

Atomic Density Distributions of Grain Boundaries in Metals and Lifetime Spectra Characteristics of Positron Annihilation

Chen Jiqiang^(1,3), Long Qiwei^(2,3,1), Zhou Jin⁽¹⁾ and Wang Kelin⁽¹⁾

⁽¹⁾ Centre for Fundamental Physics, University of Science and Technology of China, Hefei

⁽²⁾ Institute of Metal Research, Chinese Academy of Sciences, Shenyang

⁽³⁾ International Centre for Material Physics, Chinese Academy of Sciences, Shenyang

On the basis of a simple grain boundary model, the trapped states of positrons at grain boundaries in pure Aluminum are solved and the corresponding lifetime spectra of positron annihilation calculated. The correlations between the atomic density distributions of grain boundaries and the lifetime spectra are discussed, and the existent experimental results are explained theoretically.

1. INTRODUCTION

The results of positron annihilation experiments of a series of multi-crystal materials by Mckee et al. [1] and Hidalgo and De Diego et al. [2-6] show that there is always a component of lifetime τ_2 near the positron lifetime of vacancy τ_v ; for some experimental samples apparently there is another component of lifetime τ_1 : $\tau_1 < \tau_1 < \tau_2$, where τ_1 is the lifetime of the free state of the positron. According to the explanation of this fact by Hidalgo et al., grain boundary contains two types of traps. One type corresponding to τ_2 is related to the vacancy on the grain boundary. The other one corresponding to τ_1 is related to the low density region on the grain boundary, which is denser than the electron density of vacancy.

Recently, the positron lifetime spectra of superfine multi-crystal materials have been studied in experiments by Schaefer et al. [7-9], and it was discovered that the spectra could be fitted by three

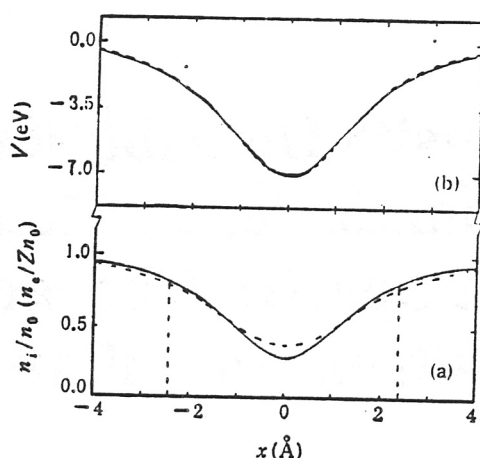


FIG.1 Grain boundaries of $\alpha = 0.7$, $\beta = 2.4$ Å. a) Distributions of atomic density (solid curve) and of electronic density (dashed curve). b) Trapping potential of positron (solid curve) can be fitted by $V = -V_0/\cosh \delta x$ (dashed curve), where $V_0 = 7.01$ eV, $1/\delta = 1.89$ Å.

components of lifetime which may be interpreted as the positron annihilations of vacancy on grain boundary, of vacancy cluster on grain boundary and at the surface of a large vacancy cluster.

The reaction of positron annihilation is considerably sensitive to grain boundary. It justifies that the lifetime spectrum of positron annihilation can be used as an experimental tool for grain boundary research. But the lifetime spectrum is rather complicated. It always has two or more lifetime components or even forms a quasi-continuous spectrum, which is quite different from the case of other defects (for example, vacancy). It is necessary for the analysis of the experimental results to clarify the correlation between the atomic configuration of grain boundary and its positron lifetime spectrum and to demonstrate the similarities or differences between the correlation with grain boundary and that with other defects. There have been no reports on these topics so far. In this paper we try to investigate this problem for Aluminum as an example because the positron annihilation research of Aluminum is quite satisfactory, its atomic and electronic structures are simple and its theoretical treatment is convenient.

2. MODEL OF GRAIN BOUNDARIES AND ITS POSITRON TRAPPED POTENTIAL

The atomic configuration of grain boundaries is so complicated that it can hardly be described in detail [10]. However, because 1) the average atomic density on grain boundaries is always lower than the density in the interior of crystalline grain and 2) the width of grain boundaries is very small compared to the size of crystalline grain, the model of two parameters (describing width and depth of grain boundaries respectively) will give basically all the characters of the atomic density distribution, such as the so-called step model [11-13], if the details of atomic arrangement are not required.

