

This article was downloaded by:[Tufts University]
[Tufts University]

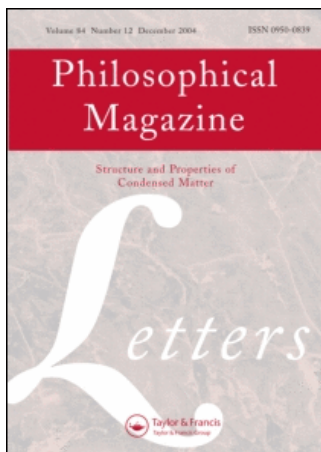
On: 24 March 2007

Access Details: [subscription number 731636168]

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Philosophical Magazine Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713695410>

Grain-boundary enthalpy of nanocrystalline selenium

K. LU; N. X. SUN

To cite this Article: K. LU and N. X. SUN , 'Grain-boundary enthalpy of nanocrystalline selenium', Philosophical Magazine Letters, 75:6, 389 - 395
xxxx:journal To link to this article: DOI: 10.1080/095008397179462

URL: <http://dx.doi.org/10.1080/095008397179462>

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article maybe used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

© Taylor and Francis 2007

Grain-boundary enthalpy of nanocrystalline selenium

By K. LU† and N. X. SUN

State Key Laboratory for Rapidly Solidified Non-equilibrium Alloys, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110015, PR China

[Received 12 November 1996 and accepted 19 February 1997]

ABSTRACT

In this letter, we report the first attempt to determine the grain-boundary enthalpy and its grain size dependence in a nanocrystalline (NC) element. Nanocrystallization of amorphous Se was achieved by isothermal annealing. Calorimetric measurements showed that the grain-boundary enthalpy decreases with a reduction in the grain size of the NC Se samples. This behaviour, which is consistent with other related measurements and computer simulation results, implies that the intrinsic nature of a grain boundary in polycrystals changes with the dimension of crystallites in the nanometre regime.

The structural characteristics and properties of the grain boundary (GB) in nanocrystalline (NC) materials have attracted increasing attention in recent years. Knowledge of the nature of GBs in NC materials is essential for understanding the structure–property relations of this new class of materials and, consequently, is important for the development of new advanced materials with novel properties. NC materials possess a large number of GBs or other interfaces that facilitate experimental investigations of the GB structure and properties.

Up to now, controversial results have been reported for the microstructure of GBs in NC materials. Early structural investigations on NC materials involving various kinds of technique (Gleiter 1989) suggest a non-equilibrium, highly disordered ‘frozen-gas-like’ GB structure that differs from those of coarse-grained polycrystalline counterparts. However, direct high-resolution electron microscopy observations combined with image simulations (Thomas *et al.* 1990), as well as precise X-ray diffraction analysis (Eastman *et al.* 1992) indicated that the atomic structures of GBs in NC materials exhibit very-low-energy configurations that are rather similar to those in conventional polycrystalline materials. These conflicting differences might originate from either different synthesis and processing conditions of the examined NC samples or use of different resolutions and interpretations of the structure analyses.

The structural characteristics of the GBs can be manifested by their average thermodynamic quantities, such as excess enthalpy, excess entropy and excess free energy. Experimentally, the average GB enthalpy in NC materials is usually determined from the heat released during a grain growth process which can be measured by differential scanning calorimetry (DSC), as reported for several metallic and oxide NC materials (Lu *et al.* 1991, Tschope *et al.* 1992, Terwilliger and Chiang 1993).

†Author for correspondence: e-mail: kelu@imr.ac.cn.

However, the accuracy of GB enthalpy values derived this way is limited by the relatively weak effect as well as by changes in microstructure (such as microstains, texture and grain size distribution) during grain growth. Sample porosities may be another major obstacle to accurate determination of the GB properties in NC materials. Nanometre-sized porosities exist in most NC materials synthesized by means of consolidation of ultrafine powders or mechanical attrition techniques (commonly utilized synthesis methods).

