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# A method for calculation of dielectric constants of ultrathin superlattices

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**Abstract.** An approach to the calculation of static dielectric constants of the  $(AC)_m(BC)_n$  ultrathin superlattices (SL) composed of III–V or II–VI semiconductors is presented. These SL are formally considered to result from artificial ordering of alternative A (B) atoms in the initial crystalline structure (ICS)—the bulk solid solution  $A_xB_{1-x}C$  with  $x = m/(m+n)$ . According to this viewpoint, the SL dielectric constants are expressed in terms of those of the ICS, and variations depending on the superperiod and degree of ordering. The changes in dielectric constants are calculated on the basis of phenomenological Landau theory of second-order phase transitions, which takes into account thermodynamic instability of the SL. We consider [001]-oriented SL with  $m+n=3$ .

## 1. Introduction

As is well known, artificial superstructures that are composed of alternate layers of two different isomorphic semiconductors possess unique physical properties, different from those of the usual bulk crystalline compounds. In a superlattice with thicknesses of layers  $d_1$  and  $d_2$ , the appearance of a new strict period  $d = d_1 + d_2$  along the direction perpendicular to the layers results in additional dimensional quantization of the SL quasiparticle spectra, as well as anisotropy of the SL macroscopic physical properties. For instance, with respect to an external static electric or long-wavelength ( $\lambda \gg d$ ) electromagnetic field, a SL composed of optically isotropic materials behaves as an optically uniaxial medium with some effective properties. In this connection a problem with regard to the calculation of SL dielectric characteristics as functions of the composition and structural parameters of the SL, such as the growth direction and the magnitude of the superperiod, has arisen. It has been solved by Levin [1] and Rytov [2] for the *thick* SL composed of isotropic alternating materials. The method allows one to obtain the spatial dispersion of the SL effective dielectric constants by solving Maxwell's equations with periodic boundary conditions imposed on the electric induction and the field components at the interfaces. A simple approach, using also boundary conditions but not taking into account both the superperiodicity and the spatial dispersion of the SL dielectric properties, has been developed in [3, 4] for anisotropic layers. Both of the methods imply that the thickness of the layers should be much greater than the unit-cell size ( $d_k \gg a_k$ ). With this condition obeyed, every layer can be considered as a continuous medium that retains the dielectric constants of the individual bulk materials,  $\varepsilon_{ij}^{(k)}$ . As a result, the SL effective dielectric constants can be expressed in terms of those corresponding to each of the individual materials:  $\varepsilon_{ij}^{eff} = f(\varepsilon_{ij}^{(1)}, \varepsilon_{ij}^{(2)})$ .

Considerable progress in the synthesis of semiconductor SL has generated a new class of these SL—*ultrathin* SL, with only a few atomic planes in a superperiod ( $d_k \approx a_k$ ). Such

a technological method of nanoscale engineering as atomic-layer-controlled epitaxy has permitted the growth of high-quality SL with a precise period, consisting of a controllable number of alternating atomic planes. Obviously, the concepts of ‘thickness of layer’ and ‘individual bulk dielectric properties’ already have no meaning for these SL. Therefore, none of the continuous approximation methods mentioned above can be used for calculation of the effective dielectric properties of these SL.

