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A comparative study of the $\Sigma = 5$ and 13 [001] twist boundaries in Cu_3Au

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Abstract. The $\Sigma = 5$ and 13 [001] twist boundaries in Cu_3Au are studied using the constant-temperature, pressure and chemical potential difference Monte Carlo method. An N -body potential and bulk-like boundary conditions are utilized. The properties studied include the stoichiometry profile, the structure factor and the average strain of the atoms along [001]. The two boundaries exhibit similar behaviour at different temperatures below the order–disorder transition. The average strain at the boundary is about 7% and diminishes rapidly, within three atomic layers. No noticeable segregation effects are observed, only a tendency of Au atoms to be depleted from the $\Sigma = 13$ boundary. Around the boundaries we find a region with lower order than the rest of the material. This region broadens as the transition temperature is approached, thus establishing the presence of wetting.

1. Introduction

The Cu–Au system is a model system for the intermetallics. It was the first system in which the ordering effect was observed [1]. Many of its properties have been extensively studied but there is renewed interest at present because new experimental results throw light onto the microscopic origin of many of its properties and because of the similarity of Cu_3Au to the load-bearing intermetallics [2]. Recent transmission electron microscopy studies have shown that wetting phenomena occur for the APBs (antiphase boundaries) and CTBs (coherent twin boundaries) [3, 4, 5]. This is very important because the internal boundaries in a material determine many of its mechanical and other properties. Currently, much interest is shown in studying the internal boundaries [6, 7, 8]. Alloy systems and intermetallics can exhibit additional effects at the internal boundaries, like segregation [9, 10].

Advances in the *ab initio* methods have made it possible to study simple boundaries in pure metals, ordered intermetallics [11] and semiconductors [12]. Despite this, the study of the boundaries in many interesting systems like intermetallics at temperatures not equal to zero necessitate the use of simpler but still realistic methods. A lot of progress has been achieved recently by using numerical statistical methods and one of the many N -body potentials to study the interfaces of the noble metals and alloys in the dilute limit [13, 14].

The order–disorder transition of the reversibly ordered intermetallic Cu_3Au was studied long ago using pair potentials extending to the second-nearest neighbours and the Monte Carlo method [15, 16]. Recently, the above work was extended by utilizing an N -body potential [17, 18, 19, 20]. Using the constant-pressure and temperature Monte Carlo method it was shown that a good description of the order–disorder transition can be obtained [18, 19, 20]. The empirical input consisted of the static properties of FCC Cu, Au and ordered Cu_3Au . All the qualitative and quantitative aspects of the order–disorder transition

agreed with the experimental findings, with the exception of the transition temperature which was found to be 25% lower than the experimental one. Because all the properties, except the transition temperature, are in agreement with experiment it was suggested that T/T_c was chosen as the control parameter.

It is the purpose of the present investigation to study two simple boundaries in Cu_3Au , to compare their effect on the order-disorder transition and to search for the presence of segregation and wetting. More specifically we investigate the $\Sigma = 5$ and 13 [001] twist boundaries. These boundaries can be obtained by rotating two semiinfinite crystals, relative to each other, around [001] with angles equal to 36.87° and 22.62° respectively. The rotation angles are special in the sense that the resulting structures have a two-dimensional periodicity along the boundary plane, with a unit cell which is a multiple of the corresponding bulk cell by the value of Σ . The physical difference between the above boundaries lies in the different geometrical arrangement of the atoms, which leads to a different periodicity along the boundary plane and a different strain field.

The method we use is the tight-binding method in the second-moment approximation [21] in conjunction with the constant-temperature, pressure and chemical potential difference Monte Carlo method [22]. From previous studies on similar materials and bulk Cu_3Au it is expected that the present model will produce a reasonably realistic description of the effect of the internal boundaries on the order-disorder transition.

In the following section we will describe the method of calculation. The results for, and the discussion on, the stoichiometry, order parameter, strains and potential energy will be given in sections 3 and 4, respectively. In section 5 we will present our conclusions.

