement in their values, so no further refinement cycle has been made. In Fig. 4, the displacements of the atoms, which exceed the standard deviation in their magnitude, are shown by the arrows attached to the atoms.* They are

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* As a result of the decrease in the standard deviation, the number of displaced atoms has increased as compared with that given in a previous paper (Iwasaki & Watanabe, 1979).
the largest for the atoms located at the 12(j)(5), 6(h)(4) and 6(h)(5) sites and are 0.018, 0.018 and 0.021 Å, respectively, which are 0.6–0.7% of the nearest-neighbor distance. The direction of the displacements changes on going from one domain to the other, but it is possible to describe the whole feature by the superposition of three possible long-period ordered structures, those of the fundamental h.c.p. lattice, but to be displaced systematically. We shall try here to represent these possible long-period ordered structures, those of the fundamental h.c.p. lattice, but to be displaced systematically. We shall try here to represent these

Many of the atoms in the Au–33% Cd alloy have been shown not to be located exactly at the positions of the fundamental h.c.p. lattice, but to be displaced systematically. We shall try here to represent these displacements in terms of displacement waves.

Similarly to the case with the concentration (occupancy) waves, we take $k_1$, $k_2$ and $k_3$ given in equation (2) as the wavevectors characterizing the displacement waves. We assume that these waves are all longitu-

### Table 3. Observed and calculated structure factors

<table>
<thead>
<tr>
<th>h0k</th>
<th>h01</th>
<th>h10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.12</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.19</td>
</tr>
<tr>
<td>4</td>
<td>0.24</td>
<td>0.21</td>
</tr>
<tr>
<td>5</td>
<td>0.28</td>
<td>0.25</td>
</tr>
<tr>
<td>6</td>
<td>0.31</td>
<td>0.26</td>
</tr>
<tr>
<td>7</td>
<td>0.34</td>
<td>0.28</td>
</tr>
<tr>
<td>8</td>
<td>0.38</td>
<td>0.31</td>
</tr>
<tr>
<td>9</td>
<td>0.41</td>
<td>0.34</td>
</tr>
<tr>
<td>10</td>
<td>0.45</td>
<td>0.38</td>
</tr>
<tr>
<td>11</td>
<td>0.49</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Reading from left to right, the columns contain the values of $h$, $F_s$ and $|F_o|$.}

### 5. Discussion

(a) Physical significance of the occupancy modulation

The results of the structure investigation described above have shown that an essential feature of the cadmium-atom distribution in the Au–33% Cd alloy can be well represented by the superposition of three concentration waves and the appearance of the limited number of superlattice reflections is a reflex of the appreciable local disordering in the atomic sites located near the antiphase domain boundaries. The reason why these selected concentration waves are induced in the alloy can be understood in the light of an electron theory of LPS (Sato & Toth, 1965). Among many possible long-period ordered structures, those which can be stabilized in alloys create energy gaps in the vicinity of the well developed, flattened Fermi surface. In the case of the Au–33% Cd alloy, the Fermi surface is shown to have the flattened parts in the (110) directions (Hirabayashi et al., 1970) and the vector $2k_F$ has its extremity close to the pair of points, 33.0 and 44.0, and their equivalents, so that an antiphase (or occupancy) modulation which gives larger structure factors to the reflections corresponding to this pair of points is the most favorable with regard to the electron energy. The concentration waves revealed here represent the modulation of this type only and preferentially form upon transition from the disordered state. The concentration waves expressed by the wavevectors corresponding to the other points in reciprocal space cannot form because they contribute little to the lowering in the electron energy.

(b) Atomic displacements in terms of displacement waves

Many of the atoms in the Au–33% Cd alloy have been shown not to be located exactly at the positions of the fundamental h.c.p. lattice, but to be displaced systematically. We shall try here to represent these displacements in terms of displacement waves.

Similarly to the case with the concentration (occupancy) waves, we take $k_1$, $k_2$ and $k_3$ given in equation (2) as the wavevectors characterizing the displacement waves. We assume that these waves are all longitu-
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dinal; the assumption has been justified for the waves in the LPS forming in the f.c.c. alloys (Kataoka & Iwasaki, 1981). The dependence of the intensity asymmetry of the split superlattice reflections on the indices, mentioned in the foregoing section, also supports the assumption, since otherwise a different dependence would appear. The displacements arising from the wave $k_1$ have components, using the Cartesian coordinates $x$ and $y$ shown in Fig. 3, expressed as

$$u_i(k_1) = \left[bsin(k_1 \cdot R_i), 0\right],$$  \hspace{1cm} (4)

where $b$ is an amplitude of the wave. The displacements arising from the other two waves have the components

$$u_i(k_2) = \left[-\frac{1}{2}bsin(k_2 \cdot R_i), \frac{\sqrt{3}}{2}bsin(k_2 \cdot R_i)\right]$$

and

$$u_i(k_3) = \left[-\frac{1}{2}bsin(k_3 \cdot R_i), -\frac{\sqrt{3}}{2}bsin(k_3 \cdot R_i)\right].$$  \hspace{1cm} (4')

Total displacements are given as a sum of the three components:

$$u(l_1, l_2) = \sum_i u_i(k_i).$$  \hspace{1cm} (5)

The displacements of the atoms in the unit cell are thus determined by the single parameter $b$. In Fig. 5 are shown schematically the displacements calculated according to equation (5) with $b = 0.010 \, \text{Å}$. The length of the arrows attached to the atoms represents the relative magnitude of the displacements. Comparison with those depicted in Fig. 4 clearly shows that the observed displacements of atoms can be reproduced well by the superposition of the three simple longitudinal displacement waves, except for the direction of the atoms in the site 12(j)(3). Inclusion of the waves of higher harmonics and those of a transverse mode would remove the discrepancy.

It is worthwhile noting that many of the atoms in the transition-metal dichalcogenides are systematically displaced. The displacement waves in hexagonal TaSe$_2$, for example, are of longitudinal mode (Moncton, Axe & DiSalvo, 1977) and they are induced by the charge-density waves existing in the compound. Although not as prominent as in TaSe$_2$ and other related compounds, charge-density waves can exist in the LPS alloys with the wavevectors determined by the Fermi-surface calipering (Sato, 1979). In the case of the Au–33%Cd alloy, these wavevectors are $k_1, k_2, k_3$ and their equivalents. We assume here that the phase of the charge-density wave consisting of conduction electrons in the alloy is coincident with the phase of the concentration wave represented by equation (3). This assumption is not unreasonable because cadmium atoms are present as divalent cations and provide lower potential minima for the conduction electrons than do monovalent gold cations and therefore the charge density will be high where the cadmium concentration is high. In Fig. 5 the locations of the maxima of the assumed charge-density waves are indicated by dotted lines. It can be seen that the displacements of the atoms are directed to the charge-density maxima, i.e. the positively charged atoms are attracted to the conductor-electron ridges. This is in substantial agreement with the direction of the cation motion observed in the transition-metal dichalcogenides (Wilson, DiSalvo & Mahajan, 1975). An approach which takes more adequately into account the coupling between the charge-density wave and the ordered atomic arrangements in the alloy will succeed in giving a more satisfactory explanation. A quantitative investigation along this line has been made on the displacement waves in the LPS forming in the f.c.c. alloys (Kataoka & Iwasaki, 1981) and an extension to the waves in the hexagonal LPS is in progress.

The authors wish to express their gratitude to Dr M. Kataoka for valuable discussions.

References


Fig. 5. Calculated displacements of atoms in the large hexagonal unit cell from the superposition of the three longitudinal displacement waves. Dotted lines represent the location of the maxima of the assumed charge-density waves.