## 2. Basic analogies

In this paper an approach to the calculation of effective dielectric constants of layered structures in the limit of ultrathin SL is proposed. It was used earlier in [5] for the calculation of SL piezoelectric constants. In what follows, we shall consider a specific [001]-oriented  $(AC)_m(BC)_n$  SL, where AC and BC are bulk pure compounds of III–V or II–VI semiconductors with zinc-blende structure. As we shall see, it is useful to imagine these SL as artificial single crystals. Indeed, they are very similar to the layered semiconductors (like GaSe and MoS<sub>2</sub>) or superstructures that often appear as a result of ordering-type phase transitions in solid alloys. The latter formal analogy is very important, and will be used below. The point is that the Landau theory of second-order phase transitions constitutes a powerful and universal instrument, which allows one to establish the relationship between dielectric tensor components of high- and low-symmetry phases:  $\varepsilon_{ij}^{LS} = \varepsilon_{ij}^{HS} + \delta\varepsilon_{ij}(\{C_\alpha\})$ . The variations  $\delta\varepsilon_{ij}(\{C_\alpha\})$  induced by the transition depend on the order parameter components (OPC)  $\{C_\alpha\}$  and some phenomenological coefficients, which are calculated for the initial high-symmetry phase. As is known [6], these OPC are the arguments of an incomplete thermodynamic Landau potential, and the rules of their transformation completely determine the reduction of symmetry under a second-order phase transition. Landau theory is traditionally used to search for the correspondence between the dielectric properties of the two *equilibrium* phases linked by the phase transition. But it should be borne in mind that this formalism is correct in a broader sense. That is, it is suitable for use in the situation where there is a *non-equilibrium* low-symmetry phase. There is only one strict requirement imposed on these two phases: the space group of the low-symmetry phase should be a subgroup of the space group of the other phase.

According to [7, 8], [001]-oriented artificial superlattices  $(AC)_m(BC)_n$  are non-equilibrium phases for all  $(m, n)$  combinations. Thus, if we can find a relatively simple and equilibrium crystalline phase such that the SL can be considered in a formal symmetry sense as a crystal *derived* from this initial crystalline structure (ICS), we could use the Landau theory formalism for our purpose, i.e. for calculation of the SL dielectric constants. It turns out that the completely disordered (random) pseudobinary solid solution  $A_xB_{1-x}C$  (with  $x = m/(m+n)$ ) which is isomorphic to the pure components AC (BC) can be chosen as the ICS. Obviously, the space group and the system of Wyckoff positions for this mixed crystal coincide with those for the pure ones ( $T_d^2$ , and the  $a$ -,  $c$ -sublattices). We consider that the  $c$ -sublattice of the ICS is occupied entirely by C-type atoms. As to the  $a$ -sublattice, it can be occupied by only the alternative A- and B-type atoms with constant probabilities  $p_A(\mathbf{r}_{la}) = x$  and  $p_B(\mathbf{r}_{la}) = 1 - x$ , where  $l$  enumerates ICS unit cells. Then the simplest SL can be *formally* considered to result from the ordering of A (B) atoms over  $a$ -positions of the ICS in the [001] direction. In a general case,  $m$  neighbouring (001) planes of the  $a$ -sublattice are occupied mostly by A atoms with variable probabilities along [001],  $p_A(\mathbf{r}_{la})$ , within the layer, and the next  $n$  planes contain mostly B atoms, also distributed with varying  $p_B(\mathbf{r}_{la})$ . In addition, we examine a particular case of ordering in which these probabilities differ for two adjacent layers, but are constant within each of them. An ideal SL is such a

completely ordered structure. To simplify the notation, we shall represent all of the above SL by the same formula as is used for the ideal SL. It should be emphasized that we use the term ‘ordering’ under the convention that it describes a set of SL with different, but fixed degrees of ordering. Below room temperature, no ordering–disordering process is actually observed in practice, due to a high activation energy of the thermal interdiffusion [9]. This means that the degree of ordering is ‘frozen’ at the moment of SL formation. However, for the sake of simplicity it is convenient to discuss the ‘ordering’ of atoms over the SL  $a$ -sublattice sites.