2. Theory and method

It is well known that pair potentials are inadequate to describe the metallic bonding. The inclusion of three-body or higher terms is very complicated and can be done in many ways. One way is the tight-binding method in the second-moment approximation. The idea is to consider the potential energy as composed of two terms, one repulsive and one binding. The repulsive term is treated as a sum of pairwise terms of the Born-Mayer type, and the binding term is produced from a simplified electronic structure model. This potential has contributions from different many-body terms. The specific form we are to use is as follows:

$$V = \sum_{\alpha} \sum_{i_{\alpha}=1}^{N_{\alpha}} \left[\sum_{\beta} \sum_{j_{\beta}=1, j_{\beta} \neq i_{\alpha}}^{N_{\beta}} A_{\alpha\beta} e^{-p_{\alpha\beta} \{r^{\alpha\beta}/d_{\alpha\beta}-1\}} - \left(\sum_{\beta} \sum_{j_{\beta}=1, j_{\beta} \neq i_{\alpha}}^{N_{\beta}} \xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta} \{r^{\alpha\beta}/d_{\alpha\beta}-1\}} \right)^{1/2} \right].$$

In the above equation α and β denote either Cu or Au, A , p , q , ξ are the potential parameters of the respective interaction terms, d is the nearest-neighbour distance of the respective material and i_{α} are the sites occupied by atoms of type α .

The square root in the binding term is related to the second moment of the density of the electronic states. Due to the approximations made one can note that the potential is not the most appropriate for cases with a strong contribution of ionic bonding or Fermi surface effects. Bonding in noble metals is within the applicability of the model [21, 23].

Computer time considerations make it necessary to use finite simulation cells. To imitate the infinite solid we have to use some kind of boundary condition. The finite range of the present potential enables us to use the so-called bulk-like boundary conditions [24]. A

special feature of these boundary conditions is that it is easy to implement the macroscopic degrees of freedom of the two crystallites which form the boundary. In addition, there is only one boundary per simulation cell.

There are two aspects which determine the size of the simulation cell. The first is the periodicity parallel to the interface; for the present case it is defined by the appropriate coincidence site lattice. The second is the extent of the perturbation induced by the interface, which is known to be $\sim 10 \text{ \AA}$ [12]. On the other hand disordering and segregation effects necessitate the simulation cell to be as large as possible. By taking into account the above constraints and using experience from the study of the order-disorder transition in bulk Cu_3Au , we have chosen the following orthogonal simulation cells: for the $\Sigma = 5a\sqrt{10} \times \sqrt{10} \times 18$ cell (in units of the lattice constant), while for the $\Sigma = 13a\sqrt{13} \times \sqrt{13} \times 18$ cell. There are 18 atomic planes on each side of the boundary.

The accuracy of the Monte Carlo results depends heavily on the number of configurations sampled. In the present work we follow the procedure used for the study of the bulk order-disorder transition [18, 19, 20]. A Monte Carlo step comprises a number of attempts to move and mute atoms chosen at random and one attempt to change the volume of the simulation box. The number of attempts to move and mute is set equal to the number of atoms in the simulation cell. We use 400 Monte Carlo steps to thermalize the system and then sample the interesting quantities for other 400 steps. The averages of these measurements represent one run. Different runs are performed using different sequences of random numbers. Each quantity presented is the average of 32 runs. It should be noted that during each run the portion of the simulation cell which represents the bulk boundary conditions is different and always in equilibrium at the given external conditions.

In order to exploit the geometry induced by the presence of the boundary, we will define various macroscopic properties for each atomic layer parallel to the interface. More specifically, these properties will be averages over the atoms on a given atomic plane. It is obvious that as long as the perturbation of the boundary is localized these properties will assume their respective bulk values away from the boundary.

In many instances ordering can be described as a modulation of the stoichiometry along some lattice direction. For ordered Cu_3Au and perpendicular to the interface there is an alternation of pure Cu and mixed Cu-Au planes. Therefore the stoichiometry should alternate between unity and one-half. On the other hand, the disordered state corresponds within fluctuations to a constant value, namely the average one. Thus, the stoichiometry is an indicator of the ordering in the system. In addition, the stoichiometry profile will show whether there are any segregation effects at the boundary. All the above are possible because we use the chemical potential difference to control the stoichiometry of the simulation cell. The values for the chemical potential difference were taken from the work on the bulk order-disorder transition [18, 19, 20].

