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Alloy scattering in ternary III-V compounds

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The mean time between scattering due to a random alloy potential is considered. The development makes use of the Warren-Cowley order parameters and uses a pseudobinary alloy model for describing the arrangement of alloy concentrations on the allowed lattice sites. The resulting mean time between scattering is found to depend inversely on the square root of temperature and energy.

I. INTRODUCTION

Alloy scattering refers to the scattering present in alloys due to the random distribution of component atoms among the available lattice sites. This scattering is in addition to the normal scattering mechanisms present in nonalloy materials. There are basically two problems in setting up a model for alloy scattering. First, one must have a model for the amount of order or disorder present in the alloy. This is done in the present work by the use of the Warren-Cowley order parameters,[1] which allows one to describe any degree of order ranging from a completely random alloy to a highly ordered alloy structure. The second problem is that of selecting an interaction or scattering potential due to the lattice disorder. Several potential models have been considered, but the one which appears most appropriate to alloy scattering is the inner-potential model of Mott.[2]

II. PSEUDOBINARY ALLOY MODEL

The model to be developed for alloy scattering is restricted to the case of ternary III-V compounds where one of the elements, denoted by C, is common to both of the constituent compounds. For example, indium in InAs-InP or arsenic in GaAs-InAs. In the cases of the alloys InSb-GaSb, InAs-GaAs, and InSb-InAs, the lattice parameter varies with composition, in mole percent, in an almost linear manner.[3,4] The crystal structure of the pure compounds is the tetrahedral zinc-blende structure and the alloys also exhibit the tetrahedral zinc-blende structure, as discussed by Goryunova *et al.*[5]

The zinc-blende lattice can be subdivided onto two interpenetrating face-centered-cubic (fcc) lattices. The side length of the cubes is the lattice parameter a and nearest-neighbor distance is $\frac{1}{4}\sqrt{3}a$. In this arrangement each atom in the lattice, except at the crystal surfaces, has four nearest neighbors with the angle between bonds at about 107.50°.

The model that will be used is of two interpenetrating fcc lattices. Denoting the general lattice vector by $\vec{\tau}$, one fcc lattice consists of the set of lattice points $\{\vec{\tau}=\vec{\gamma}\}$, and the other fcc lattice consists of the lattice points $\{\vec{\tau}=\vec{\zeta}\}$. Suppose that all of the points of the $\vec{\gamma}$ lattice are occupied by atoms of type C, but that the points of the $\vec{\zeta}$ lattice are shared between atoms of type A and type B. If the total number of lattice points on $\vec{\zeta}$ is N_ζ, and N_A, N_B denote, respectively, the number of A atoms and the number of B atoms, then

$$N_A + N_B = N_\zeta \ , \tag{1}$$

$$x = N_A/N_\zeta = C_A \ , \tag{2}$$

$$1 - x = N_B/N_\zeta = C_B \ . \tag{3}$$

In this arrangement a type-C atom may have all type-A nearest neighbors, or all type-B nearest neighbors, or a mixture of type-A and type-B nearest neighbors. The type-A or type-B atoms, however, will always have all type-C neighbors.

In effect the model is a fcc structure, lattice, of A-C and B-C molecules, with intermolecular bonding as well as intramolecular bonding. The structure described above constitutes what is referred to in this work as a "pseudobinary alloy," with the properties determined by the relative concentrations of A and B.

Nordheim[6] was the first to consider the problem of calculating the resistivity of alloys using quantum mechanical concepts. Nordheim dealt with the perfectly random crystal by introducing the concept of the virtual crystal. The actual crystal was considered to be divided into a perfectly periodic array of potentials, the virtual crystal, composed of the composition weighted potentials due to the different kinds of atoms making up the crystal, and a random part due to the difference between the actual crystal potential and the virtual crystal potential at a given lattice point. This random part was used as a perturbation potential, leading to a matrix element for transition between electron states.

