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ONE-ELECTRON ENERGY SPECTRUM IN LONG-PERIOD SUPERLATTICES

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Résumé. — On étudie le spectre d'énergie à un électron d'une structure ordonnée modulée avec un modèle unidimensionnel quand la fonction d'ordre est une fonction sinus et la périodicité n'est pas un nombre entier de mailles élémentaires. Nous utilisons la méthode de la matrice de transfert dans l'approximation du cristal virtuel. L'existence et les amplitudes relatives des *mini-gaps* sont comparées au cas d'une fonction crêteau.

Abstract. — The one-electron energy spectrum of long-period superlattices is investigated in a simple one-dimensional model when the ordering wave is a sine wave and its periodicity is not an integral number of unit cells. We use the transfer matrix method in the virtual crystal approximation. The existence and relative amplitudes of the mini-gap are compared with the *square-wave* case.

Introduction. — The occurrence of long-period superlattices or *periodic antiphase structures* is quite common in alloys of noble metals. First discovered by Johansson and Linde [1] the most typical and also the most extensively studied example of these superstructures is certainly CuAu II [2-5]. This structure is stable between the disordered and the normal ordered structure CuAu I. In the completely ordered state, the normal ordered phase CuAu I consists of planes alternately filled with Cu (α sites) and Au (β sites) along, say the Z-axis (the unit cell is shown in figure 1a). In the original description of Johansson and Linde [1], the CuAu II structure is obtained by shifting along the y-axis the normal structure by the vector $(a/2, 0, a/2)$ so that planes filled by Cu become filled by Au and so on (figure 1b). This corresponds to regular arrangement of antiphase domains of size Ma which can be described by a one-dimensional square wave variation of the order parameter $S(y)$ (figure 1c). This would correspond probably to a good description at very low temperature, however for temperatures at which the structure is stable, the variation of the order parameter is smoother. Low values of the order parameter have been observed in the antiphase boundary region [5]. The new period is just twice the domain size and in such a description M is necessarily an integral number. However experimental values obtained from X-ray diffraction appear to be non-integral [2-4]. This is generally interpreted as a mixture of domains of two different sizes M and M' , M and M' being integral [2, 6, 7].

But Jehanno and Perio [4] have shown that the structure can be described by an order function $S(y)$ of defined period $2Ma$; non-integral values of M being considered as characteristic of these long-period superlattices. It may be shown that such *order functions*

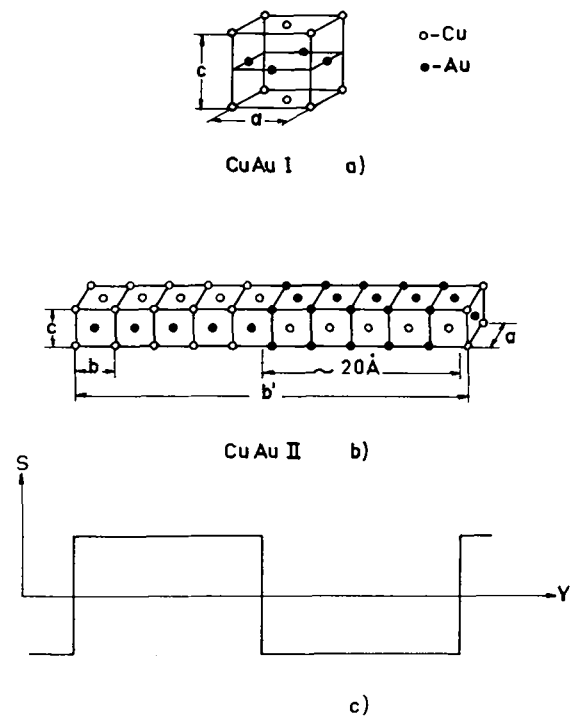


FIG. 1. — The unit cell of CuAu I (a) and of CuAu II in the Johansson and Linde description for $M = 5$ together with the order parameter profile (c).

appear as stationary states in an inhomogeneously ordered system [8]; from such thermodynamic derivation Ma can take values which are not commensurable with the lattice. On this basis, Villain [9] and Pick [10] have shown that longrange pairwise interactions between atoms are necessary to stabilize the long-period superlattices. This is in close agreement with the standard explanation [2, 11] in terms of the

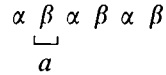
lowering of the energy of conduction electrons when the Fermi surface touches new energy gaps introduced by the superimposed periodicity of the ordering function as first suggested by Slater [12]. For arbitrary values of M , the overall structure is an *almost periodic* one and it is difficult to predict *a priori* the band structure [13]. All previous calculations of electronic states are based on the Johansson and Linde model i.e. with integral values of M [11, 14-17]. In order to attempt to clarify the effect of the ordering function $S(y)$ on the one-electron energy spectrum, the one-dimensional model proposed by Jones [15, 16] will be considered. It has been proved to have some relevance to the real situation because of the one-dimensional character of the long-period superlattice [15-17].