In this paper the following two parameter function is adopted to describe the atomic density distribution of the symmetric grain boundaries:

$$n_i(x) = n_0 \left(1 - \frac{\alpha}{\cosh \frac{2x}{\beta}} \right) \quad (1)$$

where n_0 is the atomic density of the interior of the grain, α and β are two adjustable positive parameters, and x is the coordinate variable with the origin fixed at the center of the transition region of the grain boundaries. The analytical behaviour of $n_i(x)$ is shown in Fig.1. From Eq.(1), we have

$$\frac{n_i(0)}{n_0} = 1 - \alpha, \quad \frac{n_i(\beta) - n_i(0)}{n_0 - n_i(0)} = 1 - \frac{1}{\text{ch} 2\frac{x}{\beta}} \approx 0.73,$$

which indicate that α and β can be used to describe respectively the atomic densities of the center of grain boundaries and the width of the transition region of grain boundaries. In Eq.(1) the atomic density of the transition region is considered as a continuous function of space location. Therefore it is more reasonable than that in the step model, and the following related iteration calculation will be simpler.

Carrying out the integration on both sides of Eq.(1) in the whole space,

$$\int n_i(x) dV = \int n_0 \left(1 - \frac{\alpha}{\text{ch} 2\frac{x}{\beta}} \right) dV \quad (2)$$

We can express the result in atomic number N ,

$$N - \epsilon = N - \frac{\pi}{2} n_0 \alpha \beta L^2 \quad (3)$$

where ϵ is the absent number of atoms due to the existence of grain boundaries, L^2 the area of grain surface and q the absent number of atoms per unit area of grain surface,

$$q = \epsilon / L^2 = \frac{\pi}{2} n_0 \alpha \beta \quad (4)$$

Now imagining that a grain boundary consists of vacancy array and considering that there are 4 atoms in one cell of Aluminium crystal, we have approximately

$$q' = 1 / \left(\frac{a^3}{4} \right)^{2/3} \quad (5)$$

where a is the crystal constant and P is defined as the ratio of q (over) q'

$$P = q / q' = \frac{\pi}{2} \left(\frac{a^3}{4} \right)^{2/3} n_0 \alpha \beta \quad (6)$$

P or $\alpha\beta$ can be used to measure the amount of open space (free volume) provided by the grain boundaries model.

The positron trapped potential of defect in metal consists of three parts [14]. Here, the Thomas-Fermi approximation method [15,16] is used to solve the static electric potential $e\varphi(r)$. The key point is to solve the Poisson equation:

$$\nabla^2 \varphi(r) = - \frac{Ze}{\epsilon_0} \left\{ n_i(r) - n_0 \left[1 + \frac{e}{\mu} \varphi(r) \right]^{1/2} \right\} \quad (7)$$

where Z is the atomic valence. Substituting Eq.(1) into Eq.(7), the resultant equation can be reduced into an equation of one variable and can be rewritten as

$$\frac{d^2}{dx^2} \Phi(x) - k^2 \Phi(x) = S(\Phi(x)) \quad (8)$$

where

$$S(\Phi(x)) = \kappa^2 \left\{ \frac{\alpha}{\text{ch} \frac{2x}{\beta}} + [1 + \Phi(x)]^{1/2} - \left[1 + \frac{3}{2} \Phi(x) \right] \right\} \quad (9)$$

here

$$\Phi(x) = \frac{e}{\mu} \varphi(x), \quad k^2 = \frac{3}{2} \kappa^2 = \frac{3}{2} \frac{Z e^2 n_0}{\mu \epsilon_0}.$$

Eq.(8) is a non-homogeneous and non-linear equation, which is difficult to solve, but the solution can be obtained according to the following equation by iteration numerical calculation which will be convergent quickly:

$$\Phi_n(x) = \int_0^\infty dx' G(x, x') S[\Phi_{n-1}(x')] \quad (10)$$

$$G(x, x') = -\frac{1}{k} [e^{-kx'} \text{ch} kx \theta(x' - x) + e^{-kx} \text{ch} kx' \theta(x - x')] \quad (11)$$

The change of the positron kinetic energy in the position of defect can be taken as [15]

$$V_K(r) = E_0 \left[\left(\frac{n_i(r)}{n_0} \right)^{2/3} - 1 \right] \quad (12)$$

where $E_0 = 4.8$ eV is the zero-point energy of the positron of the complete Aluminium crystal.