The scattering of suitable radiation or particles from an intermetallic is determined by the appropriate structure factor. Scattering in given directions can be used to estimate the ordering present in the intermetallic. Accordingly, we choose the following structure factor to monitor the ordering:

$$S(\mathbf{k}, l) = \frac{1}{N_l} \sum_{j=1}^{N_l} F_{\alpha_j} e^{i\mathbf{k} \cdot \mathbf{r}_j}$$

where l is the index of the plane, α_j is the type of atom occupying site j , N_l is the number of atoms on plane l and F_{α_j} is the structure factor of the atom residing on site j . The wavevector \mathbf{k} is set equal to $(2\pi/a)(2,1,1)$, $F_{\text{Cu}} = 2$ and $F_{\text{Au}} = 1$. In the case of a

simulation cell with a boundary, an appropriately rotated wavevector for each crystallite was used.

The above structure factor is proportional to the order parameter used in the Ising model study of the surface ordering of Cu_3Au [24]. It is very easy to find the values of the above structure factor for the different limiting cases. It is zero for the pure Cu planes, unity for the ordered mixed Cu–Au planes and minus one for the ordered mixed Cu–Au shifted by $(a/2)(1, 1, 0)$. Because the above property is defined for each layer it is highly possible to take positive as well as negative values. The order parameter, on the other hand, is desired to take positive values between zero and one. Therefore an appropriate choice for the order parameter is $|S(\mathbf{k}, l)|^2$. It should be noted that because of the square, the order parameter for the disordered planes will be proportional to the fluctuations of the structure factor. These fluctuations turn out to be small and thus the above order parameter can be useful. A similar order parameter was used for the study of the effect of the surfaces and internal boundaries to the melting of Si [25].

The strains produced by the presence of the boundary can be analysed in many ways. One way is to analyse them with respect to the average position of the atoms on an atomic plane in the direction perpendicular to the boundary. Due to symmetry these strains are zero for the bulk Cu_3Au . In this context the lattice relaxes in part by moving whole atomic planes and in part by moving the atoms relative to the planes. We can expect that the atomic planes adjacent to the boundary will move away from the boundary, because some atoms come close together when the two crystallites are rotated to produce the boundary. It is interesting to find out how localized this plane-averaged strain is.

3. Results and discussion

3.1. Stoichiometry, $|S|^2$, strain

The main theme of the present paper is the effect of the different geometry of two [001] twist boundaries on the ordering of the Cu–Au system. In figure 1 the stoichiometry profile for a direction perpendicular to the interface is presented at $T/T_c = 0.8$. We observe that away from the boundary the values alternate between values close to one-half and unity in both cases. Departures from the previous pattern occur only for three layers on both sides of the boundary, i.e. the stoichiometry tends to the average value. This tendency is stronger for the $\Sigma = 5$. The above shows that some Au atoms occupy the previously pure Cu planes and more Cu atoms occupy the previously mixed Cu–Au planes, indicating the presence of disorder. There is no noticeable segregation to the boundary.

In figure 2 we present the results for $T/T_c = 0.9$. One can observe that the stoichiometry deviates markedly from the perfectly ordered profile. Very far from the boundary the stoichiometry compared to that for $T/T_c = 0.8$ shows a parallel shift, while for about ten atomic layers on each side of the boundary it shows a strong layer-by-layer variation. At this temperature there is no noticeable difference between the two boundaries. The atomic layers adjacent to the boundary have stoichiometry values very close to the average stoichiometry. Also the disordered layer has increased in thickness and no segregation effects occur. For both temperatures studied here we find that the stoichiometry profile assumes the bulk values far from the boundary and therefore this is a justification of the size of the simulation cell and the boundary conditions.