### 3. The symmetry of the ordering

For further simplicity, detailed consideration is carried out only for the SL with  $m + n = 3$ . This SL differs from the ICS in such a way that one plane with an excess of A- (B-) type atoms alternates with two planes with excesses of the other (B- (A-) type) atoms. The probabilities of containing an excess of the B (A) type of atoms for these two adjacent planes can be equal or different. This leads to two different ordering structures. If  $\tau$  is the distance between two neighbouring (001) planes of the  $a$ -sublattice, then the superperiod is equal to  $\mathbf{d} = (0, 0, 3\tau)$ . The spatial modulation of the probability which represents the  $a$ -sublattice-plane occupation by the alternative atoms can be readily described in terms of static concentration waves [10]:

$$\delta p(\mathbf{r}_{la}) = C(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}_{la}) + C(-\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{r}_{la}). \quad (1)$$

Here  $p(\mathbf{r}_{la})$  is the probability for an ( $la$ ) site of the ICS  $a$ -sublattice to be occupied by an A (B) atom. In this particular case, the expansion of the modulation in a Fourier series includes a sole harmonic (wave of ordering), because it completely represents the structural variations. This harmonic can be characterized by the wavevector  $\mathbf{q} = (0, 0, 2\pi/3\tau) = \frac{1}{3}(\mathbf{b}_1 + \mathbf{b}_2)$  where the  $\{\mathbf{b}_i\}$  are the basis vectors of the ICS reciprocal lattice. It is a solution of the equation  $\mathbf{q} \cdot \mathbf{d} = 2\pi$  that results from the requirement of translational invariance:  $\delta p(\mathbf{r}_{la} + \mathbf{d}) = \delta p(\mathbf{r}_{la})$ . This  $\mathbf{q}$  belongs to the  $\Delta$  point of the ICS first Brillouin zone. It is important that the magnitude of  $\mathbf{q}$  is a rational part of the ICS reciprocal-lattice vector. Only two wavevectors,  $\pm\mathbf{q}$ , are used in expression (1). This means that only certain elements of the ICS space group  $g \in G_{\pm\mathbf{q}} = G_{\mathbf{q}} \oplus g_0 G_{\mathbf{q}} \subset G^{ICS}$  are of interest for us. Here  $G_{\mathbf{q}}$  is the wavevector group, and  $g_0 \mathbf{q} = -\mathbf{q}$ . With respect to the elements  $g \in G_{\pm\mathbf{q}}$ , a couple of wavevectors  $\pm\mathbf{q}$  form an irreducible two-arrow star. The complete permutable co-representation [11]  $D^{\pm\mathbf{q}}(g)$  induced by the identical representation of the point group  $H_{\mathbf{q}}$  of the superstructure wavevector [6, 12] is connected with this star. For an arbitrary element

$$g = \left( h / \sum_i l_i \mathbf{a}_i \right) \in G_{\pm\mathbf{q}}$$

the matrices of this co-representation have the following form:

$$\begin{pmatrix} \xi(g) & 0 \\ 0 & \xi^*(g) \end{pmatrix}$$

if  $h \in H_{\mathbf{q}}$ , and

$$\begin{pmatrix} 0 & \xi(g) \\ \xi^*(g) & 0 \end{pmatrix}$$

if  $h\mathbf{q} = -\mathbf{q}$ . Here  $\xi(g) = \exp[2\pi i(l_1 + l_2)/(m + n)]$ . The set of vectors  $\{\mathbf{a}_i\}$  is the ICS lattice basis. Two components of the order parameter,  $C_1 = C(\mathbf{q})$  and  $C_2 = C(-\mathbf{q})$ ,

are transformed according to this  $D^{\pm q}(g)$ . They describe (as is well known [6]) a spatial symmetry reduction under ordering. It follows from the reality of  $\delta p$  that  $C_2 = C_1^*$ . From the invariance of  $\delta p$  with respect to the transformation elements  $g \in G^{SL}$ , one can obtain the expression connecting the OPC with the matrices of the co-representation [11]:

