# Lattice Modulation in the $D1_a$-Type Structure of Au$_4$Cr

By Y. Watanabe and H. Iwasaki

*The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan*

## Abstract

The crystal structure of Au$_4$Cr, hitherto known to be of the $D1_a$ (Ni$_4$Mo) type, has been refined using X-ray intensity data collected on a four-circle diffractometer. Systematic displacements of Au atoms from the positions of the fundamental face-centered cubic lattice have been found with a magnitude of 0·017 Å. These are described by a superposition of sinusoidal displacement waves with the wavevectors which are the same as those of ordering waves producing the $D1_a$-type structure. The origin of the atomic displacements is discussed in the light of a theory recently developed [Kataoka & Iwasaki (1981). *J. Phys. F*, **11**, 1545–1556]. [Crystal data: Au$_{79·2}$Cr$_{20·8}$, tetragonal, $I4/m$, $a = 6·398$ (4), $c = 4·046$ (3) Å, $V = 165·6$ (3) Å$^3$, 10 atoms/cell, $D_x = 16·73$ (3) Mg m$^{-3}$, $\lambda = 0·7107$ Å, $\mu$(Mo K$\alpha$) = 203·5 mm$^{-1}$, $F(000) = 675·6$, $R = 0·084$ for 159 independent reflexions.]

## Introduction

Kataoka & Iwasaki (1981) showed, from a calculation of the energy of conduction electrons in long-period superlattice (LPS) alloys, that an interaction between charge-density waves existing in these alloys and atomic potentials induces small, periodic displacements of atoms from the positions of the fundamental face-centered cubic (f.c.c.) structure. These are called displacement waves. The theory explains well what has been observed for many LPS alloys such as CuAu, Au$_3$Cd *etc.*, and suggests that these displacement waves always accompany the formation of the LPS in alloys. Experimental investigations have since been made on two LPS alloys, Au$_3$Cd$_{1+}$ (Watanabe & Iwasaki, 1982) and Cu$_3$Sn (Watanabe, Fujinaga & Iwasaki, 1983), with the results that displacement waves, although in somewhat different form, also exist in the alloys whose fundamental structure is a hexagonal close-packed one. Of particular interest are the waves in Au$_3$Cd$_{1+}$ in which the displacements occur in such directions that, if one assumes the existence of charge-density waves synchronizing with the ordering (occupancy) waves, positively charged ions are attracted by the maxima of the electron charge density.

The $D1_a$(Ni$_4$Mo)-type structure is known as one of the ordered atomic arrangements forming in the f.c.c. alloys of composition $A_4B$ and is found in the systems Ni–Mo, Ni–W, Au–Ti, Au–Hf, Au–V, Au–Cr and Au–Mn (Schubert, 1964). It has tetragonal symmetry with a unit cell which is related to that of the fundamental f.c.c. structure by $\mathbf{a}_1 = (3\mathbf{a}_{01} - \mathbf{a}_{02})/2$, $\mathbf{a}_2 = (\mathbf{a}_{01} + 3\mathbf{a}_{02})/2$ and $\mathbf{c} = \mathbf{a}_{03}$ where $\mathbf{a}_{01}$, $\mathbf{a}_{02}$ and $\mathbf{a}_{03}$ are the unit-cell vectors of the f.c.c. structure. The ordered atomic arrangements can be described by introducing ordering waves with the wavevectors $\mathbf{k}_1 = (4\pi/5)(2\mathbf{a}_{01}^* + \mathbf{a}_{02}^*)$ and $\mathbf{k}_2 = (4\pi/5)(-\mathbf{a}_{01}^* + 2\mathbf{a}_{02}^*)$ in the f.c.c. structure, where $\mathbf{a}_{0i}^*$'s are reciprocal vectors of $\mathbf{a}_{0i}$'s (Khachaturyan, 1978). The identical atomic arrangements are produced with five other sets of wavevectors† and they are considered as orientation variants of the ordered structure. Although the $D1_a$-type structure is not classified in the LPS family, it is of interest to see whether these ordering waves are accompanied by the displacement waves as they are in the LPS alloys. Taking Au$_4$Cr as a sample material, an experimental investigation has been performed to determine precisely the atomic positional parameters in this structure and the results are described below.