The correlation potential of electron-positron is given by the following equation:

$$V_{\text{corr}}(r) = E_{\text{corr}}(n_e(r)) - E_{\text{corr}}(Z n_0) \quad (13)$$

E_{corr} is the correlation energy of electron-positron and a function of electron density n_e . This result is taken from Ref.(17) and $n_e(r)$ can be obtained from $\varphi(r)$ by the Thomas-Fermi approximation,

$$n_e(r) = Z n_0 \left[1 + \frac{e}{\mu} \varphi(r) \right]^{3/2} \quad (14)$$

Then, we obtain the trapped potential $V(r)$ of the positron in the position of defect,

$$V(r) = e\varphi(r) + V_K(r) + V_{\text{corr}}(r) \quad (15)$$

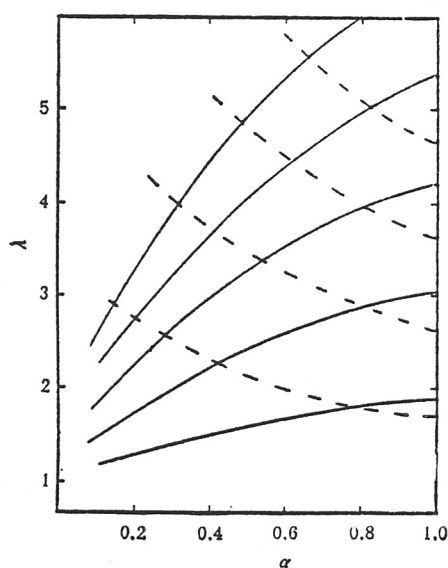


FIG.2

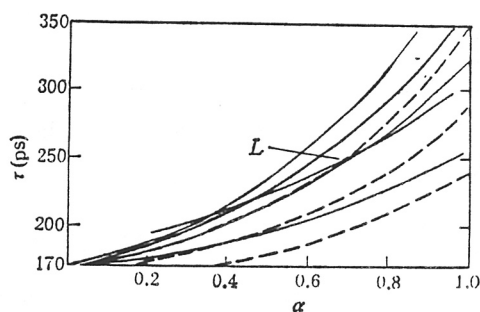


FIG.3

FIG.2 Dependence relation of α , β and λ . The solid curves from bottom to top correspond to $\beta = 1\text{\AA}, 2\text{\AA}, 3\text{\AA}, 4\text{\AA}, 5\text{\AA}$ respectively; the dashed curves are the equipotential curves of the magnitudes of open space of grain boundaries, corresponding to $P = 0.5, 1.0, 1.5, 2.0$ respectively.

FIG.3 The dependence relation of positron annihilation lifetime τ and the parameters of grain boundaries model α , β . Solid curves from top to bottom (excluding L) correspond to the positron lifetimes of the ground state of grain boundaries for $\beta = 5\text{\AA}, 3\text{\AA}, 2\text{\AA}, 1\text{\AA}$ respectively; dashed curves from top to bottom correspond to the lifetimes of their first excited states (excluding $\beta = 1\text{\AA}$). L represents the equipotential line of $P = 1$.

An example of the result of numerical calculation is given in Fig.1.

3. POSITRON TRAPPED STATE AND LIFETIME SPECTRUM OF GRAIN BOUNDARIES

In the interesting intervals of α , β values the numerical result of the positron trapped potential of grain boundaries constructed above can be fitted considerably well by an analytical function:

$$V(x) \approx -\frac{V_0}{\cosh^2 \delta x} \quad (16)$$

The depth and width of potential are described by V_0 and $1/\delta$ respectively, as shown in Fig.1(b). Thus, the wave function of positron along x direction in grain boundaries satisfies the Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - \frac{V_0}{\cosh^2 \delta x} \right) \phi_+(x) = -E_b \phi_+(x) \quad (17)$$

Its ground state solution is

$$\phi_+^{(0)}(x) = \text{ch}^{\lambda-1} \delta x \quad (18)$$

where

$$\lambda = \frac{1}{2} + \left(\frac{1}{4} + \frac{2mV_0}{\hbar^2 \delta^2} \right)^{1/2} \quad (19)$$

when $n < \lambda < n + 1$, $n = 1, 2, 3, \dots$, Eq.(17) has n solutions, and there are n trapped states correspondingly. For example, when $\lambda > 2$, there appears the second trapped state and the corresponding wave function is

$$\phi_+^{(1)}(x) = \text{sh} \lambda x \text{ch}^{\lambda-1} \delta x \quad (20)$$

From this it can be seen that the number of the trapped states is dependent on the value of λ which is in turn dependent on the values of depth V_0 and width $1/\delta$ of the trapped state, namely the values of α and β . The relations of α , β and λ are given in Fig.2.