Hall[7] reformulated Nordheim's approach to calculating residual resistivity for a binary alloy and used the Warren-Cowley order parameters. The one-electron Schrödinger wave function for an electron in a binary alloy was written with the potential $U(\vec{r})$ divided into a virtual crystal part

$$U_1(\vec{r}) = \sum_{\vec{\tau}} [C_A U_A(\vec{r} - \vec{\tau}) + C_B U_B(\vec{r} - \vec{\tau})] , \tag{4}$$

and a random potential part

$$\begin{aligned} U_2(\vec{r}) &= \Delta U(\vec{r} - \vec{\tau}) \\ &= \sum_{\vec{\tau}} C_{\vec{\tau}} [U_A(\vec{r} - \vec{\tau}) - U_B(\vec{r} - \vec{\tau})] , \end{aligned} \tag{5}$$

where $C_{\vec{\tau}}$ is a random function which is defined only at lattice sites $\vec{\tau}$. The function has the value at these points

$$C_{\vec{\tau}} = \begin{cases} (1 - C_A) & \text{for an } A \text{ atom at } \vec{\tau} , \\ \\ -C_A & \text{for a } B \text{ atom at } \vec{\tau} , \end{cases} \tag{6}$$

where, as usual, C_A is the concentration of A atoms. This function was introduced by Flinn[1] in a discussion of an electronic theory of local ordering in binary alloys. It was shown by Flinn to have the following properties:

$$\sum_{\vec{\tau}} C_{\vec{\tau}} = 0 , \tag{7}$$

$$\sum_{\vec{\tau}'} C_{\vec{\tau}'} C_{\vec{\tau}'+\vec{\tau}} = N C_A (1 - C_A) \alpha_{\vec{\tau}} , \tag{8}$$

where $\alpha_{\vec{\tau}}$ is the Warren-Cowley order parameter.

The approach of Hall was further developed by Asch and Hall.[8] This development included the change in lattice parameter with alloying and the change in effective number of conduction electrons per atom with composition. Asch and Hall have shown that the square of the transition matrix between initial and final states is given by

$$|M(\vec{K}, \vec{K}')|^2 = \sum_{\vec{\tau}}^{N} \alpha_{\vec{\tau}} J(\vec{K}, \vec{K}', \vec{\tau}) , \tag{9}$$

where

$$\alpha_{\vec{\tau}} = \sum_{\vec{\tau}'}^{N} \frac{C_{\vec{\tau}'} C_{\vec{\tau}'+\tau}}{N C_A C_B} , \tag{10}$$

$$\begin{aligned} J(\vec{K}, \vec{K}', \vec{\tau}) &= N C_A C_B \\ &\quad \times \left| \frac{1}{N\Omega} \int_{\infty \text{ volume}} \psi^*_{K'} \Delta U(\vec{r} - \vec{\tau}) \psi_K d\vec{r} \right|^2 , \end{aligned} \tag{11}$$

and $\Delta U(\vec{r} - \vec{\tau})$ is the random potential due to the alloying effect. In terms of the Bloch functions the integral expression of Eq. (11) becomes

$$\begin{aligned} J(\vec{K}, \vec{K}', \vec{\tau}) &= N C_A C_B \exp[i(\vec{K} - \vec{K}') \cdot \vec{\tau}] \\ &\quad \times \left| (1/N\Omega) \int_{\infty \text{ volume}} u^*_{K'} u_K U(\vec{r} - \vec{\tau}) \right. \\ &\qquad \left. \times \exp[i(\vec{K} - \vec{K}') \ \vec{r}] d\vec{r} \right|^2 . \end{aligned} \tag{12}$$

III. SCATTERING-POTENTIAL MODEL

Applying the virtual crystal concept of Nordheim, and treating the deviations from the perfect periodicity of the virtual crystal model as a perturbing potential, the matrix elements for a transition from state K to K' can be worked out. The matrix element squared is presented in Eq. (9) for all degrees of order which can be specified by the Warren-Cowley order-parameter set $\{\alpha_{\vec{\tau}}\}$. In the completely random alloy, the expression reduces to

$$|M(\vec{K}, \vec{K}')|^2 = \frac{C_A(1 - C_A)}{N\Omega^2} \left| \int_{\infty \text{ volume}} \psi^*_{K'} \Delta U(F) \psi_K d\vec{r} \right|^2 . \tag{13}$$

In the case where the substituted atoms, say of type A, have an effective ionic charge which differs by an amount ΔZe from that of type B, a screened potential of the form $\phi(r) = (\Delta Ze / 4\pi\epsilon r) \times \exp(-r/r_s)$ can be taken for $\Delta U(r)/e$. This leads to a relaxation time that has the same form as the Brooks-Herring type formula, except the factor n_I is replaced by $C_A(1 - C_A)/\Omega$. This type of scattering would give a mobility component which increased with temperature as $T^{3/2}$. This type of potential does not seem likely to occur for the isovalent substitutions in the III-V compound alloys. Thus a more plausible potential must be considered.

