DOI 10.5012/bkcs.2009.30.12.3016

Hardness Prediction and First Principle Study of Re-123(Re = Y, Eu, Pr, Gd) Superconductors

Weiwei Liu,†,* Y. P. Zhou, and X. L. Feng

College of Environment and Chemical Engineering, Yanshan University, Qinhuangdao 066004, P. R. China
*†Environmental Management College of China, Qinhuangdao 066004, P. R. China. *E-mail: liuww1978@yahoo.cn*
Received June 1, 2009, Accepted October 24, 2009

The chemical bond parameters of Y-123, Eu-123, Pr-123 and Gd-123 compounds have calculated using the chemical bond theory of complex crystals. Their hardness have been predicted by the chemical bond definition of hardness. The calculated results indicate that the Ba-O and RE-O types of bond have a lower covalent character and the Cu-O types of bond have greater covalency. The hardness values increase as the unit cell volume of the rare earth superconductor structures decrease.

Key Words: Superconductor, Rare earth, Hardness

Introduction

Although some new superconductors such as MgB2 and LaOFeAs have been found recently, the Re-123 (Re: rare-earth elements) superconducting compounds receive yet much attention because of its high critical temperature. Large single-grain Re-123 superconductors can trap large magnetic fields over several tesla, which is much higher than those of conventional permanent magnets, so it may be used as quasi-permanent magnets. However, the maximum trapped field is essentially limited by the mechanical properties of bulk superconductors, since a large electromagnetic force acts on the bulks when they trap large fields. The stress produced by refrigeration also causes cracking.[1] The superconducting ceramics are generally restricted because of their poor mechanical properties. Therefore, improvement of the mechanical properties of Re-123 is a major research objective. Their practical commercial use requires substantial improvement of the mechanical properties. The researchers have also always chosen the microhardness test to investigate the mechanical behavior, because it is easier to perform and not destructive. The microhardness test is one of the convenient methods for estimating the mechanical properties of materials. The prediction of hardness also helps understanding the other mechanical properties.[2-7] The macroscopic physical properties of crystals must have a direct relationship with their constituent chemical bonds. Therefore, for a given crystal, it is reasonable to investigate its origin of hardness by starting from the point of view of the chemical bond.[8-11] Recently, a new definition of the hardness of covalent crystals has been presented.[12-15]

This paper gives a theoretical prediction of hardness values of these crystals by using the chemical bond theory of complex crystals and hardness theory. It helps to understand further the other mechanical properties.

Theory

A theory describing the chemical bond of complex crystals has been developed by Zhang *et al.*[8-11,16,17] It have been successfully applied to the material properties.[18-20] Zhang[8] has pointed out that the properties of a crystal can be described by chemical bond parameters, and any complex crystal can be decomposed into different kinds of pseudo-binary crystals. In theory, the `crystal formula` is a combination of subformulae for a chemical bond. The subformula for any kind of chemical bond A-B in the multibond crystal $A_aB_b\ldots$ can be expressed by the following formula:

$$\left[\frac{N(\mathrm{B}-\mathrm{A})a}{N_{CA}}\right]\mathrm{A}\left[\frac{N(\mathrm{A}-\mathrm{B})b}{N_{CB}}\right]\mathrm{B} \qquad (1)$$

where A, B, ... represent different elements or different sites of the same element in the crystal formula. a, b, ... represent numbers of the corresponding element. N(B-A) represents the number of B ions in the A ion coordination group, and N_{CA} represents the nearest coordination number of an A ion. After decomposing the complex crystal into different kinds of pseudobinary crystals which form an isotropic system, and then introducing an effective charge to the valence electron by the Pauling bond valence method. P-V-L theory[16,17] can be used directly to calculate the chemical bond parameters in the complex crystal compound.

The average energy gap E_g^μ for every μ bond can be separated into homopolar E_h^μ and heteropolar C^μ parts[8]

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \qquad (2)$$

The ionicity f_i^μ and covalency f_c^μ of any type of chemical bond is defined as follows[8]

$$f_i^\mu = (C^\mu)^2/(E_g^\mu)^2 \qquad (3)$$

$$f_c^\mu = (E_h^\mu)^2/(E_g^\mu)^2 \qquad (4)$$

where

$$E_h^\mu = 39.74/(d^\mu)^{2.48}\ (\mathrm{eV}) \qquad (5)$$

where d^{μ} is the bond length. For any binary crystal AB_n type compounds the heteropolar C^{μ}part is defined as[8]