We will compare the existence and the relative magnitude of energy gaps in the three following cases : i) M is integer and $S(y)$ is a *square wave* ; ii) M integer but $S(y)$ becomes a *sine wave*

$$S(y) = \sin \frac{\pi y}{Ma} ;$$

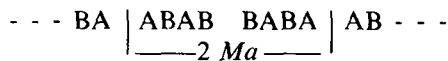
iii) we keep $S(y)$ as a *sine wave* but M has a non-integral value.

The one-dimensional model. — The one-dimensional model is simply a chain of sites of two different types alternately α and β at distance a from each other



α and β rather simulate layers of atoms so that an order parameter can be defined in each of them.

So the long period superlattice with a *square wave* for $S(y)$ and $M = 4$ corresponds to the following sequence



while the ordinary ordered state has a constant order parameter S



In the general case, we will use the virtual crystal approximation which restitutes to the lattice potential $V(y)$ the pseudo-periodicity created by $S(y)$:

$$\begin{aligned} V(y) = & \sum_{\alpha \text{ sites}} \{ P_A(y_\alpha) V_A(y - y_\alpha) + \\ & + P_B(y_\alpha) V_B(y - y_\alpha) \} + \sum_{\beta \text{ sites}} \{ P_A(y_\beta) V_A(y - y_\beta) \\ & + P_B(y_\beta) V_B(y - y_\beta) \} \end{aligned}$$

where :

$$\begin{aligned} P_A(y_\alpha) &= \frac{1 + S(y_\alpha)}{2}, & P_B(y_\alpha) &= \frac{1 - S(y_\alpha)}{2} \\ P_A(y_\beta) &= \frac{1 - S(y_\beta)}{2}, & P_B(y_\beta) &= \frac{1 + S(y_\beta)}{2} \end{aligned}$$

are the probabilities of getting respectively an atom A(B) and B(A) on site $\alpha(\beta)$ in position $y_\alpha(y_\beta)$ in a system with equal concentration of atoms A and B.

For simplification purposes, we represent the atoms by delta functions and use two sets of δ -functions of different strengths :

$$V_A(y) = \frac{\hbar^2}{2ma} P_A \delta(y)$$

$$V_B(y) = \frac{\hbar^2}{2ma} P_B \delta(y) .$$

In the numerical calculations presented in this paper we have taken $P_A = 3$ and $P_B = 1$. The results are not qualitatively affected when one chooses different sets of these parameters.

In order to make close comparison between the different cases mentioned above, we have chosen the transfer matrix method which we outline very briefly. Let the potential in a given region be $V(x)$, and $u(x)$, $v(x)$ two solutions of the Schrödinger equation such that, at a point x_0

$$\begin{aligned} u(x_0) &= 1 & v(x_0) &= 0 \\ u'(x_0) &= 0 & v'(x_0) &= 1 \end{aligned}$$

then, the wave function $\psi(x)$ and its derivative $\psi'(x)$ at a point x can be obtained from the knowledge of these functions at x_0

$$\begin{vmatrix} \psi(x) \\ \psi'(x) \end{vmatrix} = T(x, x_0) \begin{vmatrix} \psi(x_0) \\ \psi'(x_0) \end{vmatrix}$$

where

$$T(x, x_0) = \begin{vmatrix} u(x) & v(x) \\ u'(x) & v'(x) \end{vmatrix}$$

is the transfer matrix from x to x_0 .

The overall transfer matrix T is just the product of all transfer matrixes for each cell. For a really periodic structure of period b , from Bloch theorem, the two eigenvalues of the total transfer matrix are $e^{\pm ikb}$ and the condition for allowed energies is that its trace is between -2 and 2 . Similarly, for nearly periodic systems the condition is that the transfer matrix for the whole crystal has eigenvalues equal to unity to satisfy cyclic boundary conditions [18]. Numerically we stop the products of the transfer matrixes after N cells when the pseudo-periodicity of the potential is achieved (the relative change in the potential being less than ε ; we choose $\varepsilon \approx 10^{-6}$). From the value of the trace of T one gets the dispersive curve $E(k)$

$$\text{Tr } T = 2 \cos kb ,$$

where $b = Na$.