$$C_\alpha = \sum_{\beta} D_{\alpha\beta}^{\pm q}(g) C_\beta. \quad (2)$$

Those elements  $g \in G_{\pm q}$  which turn equality (2) into the identity form the SL space group  $G^{SL} \subset G_{\pm q}$ . Only some of the initial translational subgroup elements keep  $\delta p$  invariant. As a result, the SL basic vectors  $\{A_j\}$  become longer than the initial basic vectors. This corresponds to  $(m+n)$ -fold multiplication of the ICS primitive cell. So, the ordering results in a complication of the SL primitive cell in comparison with that of the ICS, due to translational invariance breaking for some sites of the  $a$ -sublattice. This is revealed in a crystal system reduction, also. It can be shown that two different sets of OPC,  $\{C_1, C_2\}$ , result in different reductions of the group symmetry. In the general case ( $C_1 \neq C_2$ ), this group belongs to the orthorhombic  $C_{2v}$  crystal system. In the other case ( $C_1 = C_2$ ), the SL has tetragonal  $D_{2d}$  symmetry [13]. Thus, a rigorous symmetry connection between the SL and the ICS is established—namely, that the SL space group is a subgroup of the ICS space group ( $T_d^2$ ). This fact permits one to obtain the relationship between the ICS and the SL dielectric constants basically within the framework of phenomenological Landau theory of second-order phase transitions.

#### 4. Thermodynamic potential

It is known [7, 8] that most of the solid solutions  $A_xB_{1-x}C$  of III–V and II–VI semiconductors with zinc-blende structure are unstable at low temperatures with respect to decomposition into the pure components  $AC + BC$ . But they become thermodynamically stable at temperatures above that of a miscibility gap ( $T > T_{MG}$ ). For some kinds of such random alloys, the maximum of the concentration dependence  $T_{MG}(x)$  is even below room temperature. For example,  $T_{MG}^{max} \approx 60$  K for the  $Ga_{0.5}Al_{0.5}As$  solution [7]. Then, for  $T > T_{MG}(x)$  the wave of the ordering can be considered as a ‘frozen’ fluctuation of the concentration from the equilibrium state. Now, as in Landau theory, we can introduce a non-equilibrium thermodynamic potential (TP) per multiplied cell  $V_{SL}$ :

$$\Phi^{SL} = \Phi_0^{ICS}(x, T) + \delta\Phi(x, T, \mathbf{E}, \{C_\alpha\})$$

where  $\Phi_0^{ICS}$  is a TP of the ICS, and  $\delta\Phi$  is the non-equilibrium variation of the TP induced by a wave of the ordering, and a macroscopic electric field  $\mathbf{E}$ . Apart from the usual thermodynamic variables  $x, T, \mathbf{E}$ , we introduce into  $\delta\Phi$  a new additional set of variables  $\{C_\alpha\}$ , i.e. the OPC which describe a deviation from the equilibrium state. According to a standard procedure, the real scalar  $\delta\Phi$  should be expanded in a power series of invariants composed of the OPC and the field components,  $\{E_i\}$ . There is only one invariant of the second power in the OPC:  $I_1 = C_1C_2$ . The nature of the problem concerned (threefold multiplication of the ICS primitive cell under ordering) enables us to construct the polynomials of degree three in  $C_\alpha$  that remain invariant under pure translations of the ICS space group (Dzyaloshinskii invariants). One of them,  $I_D = C_1^3 + C_2^3$ , is simultaneously a complete invariant. Another one,  $C_1^3 - C_2^3$ , does not possess this property, because it is transformed according to the vector irreducible representation  $A_2$  of the point group  $D_{2d}$  (i.e. like the  $z$ -component of a vector). However, two mixed polynomials, which include the electric field components and the OPC, are complete invariants:

$$I_{CE} = i^{-1}(C_1^3 - C_2^3)E_3 \quad I_{1CE} = i^{-1}(C_1^3 - C_2^3)E_1E_2$$

where  $i = \sqrt{-1}$ . Some other mixed invariants,  $I_{2CE} = (C_1 C_2) E_3^2$  and  $I_{3CE} = (C_1^3 + C_2^3) E_3^2$ , are also of interest. Finally, there is one field invariant:  $I_E = \mathbf{E}^2$ . So, the first terms in the expansion of the Landau potential up to second order in the field components and third order in the OPC have the form

$$\Phi^{SL} = \Phi_0^{ICS} + \delta\Phi_1 + \alpha I_{2CE} + \beta I_1 I_E + \frac{\gamma}{2} I_{3CE} + \frac{\nu}{2} I_D I_E + \frac{\mu}{2} I_{1CE} - \frac{V_{SL}}{8\pi} \varepsilon_0^{ICS} I_E. \quad (3)$$