## Experimental

The alloy was prepared from 99·99% pure Au and Cr by melting them in quartz capsules filled with argon gas. Small tips were cut from the ingot, remelted at 1400 K and slowly cooled. Single crystals thus grown were annealed at 543 K, which was lower by 55 K than an order–disorder transition temperature, for 52 days. According to Dutkiewicz & Thomas (1975), this heat treatment is sufficient to develop a fully ordered state in the alloy. Chemical analysis of the ingot showed the composition of the alloy to be Au–20·8 at.% Cr. This value was adopted hereafter as the composition of the crystals. The sample for X-ray diffraction study was selected from them and thinned in *aqua regia*.

Precession photographs indicated that the sample thus heat treated was no longer a single crystal but contained six orientation variants of the ordered

---

† These are $[(4\pi/5)(\mathbf{a}_{01}^* + 2\mathbf{a}_{02}^*), (4\pi/5)(-2\mathbf{a}_{01}^* + \mathbf{a}_{02}^*)]$, $[(4\pi/5) \times (2\mathbf{a}_{02}^* + \mathbf{a}_{03}^*), (4\pi/5)(-\mathbf{a}_{02}^* + 2\mathbf{a}_{03}^*)]$, $[(4\pi/5)(\mathbf{a}_{02}^* + 2\mathbf{a}_{03}^*), (4\pi/5) \times (-2\mathbf{a}_{02}^* + \mathbf{a}_{03}^*)]$, $[(4\pi/5)(2\mathbf{a}_{03}^* + \mathbf{a}_{01}^*), (4\pi/5)(-\mathbf{a}_{03}^* + 2\mathbf{a}_{01}^*)]$ and $[(4\pi/5)(\mathbf{a}_{03}^* + 2\mathbf{a}_{01}^*), (4\pi/5)(-2\mathbf{a}_{03}^* + \mathbf{a}_{01}^*)]$.

structure. An attempt to grow preferentially a particular orientation variant using a strain-annealing or other similar method was not successful, because distortion of the parent f.c.c. lattice has not been observed upon ordering in Au$_4$Cr. The structural investigation in the present work has been performed using the reflexions from one of the orientation variants. It should be noted that in other $D1_a$ ordering alloys $a_{03}/a_{01}$ (or $a_{03}/a_{02}$) always deviates from unity (Schubert, 1964).

Systematic extinction of reflexions is observed, which is consistent with the earlier assigned space group $I4/m$. 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, and $\theta$–$2\theta$ scan. The incident beam from a rotatory Mo target, operated at 50 kV and 100 mA, was monochromated by reflexion from a pyrolytic-graphite plate. 1298 reflexions were measured, of which 910 were superlattice reflexions.

The measured intensities were corrected for Lorentz and polarization effects in the usual way. There were difficulties in evaluating absorption-correction factors for the present sample containing orientation variants. Even if the size and shape of the sample were precisely known, it would not be possible to calculate the factor by a standard method for the reflexions chosen, because there is no information on how the domains belonging to different orientation variants are distributed in the sample crystal. We resorted to another method proposed by Katayama, Sakabe & Sakabe (1972) and Walker & Stuart (1983). In this method, the absorption factor is expressed as a Fourier series in the polar angles of both the incident and diffracted beams and the coefficients are determined so as to eliminate observed inequality in intensities among symmetrically equivalent reflexions. Approximate atomic positional parameters for Au$_4$Cr required in this calculation were obtained using intensities which were tentatively corrected under the assumption that the sample had a spherical shape with $\mu R = 10$. Details of the evaluation of the absorption factor are described elsewhere (Watanabe, 1984).