The lifetime of each positron trapped state is obtained from the following equation:

$$\frac{1}{\tau} = \left\{ A^2 \int_{-\infty}^{\infty} dx |\phi_+(x)|^2 [2 + 134 n_e(x)] \right\} (n_s^{-1}) \quad (21)$$

where A is the normalization coefficient of the wave function of the trapped state $\phi_+(x)$. Because the inner electrons affect the process of annihilation, an effective electron density n_{eff} is used instead of the valence electron density n_e :

$$n_{\text{eff}}(x) = n_e(x) + Z\gamma n_i(x) \quad (22)$$

Here we take $\gamma = 0.096$ [14]. The relations between α , β and the lifetimes of the positron in the ground state and in the first excited state are given in Fig.3.

4. DISCUSSION ON THE RESULTS OF CALCULATION

1) No matter what values α and β may take, there are always trapped states of positron; and as long as the free volume of grain boundaries is larger than 0.7 vacancy ($P > 0.7$), there must be more than two trapped states (see Fig.2). However, in most cases, only one trapped state was given out for vacancy by theoretical calculation (even no positron trapped state of vacancy is given in some metals [18]). Recently we have pointed out the possibility of the existence of the second trapped state (excited state) [19, 20], but its bounding energy is less than 0.037 eV and its localization at vacancy is quite weak.

2) The positron lifetime of the single vacancy of Aluminum $\tau_v = 243$ ps [18]. But Fig.3 shows that as long as the free volume of the central region of the grain boundary is not less than 0.6 vacancy, the lifetime of the ground state must be larger than τ_v . For example, for grain boundaries of $\alpha = 1$, when $P = 0.616$ and 1.232, the lifetimes of the ground state are 255 ps and 323 ps respectively, and the lifetime of the excited state for $P = 1.232$ also reaches up to 238 ps.

3) For arbitrary α (or β), as long as $0.5 < \Delta P < 1.0$, there must be $\Delta\lambda > 1$, that is, for a grain boundary with any definite depth (or width), the change of the number of trapped states and therefore the change of the components of lifetime must be more than 1, provided the change of

TABLE 1 The Positron Lifetime Spectra of Several Superfine Multi-Crystal Materials and Their Corresponding Crystal Materials, Unit of Lifetime is Picosecond (ps)

Superfine Multi-crystal material					Crystal material	
	τ_1	τ_2	I_1/I_2	τ_3	τ_t	τ_v
Cu	165±3	322±4	0.57	2600±300	112	179
Pd	142±3	321±6	0.72	700±100	96	Pt:168
Fe	185±5	337±5	0.63	4100±400	106	175
Si	212±8	400±2		10900±1500	213	266
Al	240*	390*	<1	positronium annihilation	168	243

From Ref. [7], values with * are calculated in this paper.

the free volume is larger than 0.5 but not exceeding one vacancy. However, for cases from single vacancy to a cluster of eight atomic vacancies with the symmetry of a hollow sphere, there are still only two trapped states; and the bounded energy of the excited state is very low [21]. There is only one clear component of the trapped state in the lifetime spectrum.

The calculation results of this paper reflect a great difference between grain boundaries and vacancy and cluster of vacancies. Even grain boundaries with small free space can provide multi-positron excited trapped states. Therefore there are always multi-components of lifetime in the lifetime spectrum of multi-crystal materials.

In many cases one type of defect has only one clear trapped state. People are used to relating the number of lifetime components to the number of types of defects directly, and often applying the quantitative relation of positron lifetime and the magnitude of free space to the analysis of other experimental data. It seems that it is inappropriate for these concepts to be applied to multi-crystal materials.

5. INTERPRETATION FOR EXISTENT EXPERIMENTAL RESULTS

In general, multi-crystal is always an alloy and the configurations of grain boundaries are much more complicated than those in pure metal. Nevertheless, the positron annihilation effect generally depends on the magnitude and distribution of the free volume of defects, and the two-dimensional extension of atomic distribution of grain boundaries in multi-crystal materials is predominant. Thus the experimental results of multi-crystal must reflect the fundamental characters of its grain boundaries, and the common properties of the positron annihilation lifetime spectrum of alloy multi-crystal materials can be analyzed and interpreted by use of the results of this paper.