Here  $\varepsilon_0^{ICS}$  is the dielectric constant of the optically isotropic ICS. The part of  $\delta\Phi$  including only OPC invariants and mixed invariants linear in the fields is denoted as  $\delta\Phi_1$ . It is not used in our further calculations.

We consider the ICS as a non-absorbing and non-conducting medium. In particular, this is valid for the mixed crystal  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$  with a band gap of about 2 eV [14], which, below room temperature, behaves as a dielectric with respect to electromagnetic radiation within a definite frequency range.

After introducing polar coordinates via  $C_1 = \rho \exp(i\varphi)$  and  $C_2 = \rho \exp(-i\varphi)$ , and substituting them into (3), we obtain

$$\Phi^{SL} = \Phi_0^{ICS} + \delta\Phi_1 + \rho^2 G_1(\mathbf{E}) + \rho^3 [G_2(\mathbf{E}) \cos 3\varphi + G_3(\mathbf{E}) \sin 3\varphi] - \frac{V_{SL}}{8\pi} \varepsilon_0^{ICS} \mathbf{E}^2 \quad (4)$$

where

$$\begin{aligned} G_1(\mathbf{E}) &= \beta(E_1^2 + E_2^2) + (\alpha + \beta) E_3^2 \\ G_2(\mathbf{E}) &= \nu(E_1^2 + E_2^2) + (\nu + \gamma) E_3^2 \\ G_3(\mathbf{E}) &= \mu E_1 E_2. \end{aligned}$$

The dielectric constants of the SL are determined from the second complete derivatives of  $\Phi^{SL}$  from (4) with respect to the generalized forces  $\{E_i\}$ :

$$\varepsilon_{ij}^{SL} = -\frac{4\pi}{V_{SL}} \left( \frac{\partial^2 \Phi^{SL}}{\partial E_i \partial E_j} \right)_S = \varepsilon_0^{ICS} \delta_{ij} + \delta\varepsilon_{ij}. \quad (5)$$

The subscript  $S$  denotes that derivatives are taken at zero field, and for a given degree of ordering,  $\rho = \rho_S$  and  $\varphi = \varphi_S$ . Generally speaking, the expressions for  $\varepsilon_{ij}^{SL}$  must include the derivatives of  $\rho$  and  $\varphi$  with respect to the field components. However, as already mentioned above, interplane diffusion of atoms below room temperature is in practice absent. Assuming that the fields applied to the SL are not so strong as to substantially affect the rate of the interplane diffusion, one can neglect the dependences  $\rho(\mathbf{E})$  and  $\varphi(\mathbf{E})$ . Then the complete derivative (5) is reduced to a partial one. Finally, we have from (5), with accuracy up to the third-order terms in  $\rho_S$ ,

$$\begin{aligned} \delta\varepsilon_{11} = \delta\varepsilon_{22} &= -\frac{8\pi}{V_{SL}} (\beta + \nu\rho_S \cos 3\varphi_S) \rho_S^2 \\ \delta\varepsilon_{33} &= -\frac{8\pi}{V_{SL}} [(\alpha + \beta) + (\nu + \gamma)\rho_S \cos 3\varphi_S] \rho_S^2 \\ \delta\varepsilon_{12} = \delta\varepsilon_{21} &= -\frac{4\pi}{V_{SL}} \mu \rho_S^3 \sin 3\varphi_S. \end{aligned} \quad (6)$$

It is clear from the last equality that the translational invariant  $I_{1CE}$  plays an extremely important role in the appearance of new (non-zero) components of the dielectric tensor in the SL.