### Structure refinement

In the original $D1_a$-type structure, Au atoms are allocated to $8(h)$ sites with the positional parameters $(x, y, 0)$ of space group $I4/m$ and Cr atoms to $2(a)$ sites with $(0, 0, 0)$. The values of $x$ and $y$ for the structure model in which the atoms are positioned exactly on the fundamental f.c.c. structure are given in Table 1 under the column heading 'ideal parameters'. In the real structure of Au$_4$Cr, however, evidence of deviation from the ideal model is found,

as shown in Fig. 1 which is part of a zero-layer precession photograph taken with Zr-filtered Mo $K\alpha$ radiation, in which reflexions belonging to two orientation variants are seen. The ideal model yields the structure factor of the same form for all superlattice reflexions, whereas there is an appreciable intensity asymmetry between reflexions 260 and 350, between 370 and 460, and so on.

Refinement of the structure was carried out using the program *SALS* (Nakagawa & Oyanagi, 1980) on the Tohoku University ACOS computer. There were five parameters to be refined, *i.e.* one scale factor, two atomic positional parameters and two isotropic temperature factors. No attempt was made to refine occupancy parameters of the sites by the two kinds of atom, and the full ordering scheme allowed by the alloy composition, *i.e.* Cr atoms exclusively on $2(a)$ sites and $(0.99Au + 0.01Cr)$ atoms on $8(h)$ sites, was assumed. Only superlattice reflexions, 159 of the independent ones, were used in the refinement. The function minimized was

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

$K$ being the scale factor. $w_{\mathbf{h}}$ is a weight of the form $(1/\sigma_{\mathbf{h}}^2) \times [1 - (Z_{\mathbf{h}}/CS)^2]^2$, where $\sigma_{\mathbf{h}}$ is the variance calculated from the counting statistics, $Z_{\mathbf{h}}$ the standardized residual, $S$ its median and $C$ a constant to exclude most extreme data (Tukey, 1974). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974), the values from the relativistic Hartree–Fock wavefunction being used for Au and Cr. Corrections for anomalous scattering with Mo $K\alpha$ radiation were also taken from *International Tables* (1974). Finally, the agreement
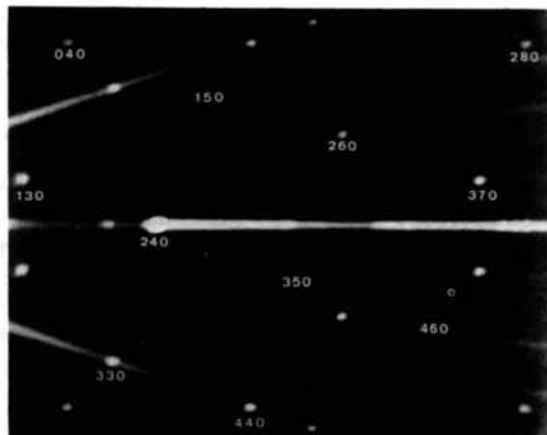


Fig. 1. Part of the X-ray precession photograph of an ordered Au–20·8 at.% Cr alloy, showing an asymmetry in intensity between superlattice reflexions 260 and 350, or 370 and 460. Unindexed reflexions are those from another orientation variant of the $D1_a$-type structure. Filtered Mo $K\alpha$ radiation was used.

Table 1. *Structural parameters for* $Au_4Cr$

| Atomic sites | Allocation of atoms | Ideal parameters | | | Final parameters | | | |
|---|---|---|---|---|---|---|---|---|
| | | $x_0$ | $y_0$ | $z_0$ | $x$ | $y$ | $z$ | $B(\text{Å}^2)$ |
| $8(h)$ | Au* | $\frac{1}{5}$ | $\frac{2}{5}$ | 0 | 0·2019 (3) | 0·3980 (3) | 0 | 0·77 (30) |
| $2(a)$ | Cr | 0 | 0 | 0 | 0 | 0 | 0 | 0·99 (176) |

* 0·99 Au + 0·01 Cr.