Long ago Mott considered the effects of substitution in dilute alloys.[2] He considered a solvent lattice in which the electron wave functions, $\psi_K = u_K(\vec{r}) \exp(i\vec{K} \cdot \vec{r})$ are solutions to the Schrödinger equation, and conduction-band electrons have energies given by

$$E(K) = \hbar^2 K^2 / 2m + E_0 , \tag{14}$$

where E_0 is the energy of the band edge. When an atom of a different potential is substituted for a "native" atom, the wave function in the Wigner-Seitz cell about the substitute will become $\psi_{K'} = u_{K'}(\vec{r}) \exp(i\vec{K}' \ r)$ and have an energy

$$E(K') = \hbar^2 K'^2 / 2m + E_0' , \tag{15}$$

corresponding to the altered wavelength, hence

K', in the altered potential region. An electron traveling from a "normal" region into the altered region will experience a change in potential. As pointed out by Mott, the problem is the same as the scattering of a beam of electrons by a potential, which he termed the "inner potential",

$$\Delta U = \begin{cases} E_0 - E_0', & r \leq r_0 , \\ 0, & r > r_0 , \end{cases} \tag{16}$$

where r_0 is the radius of the Wigner-Seitz cell (assumed spherical). This "square well" potential is used in the Appendix to derive, by means of the first Born approximation, an expression for the relaxation time due to scattering in a random alloy τ_{AR} defined by

$$\tau_{AR} = \frac{8 N_A \hbar^4 \epsilon^{-1/2}}{3\sqrt{2}\, \pi C_A (1 - C_A)(\Delta E)^2 m^{*3/2} (kT)^{1/2}} , \tag{17}$$

where $\epsilon = E/kT$. The choice of the extent of the potential ΔU is somewhat arbitrary and has been taken in the derivation as equal to the nearest-neighbor separation, or $\frac{1}{4}\sqrt{3}a$.

IV. APPLICATION TO SELECTED III-V COMPOUNDS

A decision must be made on the value of ΔE to be used in Eq. (17) in order to obtain numerical results. The energy difference could be taken as the difference in energy band gaps for the two components of the alloy. A more reasonable approach however would be to take the vacuum level as the energy reference level. If this is done E_0 and E_0' are the energy separations of the conduction band edges with respect to the vacuum level, i.e., the electron affinities of the two materials. Table I gives electron affinity values, in eV, of several III-V compound materials, taken from Neuberger.[9] If ΔE is adequately represented by $\Delta\psi$, the electron affinity difference, the data of Table I suggest little or no alloy scattering for $GaAs_xSb_{1-x}$, a relatively large alloying effect for $Ga_xIn_{1-x}As$, moderate effects for InP_xAs_{1-x}, $InAs_xSb_{1-x}$ and a somewhat smaller effect for InP_xSb_{1-x}. Before making too many predictions, however, it should be remembered that the alloying relaxation times are combined with other relaxation time for other mechanisms and it is the relative sizes of these relaxation times for a given alloy system that must be considered.

Both conventional and Monte Carlo calculations of mobility have been made for selected III-V alloys using the model discussed in this paper for alloy scattering. These calculations have considered polar optical-phonon scattering, piezoelectric scattering, ionized impurity scattering, and intervalley scattering as well as alloy scattering. The percentages of total scattering events attributable to alloy scattering has ranged from a few percent to as much as 25% depending on the ternary material and the composition. Monte Carlo transport calculations in such materials as $InAs_{1-x}P_x$ have shown that alloy scattering is more important at high electric fields than for the low-field mobility. Details of this work are being published elsewhere.[10,11]

TABLE I. Electron affinity values (in eV) for some III-V compound materials.[9]