In the general case of ordering, as  $\varphi_S \neq 0$  and  $\rho_S < 1/3$ , some off-diagonal components of the dielectric tensor from (6) are non-zero. By using rotation through  $\pi/4$  about the  $OZ$ -axis, the tensor  $\varepsilon_{ij}^{SL}$  can be transformed into a standard form [15], with three different

on-diagonal components as expected for an anisotropic two-axes optical medium which belongs to the polar orthorhombic crystal class  $C_{2v}$ :

$$\tilde{\varepsilon}_{11}^{SL} = \varepsilon_{11}^{SL} + \varepsilon_{12}^{SL} \quad \tilde{\varepsilon}_{22}^{SL} = \varepsilon_{11}^{SL} - \varepsilon_{12}^{SL} \quad \tilde{\varepsilon}_{33}^{SL} = \varepsilon_{33}^{SL}.$$

In the other case ( $\varphi_S = 0$  and  $\rho_S = 1/3$ ), i.e. in an ideally ordered SL with the tetragonal crystal class  $D_{2d}$ , the expressions (6) are simplified as for a one-axis optical medium, so the non-zero components are  $\varepsilon_{11}^{SL} = \varepsilon_{22}^{SL} \neq \varepsilon_{33}^{SL}$ .

The phenomenological coefficients  $\alpha$ ,  $\beta$ ,  $\nu$ ,  $\gamma$ , and  $\mu$  can be calculated by using the expression for the free energy derived by standard methods of statistical mechanics [16] applied to a specific model for the random pseudobinary alloy  $A_xB_{1-x}C$ . However, the calculation of the TP coefficients using a microscopic alloy model is beyond the scope of this paper. We only mention here that these coefficients can be expressed in terms of a small number of combinations of interatomic interaction energies, such as the mixing energy, that have been calculated for some III–V and II–VI semiconductor alloys in [17] by a pseudopotential method.

## 5. Concluding remarks

A new phenomenological method is proposed for calculating effective static dielectric constants of the ultrathin SL  $(AC)_m(BC)_n$  with only three atomic planes in the superperiod. For such a SL, layers of alternative materials cannot be considered within the continuous-medium model that is used for the calculation of the dielectric properties of thick SL. But it was shown that ultrathin SL can be represented formally as a result of ‘ordering’ of alternative atoms in the initial solid solution  $A_xB_{1-x}C$ , which is thermodynamically an equilibrium phase above the miscibility-gap temperature at  $x = m/(m + n)$ . In contrast, these SL, as artificial objects, are non-equilibrium structures. Their thermodynamic states can be described by an incomplete TP, which is a function of the order parameter determining the deviation from the equilibrium state, as well as a symmetry reduction occurring as a result of ordering. This viewpoint for the SL provides a natural and convenient way (like in the Landau theory of ordering-type phase transitions) to express the static dielectric constants of the SL,  $\varepsilon_{ij}^{SL}$ , in terms of those of the ICS,  $\varepsilon_0^{ICS}$ , and the variations  $\delta\varepsilon_{ij}$  depending on the concentration-wave amplitude  $\rho_S$  and the superperiod  $d$ .

Thereby, the complicated initial problem is split into two simpler parts. In the first step, the proposed phenomenological approach allows one to take account of the symmetry of the ordering comprehensively. The variations in the dielectric constants are represented as a power series in the OPC, with some phenomenological coefficients. The importance of Dzyaloshinskii invariants as regards the appearance of non-zero dielectric tensor components is demonstrated. We believe that here the value of the ICS dielectric constant  $\varepsilon_0^{ICS}(x)$  is known. For example, it can be measured for real solid solutions. A set of phenomenological coefficients can be calculated independently of the first step by the well developed methods of statistical mechanics applied to a concrete model of the solid solution. This second step towards a complete solution of the problem will be published later [18]. It should be emphasized that the main goal of this paper was to show (in principle) the necessity and feasibility of using this approach for the calculation of the SL dielectric properties as perturbations of the ICS ones.

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