1) Some theoretical calculations and experimental observations [13] show that the half-width of grain boundaries of the pure Aluminum sample is approximately 1.5--3.5 Å, and its average atomic density of grain boundaries is not less than 0.75 n_0 . Applying the grain boundaries model of Eq.(1) to describe it, the values of α and β are roughly about 0.5 and 3 Å respectively. According to the calculation of this paper, the number n of lifetime components given by each grain boundary configuration satisfies the relation $1 \leq n \leq 3$, and the value τ of lifetime satisfies $\tau_t < \tau < \tau_v$. As there are many configurations of grain boundaries in practical multi-crystal materials, and the lifetime magnitude and the number of lifetime components are quite different for different configurations, the lifetime spectrum having so many components that it looks like a continuous one. This result is consistent with the phenomenon of a continuous spectrum observed in the experiments [1-6]. Compared to the interpretation by Hidalgo et al., the free volume of grain

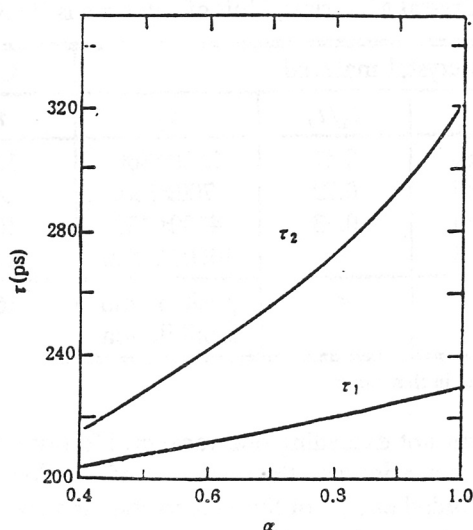


FIG.4 When the free volume concentrates toward the middle of grain boundaries (e.g. α increasing and β decreasing), the positron lifetimes of the ground state and the first excited state of grain boundaries τ_2 and τ_1 for $\alpha\beta = 1.9\text{\AA}$ get larger; especially the value of τ_2 rises quickly.

boundaries corresponding to a continuous spectrum is considerably less than vacancy, and it is supported by the theory and experiment of grain boundary structure.

2) McKee et al. gave out only a single lifetime component near τ_v for Zn-Al alloy with larger crystalline grain, whereas Hidalgo et al. gave out a continuous spectrum for Zn-Al-Mg alloy with small crystalline grain and also showed a long lifetime component $\tau_2 \sim \tau_v$. The smaller the crystalline grain, the stronger the τ_2 component. Considering the discussion of 1), it seems that the above experimental result does not come from the grain boundary itself. However, there is not a large amount of other independent defects in samples guaranteed by the technology, and even the experimental results by McKee et al. have been proved to belong to grain boundaries [22]. Thus it can be assumed that grain boundary always contains vacancies. When crystalline grains are large enough (for example, $1.5\text{ }\mu\text{m}$), and the free volume of grain boundary is small enough, the continuous part of the lifetime spectrum becomes extremely narrow, and is difficult to distinguish from free state. When grains become smaller, the vacancy concentration and free volume of grain boundaries increase, thus making the τ_2 component to become more prominent, the continuous spectrum to get wider and the upper limit of τ_2 even to approach τ_v .

3) Investigating the superfine multi-crystal materials along the line of 2), it can be assumed that the free volume of grain boundaries and vacancy concentration become larger, and the latter may be so large that the configuration of grain boundaries in sample can be considered as normal grain boundaries covered by a layer of vacancy. Using Eq.(1) to describe these special grain boundaries has underestimated the concentration of the free volume in the middle of the transition region of the grain boundaries. But still the calculated result of this paper has some enlightening significance. For $\alpha = 1$ grain boundary, when $\beta = 1.9\text{ \AA}$ (radius of Aluminium vacancy is roughly 1.6 \AA), there are two positron trapped states with lifetimes of $\tau_1 = 230\text{ ps}$ and $\tau_2 = 320\text{ ps}$ respectively. Assuming the free volume keeps its magnitude unchanged but concentrates toward the center of grain boundaries, the existence of the two trapped states remains unchanged as shown in Figs.2 and 3. However, the lifetimes will become higher, especially the positron lifetime of the ground state. It