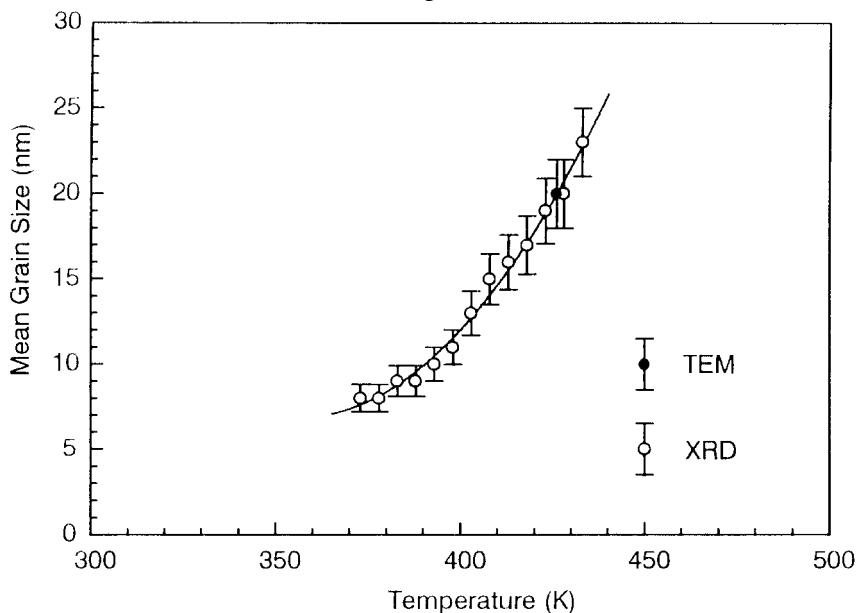
Among various synthesis methods for NC materials, the complete crystallization of amorphous solids has been shown to be one effective way of producing porosity-free NC materials (Sui *et al.* 1991, Lu 1996). Furthermore, nanocrystallization of amorphous solids provides a unique approach for determining thermodynamic properties of GBs in porous-free NC materials. In this letter, we report the first attempt to derive the average GB enthalpy and its grain size dependence in a NC element, namely Se. The basic idea of this approach is to measure the total excess enthalpy in the NC material by comparing the enthalpy changes for a nanocrystallization (amorphous-to-NC) and a conventional crystallization (amorphous-to-crystalline) process. An average GB enthalpy may be derived from the difference in the enthalpy changes.

A bulk amorphous Se bar, 10 mm in diameter and 100 mm in length, was produced by means of the melt-quenching technique. Pure polycrystalline Se (with a purity better than 99.999%) was sealed in a quartz ampoule evacuated to about 10^{-5} Torr, melted for 1 h at 673 K and then quenched into a mixture of ice and water. The as-quenched amorphous Se bar was put into a water bath at 304 K for 400 h to allow full relaxation before heat capacity and nanocrystallization measurements. X-ray diffraction (XRD) and transmission electron microscopy (TEM) observations confirmed that the whole sample was in the amorphous state.

Isothermal annealing in a flowing Ar atmosphere was performed for crystallization of the amorphous Se, which was monitored using a differential scanning calorimeter (Perkin-Elmer DSC-7). The temperature (with an accuracy of ± 0.02 K) and energy (± 0.04 mJ s $^{-1}$) scales of the DSC-7 were calibrated by means of pure In and Zn standard samples. The isothermal annealing procedure consists in rapidly heating the amorphous sample at a rate of 160 K min to the desired annealing temperature, holding for a certain period of time until the sample is fully crystallized (exothermic peak in the DSC signals completely finished) and then cooling rapidly to room temperature. Various annealing temperatures from 373 to 433 K were used to form NC Se samples with different grain sizes.

The average grain size of the fully crystallized Se was determined by means of TEM observations and quantitative XRD experiments (for details see our previous publications (Zhang *et al.* 1995a,b)). The resultant grain sizes obtained from both methods coincide very well. Figure 1 shows results (by both XRD and TEM) of the mean grain sizes in NC Se samples crystallized at different annealing temperatures. The mean grain size values from the XRD measurement were calculated in terms of the XRD (104), (210) and (003) lines. It is seen that the mean grain size increases significantly with increasing annealing temperature. When the annealing temperature is below 370 K or above 440 K, the crystallization process cannot be accurately monitored by DSC owing to the slow crystallization rate (below 370 K) or partial crystallization during the heating procedure (above 440 K).