Table 2. *Interatomic distances* (Å) *in* $Au_4Cr$

| Au* – Au* | | Au* – Cr | |
|---|---|---|---|
| 2·850 (3) | in the same | 2·855 (3) | in the same |
| 2·894 (3) | (002) plane | | (002) plane |
| 2·839 (3) | in adjacent | 2·856 (2) | in adjacent |
| 2·878 (2) | (002) planes | | (002) planes |

* 0·99 Au + 0·01 Cr.

factor $R$ decreased to 0·084, where $R = \sum_h |F_o(\mathbf{h}) - |F_c(\mathbf{h})||/\sum_h F_o(\mathbf{h})$.

The final, refined atomic positional parameters and temperature factors are given in Table 1.* It can be seen that $x$ and $y$ of the Au atoms have values deviating significantly from the ideal parameters. The asymmetry in intensity of the superlattice reflexions is thus shown to arise from the displacements of these atoms from the ideal positions. The parameter $K$ is 1·29(5).

In the ideal model of $D1_a$-type $Au_4Cr$, each Au atom is surrounded by nine Au atoms and three Cr atoms all at the same distance, 2·861 Å. Displacements of atoms result in a decrease in four of the Au–Au distances and an increase in five of them, while the Au–Cr distance decreases only slightly, as shown in Table 2.

## Displacements of atoms in the $D1_a$-type structure of $Au_4Cr$

Fig. 2 depicts the atomic arrangements of $D1_a$-type $Au_4Cr$ projected onto the (001) plane. Thick lines represent the size of the $D1_a$ unit cell and thin lines that of the fundamental f.c.c. unit cell. Arrows attached to atoms show the directions of the displacements. Their magnitude is 0·017 Å. It should be noted that the atoms move in the $\langle 110 \rangle$ directions of the ordered structure or in the $\langle 210 \rangle$ directions of the fundamental f.c.c. structure. Any attempt to interpret the displacements in terms of a repulsion arising from the atomic-size disparity between Au and Cr atoms is not successful. Their origin may be found in other factors, as will be discussed below.

In the study of the displacement-type lattice modulation in $Au_3Cd_{1+}$ (Watanabe & Iwasaki, 1982), it

was shown that the atomic displacements can be described as a superposition of sinusoidal displacement waves which have an intimate relation with the ordering (occupancy) waves. An analysis is made here to seek the relation in $Au_4Cr$. The ordered arrangements of atoms are expressed by a superposition of two sinusoidal waves,

$$c(\mathbf{R}_l) - c_0 = 2F(\cos \mathbf{k}_1 . \mathbf{R}_l + \cos \mathbf{k}_2 . \mathbf{R}_l), \quad (2)$$

where $c(\mathbf{R}_l)$ represents a concentration of Cr atoms at the site $\mathbf{R}_l = \frac{1}{2}(l_1 \mathbf{a}_{01} + l_2 \mathbf{a}_{02} + l_3 \mathbf{a}_{03})$ with $l_1 + l_2 + l_3 =$ even integer, $c_0$ the mean Cr concentration of the alloy and $\mathbf{k}_1$ and $\mathbf{k}_2$ the wavevectors given in the *Introduction*. $F$ and $c_0$ are respectively 0·198 and 0·208 for our $Au_4Cr$ alloy. On the other hand, we decompose the displacement $\mathbf{u}_l$ of the atom at the site $\mathbf{R}_l$ into the components $u_{l1}$ and $u_{l2}$ respectively along the $\mathbf{a}_{01}$ and $\mathbf{a}_{02}$ axes and assume their form to be

$$u_{l1} = A_0 + A_1 \sin (\mathbf{k}_1 . \mathbf{R}_l + \varphi_1)$$
$$+ A_2 \sin (\mathbf{k}_2 . \mathbf{R}_l + \varphi_2) \quad (3)$$
$$u_{l2} = A_0' + A_1' \sin (\mathbf{k}_1 . \mathbf{R}_l + \varphi_1')$$
$$+ A_2' \sin (\mathbf{k}_2 . \mathbf{R}_l + \varphi_2'). \quad (4)$$