Each cell is defined such that the atom is at the center of the cell. The transfer matrix for a delta function is simply

$$\eta \rightarrow 0 \begin{cases} T(y_i + \eta, y_i - \eta) = \begin{vmatrix} 1 & 0 \\ \gamma_i & 1 \end{vmatrix} \\ i = \alpha, \beta \end{cases}$$

and

$$\begin{aligned} \gamma_i &= \frac{1}{a} \frac{P_A + P_B}{2} + S(y_i) \frac{P_A - P_B}{2} \quad \text{for } i = \alpha \\ &= \frac{1}{a} \frac{P_A + P_B}{2} - S(y_i) \frac{P_A - P_B}{2} \quad \text{for } i = \beta. \end{aligned}$$

For a constant $V = 0$ potential

$$T(x, x_0) = \begin{vmatrix} \cos \alpha(x - x_0) & \frac{1}{\alpha} \sin \alpha(x - x_0) \\ -\alpha \sin \alpha(x - x_0) & \cos \alpha(x - x_0) \end{vmatrix}$$

$$\alpha^2 = \frac{2mE}{\hbar^2}, E \text{ being the energy eigenvalue.}$$

So that the transfer matrix for a cell centered at y_i becomes :

$$T(y_i) = \begin{vmatrix} \cos \alpha a + \frac{\gamma_i}{\alpha} \sin \alpha a & \frac{1}{\alpha} \sin \alpha(x - x_0) \\ -\alpha \sin \alpha a + \gamma_i \cos \alpha a & \cos \alpha a \end{vmatrix}$$

For square wave functions $S(y)$ (case i), $\text{Tr } T$ can be evaluated for any integral value of the period M [16].

Results and discussion. — i) JOHANSSON AND LINDE MODEL : square wave. — For illustration, the dispersion curves $E(k)$ are shown on figure 2 for $M = 4$, together with $E(k)$ for the usual ordered state (constant order parameter). Qualitatively we retrieve

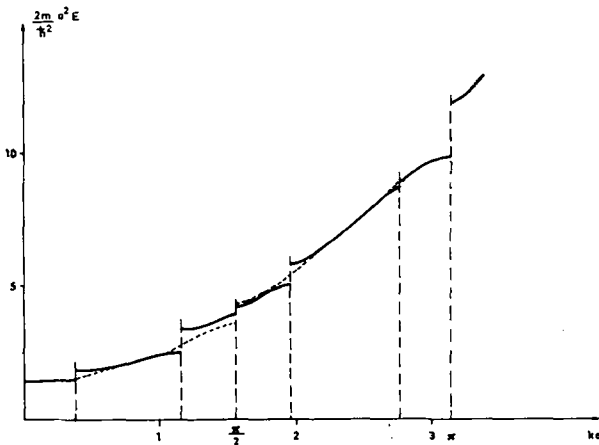


FIG. 2. — $E(k)$ for $M = 4$. $S(y)$ being a square wave as represented on figure 1c. The broken curve shows the band structure for the ordinary ordered state (constant order parameter).

the results of Jones [15, 16] except for the gap at $k = \pi/2 a$ i.e. where the ordered state has a gap. This gap at $k = \pi/2 a$ is considerably smaller than in the ordered system. In fact, for the ordered state sufficiently high values of S are necessary to get a gap as shown in the coherent potential approximation [19] and this indicates the limitations of the virtual crystal approximation. New energy gaps appear at

$$k = \frac{(2n + 1)\pi}{2Ma} \quad (n = 0, 1, \dots, M - 1).$$

The same result can be obtained with a tight binding calculation [20].

ii) $S = \sin \pi y/Ma$ WITH M INTEGER. — The band structure is represented on figure 3 for $M = 4$. We see clearly that the amplitudes of the gaps are deeply modified as compared with case i) (table I).

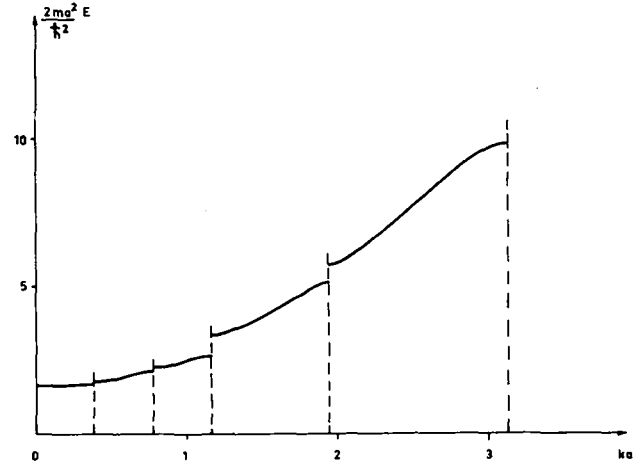


FIG. 3. — $E(k)$ for $S(y) = \sin \pi y/Ma$, $M = 4$.