Fig. 1



Mean grain size against the annealing temperature in the as-crystallized NC Se, determined by TEM (●) and XRD analysis (○).

According to classical thermodynamics theory, the enthalpy change for a usual crystallization process, that is a transformation from an undercooled liquid to a crystalline state can be described by

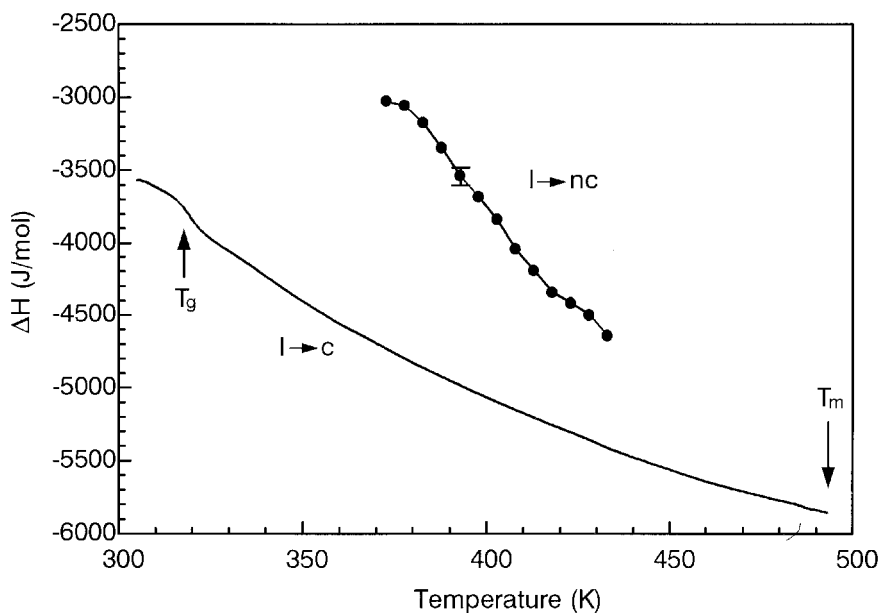
$$\Delta H^{l \rightarrow c} = \Delta H_f - \int_{T_m}^T (c_p^l - c_p^c) dT, \quad (1)$$

where ΔH_f is the enthalpy change for fusion at the melting temperature T_m , and c_p^l and c_p^c are the molar heat capacities for the liquid and the crystal respectively.

Heat capacities for the amorphous, the coarse-grained polycrystalline and the NC specimens were experimentally determined in the temperature range 225–500 K, as reported elsewhere (Sun and Lu 1996). Measurements show that the excess molar heat capacity of the undercooled liquid Se with respect to the conventional polycrystalline state, $\Delta c_p^l = c_p^l - c_p^c$, rises steadily with decreasing temperature. In the temperature range 320–493 K, the variation in Δc_p^l with T can be adequately fitted by a linear expression of the form $\Delta c_p^l = 43.6 - 0.079T$ ($\text{J mol}^{-1} \text{K}^{-1}$). Below the glass transition temperature ($T_g = 318$ K), the excess heat capacity of the amorphous Se decreases with a reduction in temperature. Based on the measured excess heat capacity of the undercooled liquid Se and the enthalpy change for fusion, $\Delta H_f = 5.87 \text{ kJ mol}^{-1}$ (Bairn *et al.* 1977), the temperature dependence of $\Delta H^{l \rightarrow c}$ can be determined, as shown in fig. 2.

The isothermal nanocrystallization process (i.e. the undercooled liquid-to-NC transformation) of the amorphous sample Se exhibits a single exothermic peak in DSC and its enthalpy change $\Delta H^{l \rightarrow nc}$ can be obtained by integrating the area under the peak. Figure 2 displays the results of the enthalpy change as a function of

Fig. 2



Temperature dependence of the enthalpy changes for the undercooled liquid-to-crystal (l→c) and the undercooled liquid-to-nanocrystalline (l→nc) transformations in Se. T_g and T_m are the glass transition temperature for the amorphous Se and melting temperature for Se respectively.