Going to the order parameter $T/T_c = 0.8$, figure 3, we notice that the region around the boundary is indeed disordered. Away from the boundary, both cases show on average similar values, which are close to the bulk values. Only within three layers on both sides

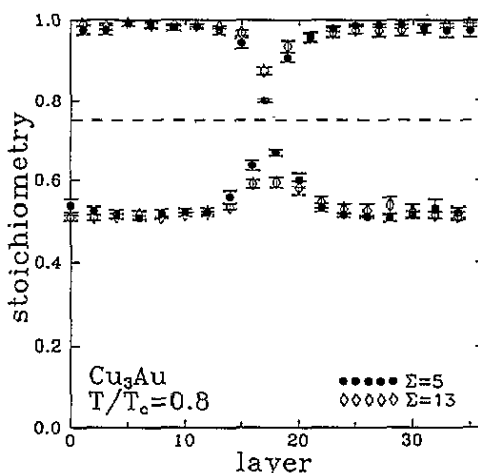


Figure 1. Stoichiometry of each plane parallel to the interface for $\Sigma = 5$ and 13 at $T/T_c = 0.8$.

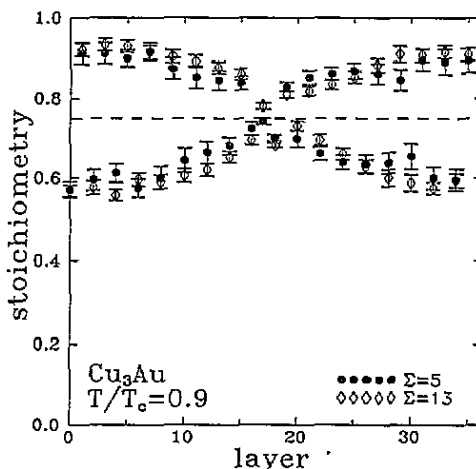


Figure 2. Same as figure 1 but at $T/T_c = 0.9$.

of the boundary does the order parameter drop to zero. Therefore, there are some atomic layers at the boundary where disordering has taken place. The drop of the order parameter is not related to the strains near the boundary, since the order parameter is not sensitive to the small displacements from the FCC structure, but to chemical disordering. Similarly to the stoichiometry profile the order parameter for $T/T_c = 0.9$, figure 4, shows a parallel shift away from the boundary and gradually tends to zero within ten layers on each side of the boundary. This picture is reminiscent of the results for the Cu_3Au [001] surface [24] and it is usually called wetting.

The average strain of each plane along [001] is presented in figures 5 and 6 for $T/T_c = 0.8$ and 0.9 respectively. The two boundaries show remarkably similar behaviour which is independent of temperature. One can notice that there are no long-range strains and that the average strain along [001] drops to zero within three layers from the boundary. The two layers adjacent to the boundary show an increase of their relative separation by as much as 7% of the lattice constant. From the above we can conclude that plane-averaged strains

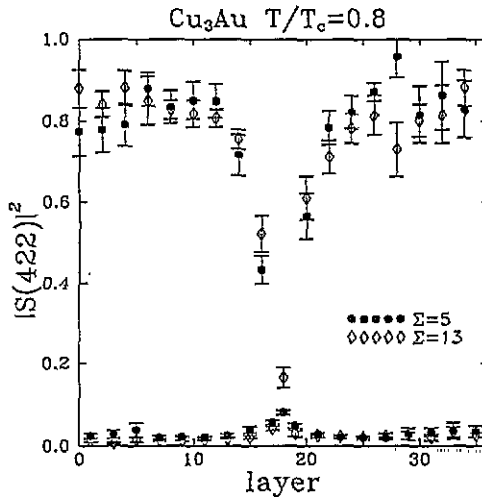


Figure 3. Order parameter of each plane parallel to the interface for $\Sigma = 5$ and 13 at $T/T_c = 0.8$.

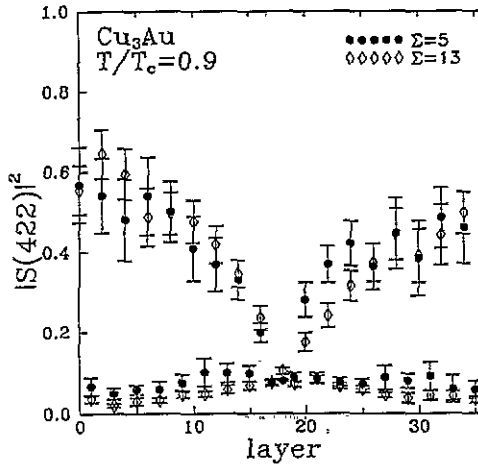


Figure 4. Same as figure 3 but at $T/T_c = 0.9$.

along [001] induced by the boundary are very localized near the boundary and independent of the disordering. The last conclusion comes from the fact that the disordered region extends to more atomic planes than the averaged strains along [001].