TABLE I

k	$\frac{\pi}{8a}$	$\frac{\pi}{4a}$	$\frac{3\pi}{8a}$	$\frac{\pi}{2a}$	$\frac{5\pi}{8a}$	$\frac{3\pi}{4a}$	$\frac{7\pi}{8a}$
Square wave	0.38	0	0.9	0.27	0.8	0	0.18
Sine wave	< 0.03	0.09	0.72	≈ 0.02	0.64	< 0.03	< 0.03

The gaps at $k = \pi/8 a$ and $7\pi/8 a$ are now very small, and, although small, gaps appear at $k = \pi/4 a$ and $3\pi/4 a$. The gap at $k = \pi/2 a$ becomes considerably narrower than in the previous case. These important changes are illustrated even more clearly by the density of states (figure 4). This shows the important role played by the gradient of the order parameter in determining the electron energy spectrum.

iii) We keep the same profile $S(y)$ but M takes non-integral values. The band structure changes slightly; the position as well as the amplitude of the major gaps varies in a regular fashion. The case $M = 4.2$ is plotted on figure 5. The lowest gap appears at a slightly higher value of k (between $0.42/a$ and $0.465/a$ instead of $\pi/8 a$), while the next one appears at a lower value (between $0.729/a$ and $0.77/a$ instead of $\pi/4$) and are very small. The gaps around $3\pi/8 a$ and $5\pi/8 a$ remain important, while other gaps, too small, do not appear in our calculation. The effect amplifies for $M = 4.4, 4.6, \dots$

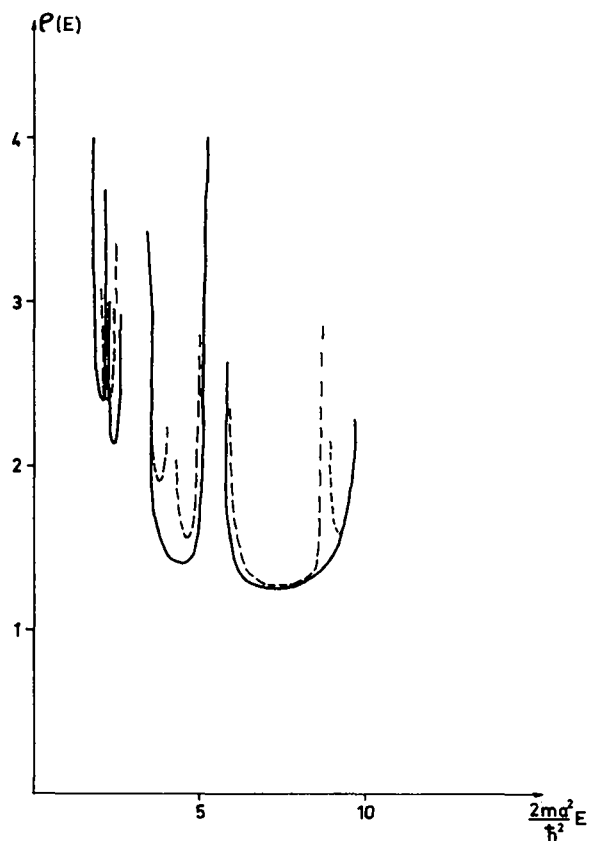


FIG. 4. — Density of states obtained from $E(k)$ plotted in figure 2 (dashed line) and figure 3 (full line).

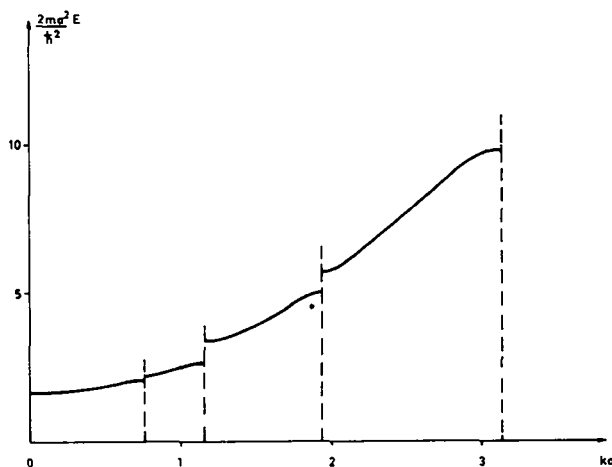


FIG. 5. — $E(k)$ for $S(y) = \sin \pi y/Ma$, $M = 4.2$.

The problem we have considered here presents some similarity with *frozen* spin density waves as in Chromium for instance [21]. The position and the relative amplitude of the energy gaps are found different from what is normally expected from a perturbation method [22]. First order gaps should occur at $\pm \frac{1}{2} \frac{\pi}{Ma}$. The results show that the profile of the order parameter plays a determining role, probably as or even more crucial than its period.

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