annealing temperature. The heat released during nanocrystallization of the undercooled liquid (i.e. the absolute value of $\Delta H^{l \rightarrow nc}$) increases steadily at higher annealing temperatures, from 3.03 kJ mol^{-1} (at 373 K) to 4.64 kJ mol^{-1} (at 433 K). It is seen that the temperature dependence of $\Delta H^{l \rightarrow nc}$ evidently deviates from that of $\Delta H^{l \rightarrow c}$, and the difference between the two enthalpy changes, $\Delta H^* = \Delta H^{l \rightarrow nc} - \Delta H^{l \rightarrow c}$, decreases with increasing annealing temperature. The maximum value of ΔH^* reaches 1.80 kJ mol^{-1} , which is about 30% of ΔH_f , at the lowest annealing temperature (373 K).

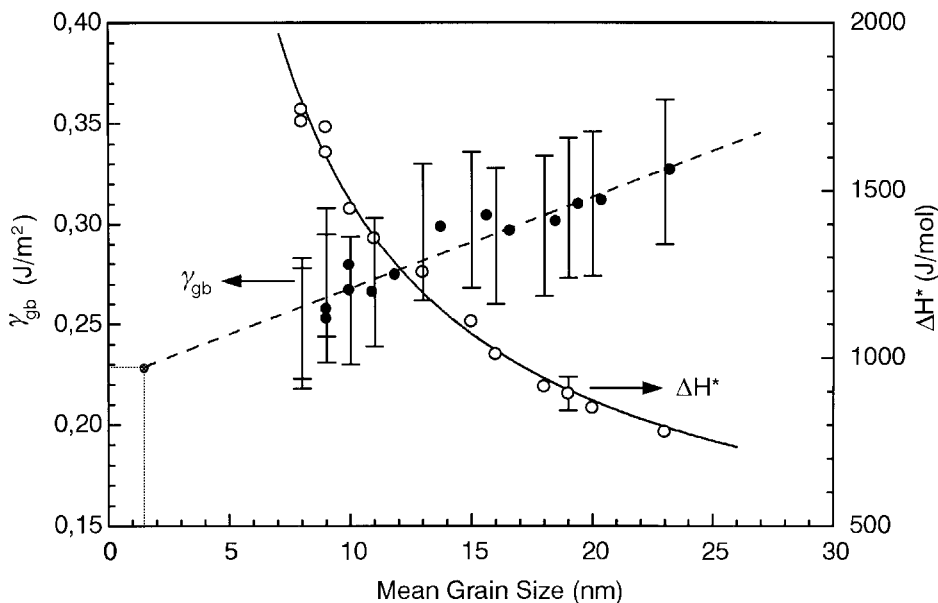
Such a significant divergence of the enthalpy changes between the two transformation processes might be reasonably attributed to the excess enthalpy stored in the NC Se sample, which increases from about 13% to 30% of ΔH_f when the mean grain size decreases from 23 to 8 nm, as shown in fig. 3. Suppose that the excess enthalpy of the NC sample is concentrated in the high density of GBs, then one can obtain the average GB enthalpy from

$$\gamma_{gb} = \frac{\Delta H^*}{A_{gb}}, \quad (2)$$

where A_{gb} is the total GB area, which is related to the mean grain size d by $A_{gb} = 2gV_m/d$, in which g is a geometrical factor depending on the grain shape and the grain size distribution (here g is taken as 1.67), and V_m is the molar volume.

Figure 3 shows the results of the average GB enthalpies for the NC Se samples with various grain sizes. The average GB enthalpies γ_{gb} obtained are rather small

Fig. 3



Variations in the excess enthalpy $\Delta H^* (= \Delta H^{l \rightarrow nc} - \Delta H^{l \rightarrow c})$ and the GB enthalpy γ_{gb} with the mean grain size in the NC Se samples.

and comparable with those of large-angle GBs in conventional polycrystals (Wagner and Chalmers 1960). From fig. 3, it is seen that the average GB enthalpy in NC Se decreases with a reduction in grain size, from about 0.33 J m^{-2} with $d = 23 \text{ nm}$ to 0.25 J m^{-2} with 8 nm . Such a significant decrease in γ_{gb} (by about 25%) indicates that the effective GB energy in NC Se with finer grains is smaller despite the fact that the total excess enthalpy ΔH^* is greater.