3.2. Energetics

In comparing the stability of different boundaries it is necessary to calculate the Gibbs free energy. This quantity is very difficult to obtain. Consequently, either one uses the readily available potential energy or utilizes one of the available approximate methods to obtain the Gibbs free energy [26]. Here we will present some results on the potential energy of some boundaries and their temperature dependence. From now on the term 'boundary energy' will be used to denote the potential energy of the boundary. The boundary energy of different boundaries and for different temperatures as a function of the rotation angle is

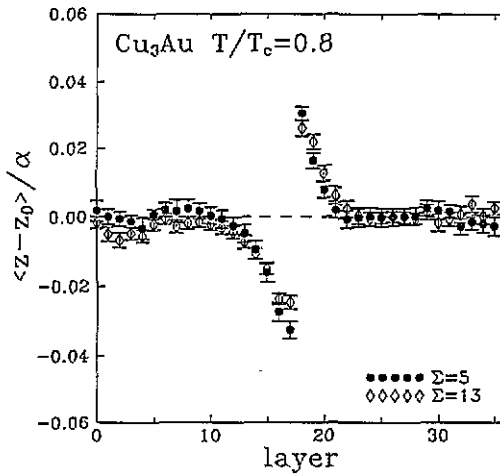


Figure 5. Plane-averaged strains along [001] for $\Sigma = 5$ and 13 at $T/T_c = 0.8$.

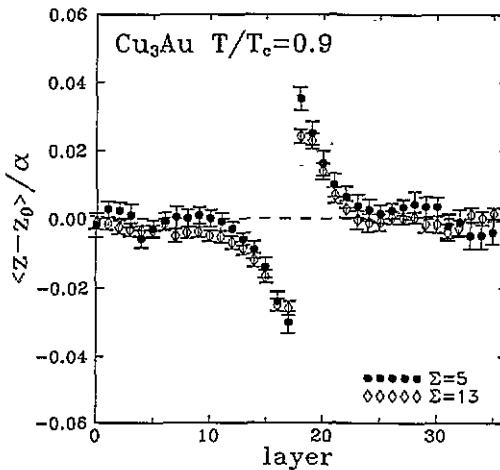


Figure 6. Same as figure 5 but at $T/T_c = 0.9$.

given in figure 7. At $T = 0$ K the boundary energy shows a smooth change with the angle and increases as the angle increases. The corresponding unrelaxed results, not displayed here, show almost no dependence on the angle and their values are higher than the relaxed results by a factor of three. Similar behaviour was found for the boundary energies of pure metals. As temperature increases the boundary energy increases similarly for $\Sigma = 5$ and 13. For $T/T_c = 0.8$ we observe a parallel shift. The results for $T/T_c = 0.9$ have larger error bars and it is difficult to find a trend.

4. Discussion

Common to all the above results is that the perturbation induced by the boundary is localized and that the two boundaries show very similar behaviour. The deviations of the order parameter and stoichiometry profile from their bulk values extend increasingly further from the boundary as one approaches the transition temperature. On the other hand