It is readily shown that putting $A_0 = A_0' = 0$, $\varphi_1 = \varphi_1' = \varphi_2 = \varphi_2' = 0$, $A_1 = A_2' = -0·0157$ Å and $A_2 = -A_1' = -0·0014$ Å reproduces well the experimentally determined displacements of the atoms. The relative
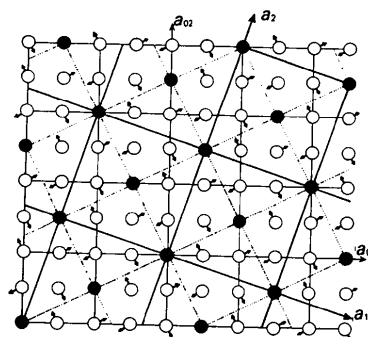


Fig. 2. Atomic arrangements of $Au_4Cr$ projected onto the (001) plane. Open and solid circles represent respectively Au and Cr atoms. Arrows attached to the atoms show the directions of the displacements. Thick lines show the size of the $D1_a$ unit cell and thin lines that of the fundamental f.c.c. unit cell. Dotted lines show the traces of the maxima of electron charge density calculated on the basis of a theory developed by Kataoka & Iwasaki (1981).

magnitude of the coefficients of the sine terms in equations (3) or (4) suggests that both $u_{l1}$ and $u_{l2}$ are regarded as waves having an approximately longitudinal nature. The relation between equation (2) and equations (3) and (4) above is similar to the relation between equation (1) and equations (4) and (4′) found in $Au_3Cd_{1+}$ (Watanabe & Iwasaki, 1982).

Kataoka & Iwasaki (1981) gave a formulation which represents a periodic change in electron charge density $\rho(r)$ in alloys when an LPS is formed. We apply that formula to the present case of the $D1_a$-type superlattice. The change is written as

$$\delta\rho(\mathbf{r}) = N^{-1}\sum_{l}\sum_{g}\sum_{k} \nu_g(\mathbf{k})\zeta S(\mathbf{R}_l)\cos\left[(\mathbf{k}+\mathbf{g}).(\mathbf{r}-\mathbf{R}_l)\right],$$

$$(5)$$

where $N$ is the total number of atoms, $\mathbf{g}$ a reciprocal-lattice vector of the f.c.c. structure, $\mathbf{k}$ a wavevector in the first Brillouin zone. $\nu_g(\mathbf{k})$ is a quantity containing the dielectric constant of the conduction electron system. $\zeta S(\mathbf{R}_l)$ represents an ordering scheme of atoms, which can here be put equal to $c_0 - c(\mathbf{R}_l)$. If we take only the dominant term $\mathbf{g} = 0$ in equation (5) and neglect the $\mathbf{k}$ dependence of $\nu_0(\mathbf{k})$, we obtain

$$\delta\rho(\mathbf{r}) = -F\nu_0(\cos\mathbf{k}_1.\mathbf{r}+\cos\mathbf{k}_2.\mathbf{r})$$

$$-N^{-1}F\nu_0\sum_{l}\{\cos[\mathbf{k}_1.(\mathbf{r}-2\mathbf{R}_l)]$$

$$+\cos[\mathbf{k}_2.(\mathbf{r}-2\mathbf{R}_l)]$$

$$+\cos[\mathbf{k}_1.\mathbf{r}-(\mathbf{k}_1-\mathbf{k}_2).\mathbf{R}_l]$$

$$+\cos[\mathbf{k}_1.\mathbf{r}-(\mathbf{k}_1+\mathbf{k}_2).\mathbf{R}_l]$$

$$+\cos[\mathbf{k}_2.\mathbf{r}-(\mathbf{k}_2-\mathbf{k}_1).\mathbf{R}_l]$$

$$+\cos[\mathbf{k}_2.\mathbf{r}-(\mathbf{k}_2+\mathbf{k}_1).\mathbf{R}_l]\}. \qquad (6)$$