Material	GaAs	GaSb	InP	InAs	InSb
electron affinity (eV)	4.07	4.06	4.40	4.90	4.59

The presence or importance of alloy scattering is difficult to experimentally verify by the predicted $\sqrt{T}$ dependence of Eq. (17). This is due to several factors. First, even when alloy scattering is important it does not appear to be the dominant scattering mechanism to the point where other scattering processes can be neglected. Second, at low temperatures, scattering is usually dominated by ionized impurity scattering which has a $T^{3/2}$ temperature dependence and decreases more rapidly at low temperatures than does the alloy scattering. Finally at high temperatures, scattering is dominated by phonon scattering with a $T^{-1/2}$ dependence. Thus the temperature range over which alloy scattering is important does not usually appear to be wide enough to uniquely identify the $\sqrt{T}$ temperature dependence. The most convincing evidence for the importance of alloy scattering has been the need for an additional scattering process to explain the experimentally observed mobility values for semiconductor alloys.[10,12]

APPENDIX: CALCULATION OF RELAXATION TIME FOR INNER POTENTIAL SCATTERING

Using the Born approximation to calculate the matrix element for a transition due to a "square well" potential of strength ΔE and extent $r \leq r_0$,

$$m(K, K') = \int_{\infty\,\text{volume}} e^{i \Delta \vec{K} \cdot \vec{r}}\, \Delta U \, d\vec{r},$$

and (A1)

$$\Delta\vec{K} = (\vec{K} - \vec{K}') ,$$

$$d\vec{r} = r^2 dr \sin\theta \, d\theta \, d\phi .$$

Due to azimuthal symmetry, integration on ϕ

gives a factor 2π. Taking θ as the angle between $\Delta\vec{K}$ and $\vec{K}'$,

$$m(\vec{K},\vec{K}') = 4\pi \frac{\Delta E}{\Delta K} \int_0^\infty \sin(\Delta K r)\, r\, dr\ ,$$

$$m(\vec{K},\vec{K}') = 4\pi[\Delta E/(\Delta K)^3] \times (\sin\Delta K r_0 - \Delta K r_0 \cos\Delta K r_0)\ . \tag{A2}$$

For $\Delta K r_0$ real the series expansions of $\sin x$ and $\cos x$ yield

$$\sin x = x - x^3/3! + x^5/5! - x^7/7! \cdots\ ,$$

$$x\cos x = x - x^3/2! + x^5/4! - x^7/6! + \cdots\ .$$

Subtraction term by term yields

$$\sin x - x\cos x = 2x^3/3! - 4x^5/5! + \cdots\ . \tag{A3}$$

Substitution of Eq. (A3) into Eq. (A2) gives

$$m(K,K') = 4\pi(\Delta E)\, r_0^3 (\tfrac{1}{3} - \tfrac{1}{30}\Delta K^2 r_0^2 + \cdots)\ . \tag{A4}$$

The square of the matrix element is

$$|m(K,K')|^2 = 16\pi^2(\Delta E)^2 r_0^6 (\tfrac{1}{9} - \tfrac{1}{45}\Delta K^2 r_0^2 + \cdots)\ . \tag{A5}$$

The neglect of higher-order terms can be justified on the basis that $r_0 \simeq 2.5\times10^{-10}$ meters and $\Delta K_{\text{max}} \simeq (3kT\times 2m^*/\hbar^2)^{1/2}$. Therefore, $(\Delta K r_0)_{\text{max}} \simeq 8.5 \times 10^{-2}$ and to a good approximation

$$|m(K,K')| = \tfrac{16}{9}\pi^2(\Delta E)^2 r_0^6\ . \tag{A6}$$

The choice of the value for r_0 is somewhat arbitrary. Substitution of a "foreign" atom of the same valence as a "native" atom in the center of a tetrahedral unit would be expected to change the energy levels at least out to the nearest neighbors, or $r_0 = \frac{1}{4}\sqrt{3}\, a$. Using this value,

$$|m(\vec{K},\vec{K}')|^2 = \tfrac{3}{16}\pi^2\, \Omega^2(\Delta E)^2\ . \tag{A7}$$

Assuming the *random* case gives

$$|M(K,K')|^2 = 3\pi^2 C_A(1 - C_A)(\Delta E)^2/16N\ . \tag{A8}$$

Evaluating the collision integral term for the Boltzmann transport equation gives the relaxation time expression

$$\tau_{AR} = \frac{8N_A\hbar^4\epsilon^{-1/2}}{3\sqrt{2}\,\pi C_A(1-C_A)(\Delta E)^2 m^{*3/2}(kT)^{1/2}}\ . \tag{A9}$$

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