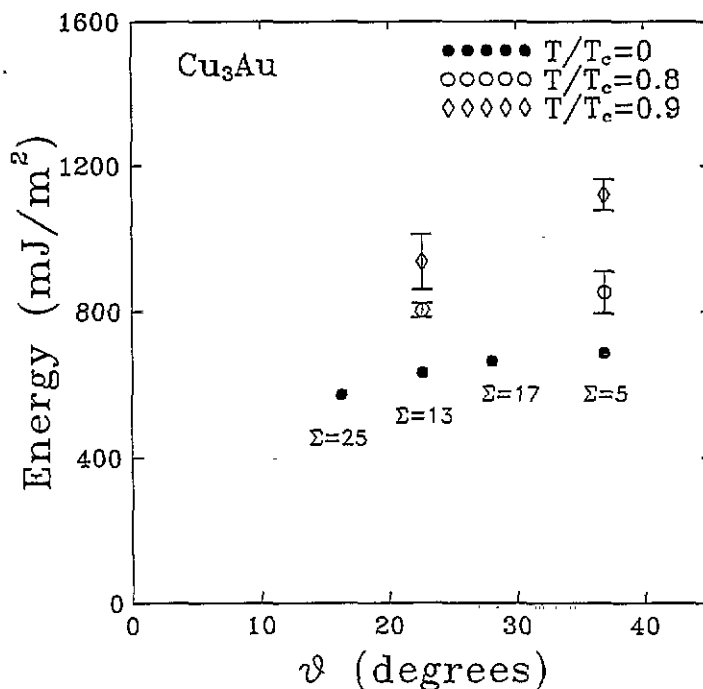


Figure 7. Boundary energy as a function of rotation angle and for different temperatures.

the localization of the plane-averaged strains along [001] is independent of temperature. To understand the above we will use the facts that the atomic radius difference between Au and Cu is almost 10% with Au being the larger atom and that the disordered state has higher potential energy than the ordered one for $T/T_c < 1$. Because of the different behaviour of the order parameter and stoichiometry from the plane-averaged strains we will discuss first the effect of the boundaries on the stoichiometry and order parameter.

Segregation is expected to occur at boundaries and surfaces because compared to the bulk the geometrical environment is different. Work on the effect of the [001] twist boundaries in Cu-Ni alloys has shown that Cu atoms which are larger than Ni atoms always segregate to the boundary [27]. The sites which are preferentially occupied by the segregated atoms are those which have tensile stresses. These are the coincidence sites and some neighbouring sites. The case of an intermetallic is a little different. Here the preferred state at temperatures lower than the transition temperature is the ordered state. As a result segregation of Au atoms to an interface in Cu_3Au is not to be favoured. On the other hand, the ordered unrelaxed boundary has coincidence sites on both planes adjacent to it, which are occupied by Cu atoms for the pure Cu plane and Cu and Au atoms for the mixed plane. It is reasonable to expect that as the temperature rises the coincidence sites will be occupied by the Au atoms. Obviously the fraction of the coincidence sites and their neighbouring sites is less than one-half. Therefore Au atoms are expected to leave the mixed plane adjacent to the boundary and start to occupy the coincidence sites of the previously pure Cu plane. There are two consequences: firstly, that stoichiometry should approach the average at the boundary and secondly, the planes adjacent to the boundary will disorder. This is exactly what the present results show. Experimentally, by studying APBs and CTBs in Cu_3Au it was observed that these boundaries wet some kelvins below the

transition temperature [3, 4]. The wetting phenomena exhibited by the present model are in this direction.

We now turn to consider the plane-averaged strains along [001] which is the only relaxation mode investigated in the present study. This mode is specifically related to the boundary. The other strains that will be produced by the boundary are expected to be similar in size to the strains induced by disordering, because of the large difference between the atomic radii of Cu and Au. It is remarkable that this relaxation vanishes quickly away from the boundary and that it shows no temperature dependence in either its magnitude or its localization. The geometrical constraint due to the presence of the boundary is expected to be independent of the temperature for temperatures well below the melting point. Also, it is important only for those atoms which are close to the boundary. How far this extends can be deduced from studies of the vacancy formation energies utilizing *ab initio* methods. This is necessary because the present result may be an artifact of the finite range of the potential used. From *ab initio* calculations it was found that the interaction between vacancies diminishes for distances which correspond to the seventh-neighbour distance [28]. Assuming that the change in the geometrical arrangement at the boundary would have similar results we can say that the strain should be localized to within some atomic layers from the boundary. This is exactly what we found, and therefore it seems that it is an intrinsic property of the boundary and not of the potential. Also it is independent of the ordering since it is only related to the local geometry of the boundary. The temperature independence of the plane-averaged strains is a consequence of the fact that the temperatures studied are well below the melting point and therefore the geometrical constraints will also be the same, independent of temperature.