In the evaluation process, it is assumed that all the excess enthalpy stored in the NC sample is concentrated in the GBs and the nanometre-sized crystallites are considered to have the same lattice structure as their coarse-grained counterparts. In fact, the lattice structure of the NC grains is distorted when the grain size is reduced into the nanometre regime, as observed in several NC materials, including element Se (Sui and Lu 1994, Zhang *et al.* 1995c). It was detected that the degree lattice distortion (the lattice parameter a is increased and c is depressed) increases with a reduction in grain size in the NC Se sample. Taking this effect into account, one may obtain an even smaller GB enthalpy for NC Se samples with finer grains, because a part of the excess enthalpy will be distributed into the NC distorted crystallites. Thus the decreasing tendency of γ_{gb} with increasing grain size may be even stronger than that in fig. 3.

Measurements of the grain size dependence of GB enthalpy in NC elements are not available in the literature, and only a few related works have been reported. In a Ni-P NC alloy with two nanophases of Ni and Ni₃P, the Ni-Ni₃P interfacial enthalpy was found to decrease with reduction in grain size, from about 0.47 J m^{-2} (with a mean Ni₃P grain size of 60 nm) to 0.16 J m^{-2} (6.5 nm), with a decreasing rate $\delta\gamma_{gb}/\delta d$ of about $5.8 \times 10^6 \text{ J m}^{-3}$ (Lu *et al.* 1993). Terwilliger and

Chiang (1993) reported a similar phenomenon in a NC TiO₂ made by consolidation of ultrafine powders, that is when the grain size changes from 76 to 34 nm, the mean GB enthalpy decreases from 1.55 to 1.28 J m⁻², with a slope of about 6.4 × 10⁶ J m⁻³. The decreasing rate of $\delta\gamma_{\text{gb}}/\delta d$ in the present NC Se (5.2 × 10⁶ J m⁻³) is comparable with those reported for the above two cases. However, in the case of Ni-P and TiO₂, other possible influencing factors (such as segregation of an element on the GBs) on the GB enthalpy change could not be ruled out. By measuring the grain size dependence of the electrical resistivity in a NC element Pd consolidated from ultrafine powders, Birringer *et al.* (1995) noticed that the specific excess volume of GBs (which is directly related to the GB enthalpy) is smaller for samples with finer grains. More recently, computer simulations of a model NC material carried out by Wang *et al.* (1996) also indicated that the effective GB energy decreases with reduction in grain size. Therefore it can be concluded that the result of a decreasing GB enthalpy with reduction in grain size in NC Se consistent with the observations in the literature.

A decreasing GB enthalpy implies a denser GB structure with a lower-energy configuration when the grain size becomes smaller. For the GBs formed during crystallization of an amorphous solid, it is normally anticipated that denser GBs may be formed with annealing at higher temperatures, as the atomic diffusion will be much enhanced at elevated temperatures, and hence the atoms may have a higher mobility and accommodate themselves to the relatively lower-energy configurations during the GB formation process. However, the opposite behaviour is obtained experimentally, with a denser GB structure with a lower-energy configuration being formed at lower annealing temperatures. This implies that atomic diffusion does not play a dominant role in the GB formation process. On the other hand, a decrease in grain size in the nanometre regime would enhance the activity of grains. Any movement or rearrangement of the nanometre sized crystallites to form an interface with a low-energy configuration would be facilitated by smaller grains. This might also hold for the NC samples made by consolidation of ultrafine powders, where the GBs are formed under compression at low temperatures, as rather similar behaviours were observed for the GB energy as described above.

According to the two-state model for the NC material, Wang *et al.* (1996) obtained a very simple relationship between the effective GB energy and grain size:

$$\gamma = \gamma^{\infty} - \frac{c}{d}, \quad (3)$$

where c is a constant (of the order of 10⁻⁹ J m⁻¹), γ^{∞} is the GB energy for the infinite grain size, which is normally about 10⁻¹ J m⁻². It is clear that the effective GB energy will decrease significantly with reduction in grain size below 100 nm. This agrees with our experimental observations. In fact, such a variation in the GB structure with grain size has been successfully utilized in interpretation of some properties of NC materials, such as the abnormal Hall-Petch relationship (Lu and Sui 1993) and the intrinsic thermal stability (Lu 1993).