is estimated from Fig.4 that if τ_1 reaches 240 ps τ_2 will be raised to roughly 390 ps. On the other hand, considering that there exist vacancies on normal grain boundaries, grain boundaries of superfine materials have larger cluster of vacancy which contributes to the long lifetime component τ_3 for positronium. This explains very well the experimental lifetime spectrum of superfine materials (see Table 1) from a point of view different from that of Schaefer et al.: (i) there are and only are three lifetime components; (ii) τ_1 and τ_2 come from the same defect but with different bounding energies of positron states, and their spectrum strengths have a ratio of $I_1/I_2 < 1$; (iii) the differences between τ_1 , τ_2 and τ_3 are roughly the same for each material.

6. CONCLUSION

The conclusions of this paper are: the grain boundaries tend to provide many trapped states with different bounding energies of positrons. Thus the basic character of the life-time spectrum of positron annihilation of multi-crystal materials is that there are many lifetime components. From this, the following inferences can be drawn: 1) the lifetime spectrum of multi-crystal materials, which is determined by the theory of grain boundaries structure and the parameters of grain boundary structure given by experiments, has a quasi-continuous value between τ_1 and τ_3 ; 2) the grain boundary contains vacancy and the smaller the crystalline grain, the larger the free volume of grain boundaries and the concentration of vacancy at grain boundaries and 3) the model in which the normal grain boundary is covered by a layer of vacancies and embellished by clusters of vacancies with large size can be used to describe the grain boundary micro-structure of superfine materials.

REFERENCES

- [1] B. T. A. Mckee, G. J. C. Carpenter, J. F. Watters and R. J. Schultz, *Philos. Mag.* A41(1980)65.
- [2] C. Hidalgo, N. de Diego and M. A. Ochando, *Phys. Stat. Sol. (a)*, 83(1984)K93.
- [3] C. Hidalgo and N. de Diego, *Phys. Stat. Sol. (a)*, 80(1983)K145.
- [4] C. Hidalgo, N. de Diego and M. A. Ochando, *Solid St. Commun.* 49(1984)611.
- [5] C. Hidalgo, N. de Diego and F. Plazaola, *Phys. Rev.* B31(1985)6941.
- [6] N. de Diego and C. Hidalgo, *Philos. Mag.* A53(1986)123.
- [7] H.-E. Schaefer, R. Wurschum, R. Birringer and H. Gleiter, Invited talk at International Conference on Energy Pulse and Particles Beam Modification of Materials, Dresden, (1987), To be published in *Physics Research*, Akademik-Verlag, Berlin.
- [8] H.-E. Schaefer, R. Wurschum, *Phys. Lett.* A119(1987)370.
- [9] R. Wurschum, M. Scheytt and H.-E. Schaefer, *Phys. Stat. Sol. (a)*, 102(1987)119.
- [10] G. A. Chadwick and D. A. Smith (editors), *Grain boundary structure and properties*, Academic Press, (1976).
- [11] J. H. Rose, John Ferrante and John R. Smith, *Phys. Rev. Lett.* 47(1981)675.
- [12] John Ferrante and John R. Smith, *Phys. Rev.* B19(1979)3911.
- [13] John R. Smith and John Ferrante, *Phys. Rev.* B19(1986)2238.
- [14] P. Hautajarvi, J. Heinio, M. Manninen and R. Nieminen, *Philos. Mag.*, 35(1977)973.
- [15] J. Arponen, P. Hautajarvi, R. Nieminen and E. Pajanne, *J. Phys. F: Metal Phys.* 2(1973)2092.
- [16] Chen Jiqiang, Long Qiwei and Wang Kelin, *Chinese Science Bulletin* (in Chinese), 32(1987)661.
- [17] P. Bhattacharyya and K. S. Singwi, *Phys. Lett.* A41(1972)457.
- [18] M. Manninen, R. Nieminen, P. Hautajarvi and J. Arponen, *Phys. Rev.* B12, 10(1975)4012.
- [19] J. Q. Shen, C. W. Lung, Preprint of ICTP, IC/88/298.

- [20] J. Q. Shen, C. W. Lung and K. L. Wang, Proceedings of International Workshop on Physics of Materials, (1988)127.
- [21] P. Jean, M. J. Ponnambalam, M. Manninen, *Phys. Rev. B* **24**, 5(1981)2884.
- [22] C. Hidalgo and N. de Diego, *Apply. Phys. A* **27**(1982)149.