The second term on the right-hand side of this equation consists of cosine terms having various phase factors and they almost cancel each other at every site in the alloy crystal, leaving only the first term. Comparing its form with equation (2), one can see that the electron charge density forms waves which synchronize with the ordering (occupancy) waves. The sign of $\nu_0$ depends on the difference between the effective valences of the Au and Cr atoms. According to a magnetic measurement by Giansoldati (1954), Cr atoms in Au have nearly four $3d$ electrons, leaving two electrons in the $4s$ band. This fact suggests that the effective valence of Cr atoms is larger than that of Au atoms and therefore $\nu_0$ is negative. Dotted lines in Fig. 2 represent the traces of the maxima of the charge density given by equation (6). Au atoms in $Au_4Cr$ of the $D1_a$-type structure are thus shown

to move as if they are attracted to the maxima of the charge density.

In earlier structural investigations of $Ni_4Mo$ (Harker, 1944) and $Ni_4W$ (Epremian & Harker, 1949), the atoms were placed on the ideal positions of the $D1_a$-type structure. It was shown there that no improvement in an agreement between observed and calculated intensities was obtained if they were displaced, but the accuracy of their intensity measurement was not high enough to exclude the possibility of the existence of small displacements. Extensive structural investigations of these alloys and other Au-based $D1_a$ ordering alloys will reveal the displacement waves as found in $Au_4Cr$.

**References**

DUTKIEWICZ, J. & THOMAS, G. (1975). *Metall. Trans.* **6A**, 1919–1928.
EPREMIAN, E. & HARKER, D. (1949). *Trans. Am. Inst. Min. Metall. Pet. Eng.* **185**, 267–273.
GIANSOLDATI, A. (1954). *Ark. Phys.* **8**, 151–154.
HARKER, D. (1944). *J. Chem. Phys.* **12**, 315–317.
*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–97, 149–150. Birmingham: Kynoch Press.
KATAOKA, M. & IWASAKI, H. (1981). *J. Phys. F*, **11**, 1545–1556.
KATAYAMA, C., SAKABE, N. & SAKABE, K. (1972). *Acta Cryst.* **A28**, S207.
KHACHATURYAN, A. G. (1978). *Progress in Materials Science*, Vol. 22, edited by B. CHALMERS, J. W. CHRISTIAN & T. B. MASSALSKI, pp. 1–150. New York: Pergamon Press.
NAKAGAWA, T. & OYANAGI, Y. (1980). *Program System SALS for Nonlinear Least-Squares Fitting in Experimental Sciences. Recent Developments in Statistical Inference and Data Analysis*, edited by K. MATUSITA, pp. 221–225. Amsterdam: North-Holland.
SCHUBERT, K. (1964). *Kristallstrukturen zweikomponentiger Phasen*, p. 102. Berlin: Springer-Verlag.
TUKEY, J. W. (1974). *Introduction to Today's Data Analysis. Proceedings of the Conference on Critical Evaluation of Chemical and Physical Structural Information*, edited by D. R. LIDE JR & M. A. PAUL, pp. 3–14. Washington: National Academy of Sciences.
WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
WATANABE, Y. (1984). In preparation.
WATANABE, Y., FUJINAGA, Y. & IWASAKI, H. (1983). *Acta Cryst.* **B39**, 306–311.
WATANABE, Y. & IWASAKI, H. (1982). *J. Appl. Cryst.* **15**, 174–181.