By extrapolating the variation in γ_{gb} with d (as a straight line) to the dimension of the short-range ordering in the amorphous solid (about 1.5 nm), one may obtain a GB enthalpy of about 0.23 J m⁻², which is equivalent to 3.80 kJ mol⁻¹ by taking the GB thickness as approximately 1 nm. This value is very close to the excess enthalpy (3.70 kJ mol⁻¹) of amorphous Se at the glass transition temperature. In other words, when the crystallite size in the NC Se becomes comparable with that of the short-range ordering, the excess enthalpy of the GB will approach that of the amorphous

solid. This coincidence implies that the enthalpy difference will vanish between the amorphous solid and the NC material with grains so small that most atoms are located on the GBs. The implication supports the computer simulation results that the NC-to-amorphous solid transformation is a reversible energy-based transition that is controlled by a critical grain size. Meanwhile, it can be anticipated that the low limit of the GB enthalpy in NC materials might be the excess enthalpy of the amorphous solid of the same composition which, to some extent, is in agreement with the conclusion from computer simulations that the GB structure (in a NC element Si) is 'amorphous like' (Wolf *et al.* 1997).

ACKNOWLEDGEMENTS

This work was financially supported by the National Science Foundation of China and the Chinese Academy of Sciences. We are grateful to Professor J. H. Perepezko, Professor Q. Jiang and Dr R. Lück for stimulating discussions.

REFERENCES

- BARIN, I., KNACKE, O., and KUBASCHEWSKI, O., 1977, *Thermochemical Properties of Inorganic Substances, Supplement* (Berlin; Springer).
- BIRNINGER, R., KRILL, C. E., and KLINGEL, M., 1995, *Phil. Mag. Lett.*, **72**, 71.
- EASTMAN, J. A., FITZSIMMONS, M. R., and THOMPSON, L. J., 1992, *Phil. Mag. B*, **66**, 667.
- GLEITER, H., 1989, *Prog. Mater. Sci.*, **33**, 223.
- LU, K., 1993, *Nanostruct. Mater.*, **2**, 643; 1996, *Mater. Sci. Engng Rep.*, **R16**, 161.
- LU, K., LÜCK, R., and PREDEL, B., 1993, *Scripta metall. mater.*, **28**, 1387.
- LU, K., and SUI, M. L., 1993, *Scripta metall. mater.*, **28**, 1465.
- LU, K., WEI, W. D., and WANG, J. T., 1991, *J. appl. Phys.*, **69**, 7345.
- SUI, M. L., and LU, K., 1994, *Mater. Sci. Engng*, **A179–180**, 541.
- SUI, M. L., LU, K., DENG, W., XIONG, L. Y., PATU, S., and HE, Y. Z., 1991, *Phys. Rev. B*, **44**, 6466.
- SUN, N. X., and LU, K., 1996, *Phys. Rev. B*, **54**, 6058.
- TERWILLIGER, C. D., and CHIANG, Y. M., 1993, *Materials Research Society Symposium Proceedings*, Vol. 286 (Pittsburgh, Pennsylvania: Materials Research Society), p. 15.
- THOMAS, G. J., SIEGEL, R. W., and EASTMAN, J. A., 1990, *Scripta metall.*, **24**, 201.
- TSCHOPE, A., BIRNINGER, R., and GLEITER, H., 1992, *J. appl. Phys.*, **71**, 5391.
- WAGNER, R. S., and CHALMERS, B., 1960, *J. appl. Phys.*, **31**, 581.
- WANG, J., WOLF, D., and GLEITER, H., 1996, *Phil. Mag. A*, **73**, 517.
- WOLF, D., *et al.* 1997, *Nanostruct. Mater.* (to be published).
- ZHANG, H. Y., HU, Z. Q., and LU, K., 1995a, *J. appl. Phys.*, **77**, 2811; 1995b, *Nanostruct. Mater.*, **5**, 41.
- ZHANG, H. Y., LU, K., and HU, Z. Q., 1995c, *J. Phys.: condens Matter*, **7**, 5327.