5. Conclusions

The study of $\Sigma = 5$ and 13 [001] twist boundaries in Cu_3Au has shown that both boundaries affect the stoichiometry profile, order parameter and the plane-averaged strains along [001]. Although the perturbation is localized near the boundary the localization length diverges for the order parameter and the stoichiometry profile as the order-disorder transition temperature is approached. The plane-averaged strains along [001] show localization and magnitude independent of the temperature. All the above effects can be understood to arise from the large difference between the atomic sizes of Au and Cu and the geometry of the boundary. The wetting observed in both boundaries is in accordance with the experimental observation for APBs and CTBs.

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References

- [1] Kumakov N, Zencuzny S and Zasedev M 1916 *J. Inst. Met.* **15** 305
- [2] Cahn R W 1991 *MRS Bull.* May, p 18
- [3] Antonopoulos J G, Schapink F W and Tichelaar F D 1990 *Phil. Mag. Lett.* **61** 195
- [4] Tichelaar F D 1990 *PhD Thesis*
- [5] Putaux J L, Thibault J, Jacques A and George A 1993 *Mater. Sci. Forum* **126-128** 73
- [6] Luzzi D E, Yan Min, Sob M and Vitek V 1991 *Phys. Rev. Lett.* **67** 1894

- [7] Ernst F, Finnis M W, Hofmann D, Maschik T, Schonberger U, Wolf U and Methfessel M 1992 *Phys. Rev. Lett.* **69** 620
- [8] Ducastelle F, Ricolleau C and Loiseau A 1993 *Proc. Int. Workshop on Reactive-Diffusive Transformations (Aussois, 1993)*
- [9] Wang H Y, Najafabadi R, Srolovitz D J and LeSar R 1993 *Interface Sci.* **1** 31
- [10] Hu J G and Seidman D N 1990 *Phys. Rev. Lett.* **65** 1615
- [11] Paxton A T 1992 *Phys. World* **5** 35
- [12] Payne M C, Bristowe P D and Joannopoulos J D 1987 *Phys. Rev. Lett.* **58** 1348
- [13] Ackland G J, Tichy G, Vitek V and Finnis M W 1987 *Phil. Mag. A* **56** 735
- [14] Daw M S, Baskes M I and Wolf W G 1985 *Proc. Special Symp. on Modelling Environmental Effects on Crack Initiation and Propagation (Toronto)* (New York: AIME)
- [15] Cowley J M 1950 *J. Appl. Phys.* **21** 24
- [16] Sundaram V S, Farrell B, Alben R S and Robertson W D 1973 *Phys. Rev. Lett.* **31** 1136
- [17] Rey-Losada C, Hayoun M and Pontikis V 1992 *Proc. MRS Fall Meeting (Boston, 1992)*
- [18] Polatoglou H M 1993 *13th Gen. Conf. Condens. Matter Div. EPS (Regensburg, 1993)*
- [19] Polatoglou H M and Bleris G L 1994 *Solid State Commun.* **90** 425
- [20] Polatoglou H M and Bleris G L 1994 *Interface Sci.* at press
- [21] Rosato V, Guillope M and Legrand B 1989 *Phil. Mag. A* **59** 321
- [22] Bacher P, Wynblatt P and Foiles S M 1991 *Acta Metall. Mater.* **39** 2681
- [23] Loisel B, Gorse D, Pontikis V and Lapujoulade J 1989 *Surf. Sci.* **221** 365
- [24] Sundaram V S, Alben R S and Robertson W D 1974 *Surf. Sci.* **46** 653
- [25] Phillpot S R, Yip S and Wolf D 1989 *Comput. Phys. Nov./Dec.*, p 20
- [26] Sutton A P 1992 *Phil. Trans. R. Soc. A* **341** 233
- [27] Wang H Y, Najafabadi R, Srolovitz D J and LeSar R 1993 *Acta Metall. Mater.* **41** 2533
- [28] de Vita A and Gillan M J 1991 *J. Phys.: Condens. Matter* **3** 6225