$$C^{\mu} = 14.4b^{\mu}[(Z_A^{\mu})^* + \Delta Z_A^{\mu} - n(Z_B^{\mu})^*]e^{-k_s^{\mu}r_0^{\mu}} / r_0^{\mu} \text{ (eV)} \quad (6)$$

$$r_0^{\mu} = d^{\mu} / 2 \quad (7)$$

$$k_s^{\mu} = (4k_F^{\mu} / \pi a_B)^{1/2} \quad (8)$$

$$(k_F^{\mu})^3 = 3\pi^2 N_e^{\mu} \quad (9)$$

where $(Z_A^{\mu})^*$ is the number of effective valence electrons of A ion. ΔZ_A^{μ} is correction factors from d electron effects such as the crystal field stable energy and Janh-Teller effect.[9] n is the ratio of element B to element A in the subformula. k_s^{μ} is Thomas-Fermi screening wave number of valence electron in binary crystal composed of only one type of bond μ. a_B is the Bohr radius, k_F^{μ} is Fermi wave number of valence electron in binary crystal composed of only one type of bond μ. N_e^{μ} is the numbers of valence electrons of type μ bond per cubic angstroms, b^{μ} is proportional to the square of the average coordination number N_c^{μ}

$$b^{\mu} = \beta(N_c^{\mu})^2$$
$$N_c^{\mu} = N_{CA}^{\mu} /(1+n) + nN_{CB}^{\mu} /(1+n) \quad (10)$$

where b^{μ} depends on a given crystal structure.

The hardness of psuedobinary compound composed of μ-type bond can be calculated as follow:[12-15]

$$H_v(\text{GPa}) = 556\frac{N_a e^{-1.191f_i}}{d^{2.5}} = 350\frac{(N_e)^{2/3} e^{-1.191f_i}}{d^{2.5}} \quad (11)$$

where N_a is the number of bond per unit area. N_e^{μ} is expressed as follows

$$N_e^{\mu} = (n_e^{\mu})^* / v_b^{\mu} \quad (12)$$

$$(n_e^{\mu})^* = [(Z_A^{\mu})^* / N_{CA}^{\mu} + (Z_B^{\mu})^* / N_{CB}^{\mu}] \quad (13)$$

$$v_b^{\mu} = (d^{\mu})^3 / \sum_{\nu}[(d^{\nu})^3 N_b^{\nu}] \quad (14)$$

where $(n_e^{\mu})^*$ is the number of effective valence electrons per μ bond. v_b^{μ} is the bond volume.

The hardness of multicomponent compound systems can be expressed as an average of hardness of all binary systems in the solid. Hardness surely involves the cooperative softening of many bonds. When there are differences in the strength among different types of bonds, the trend of breaking the bonds will start from a softer one. Therefore, the hardness H_v of complex crystals should be calculated by a geometric average of all bonds as follow:[12]

$$H_v = [\prod_{\mu}^{\mu}(H_v^{\mu})^{n^{\mu}}]^{1/\sum n^{\mu}} \quad (15)$$

where n^{μ} is the number of bond of type μ composing the actual complex crystal.

Results and Discussion

According to theory,[8] Re-123 can be decomposed into the sum of pseudobinary crystals as follows:

$$\begin{aligned} REBa_2Cu_3O_7 &= REBa_2Cu(1)Cu(2)_2O(1)_2O(2)_2O(3)_2O(4) \\ &= 4/5BaO(1)_{5/3} + 2/5BaO(2)_{5/3} \\ &\quad + 2/5BaO(3)_{5/3} + 2/5BaO(4)_{5/3} \\ &\quad + 1/2REO(2)_{4/3} + 1/2REO(3)_{4/3} \\ &\quad + 1/2Cu(1)O(4)_{2/3} + 1/2Cu(1)O(1)_{2/3} \\ &\quad + 2/5Cu(2)O(1)_{5/6} + 4/5Cu(2)O(2)_{5/6} \\ &\quad + 4/5Cu(2)O(3)_{5/6} \end{aligned}$$

The calculated chemical bond covalency of each type of constituent chemical bond and the hardness of pseudobinary crystals composed of corresponding constituent bond are listed in Table 1. Table 2, Table 3, Table 4 for Y-123. Eu-123. Pr-123 and Gd-123, respectively. From Table 1, Table 2, Table 3. Table

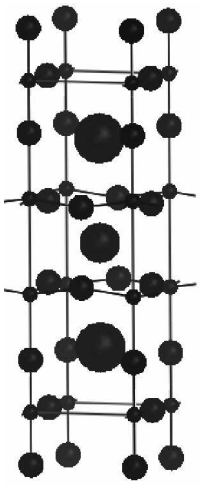

Figure 1. Structure of Re-123.

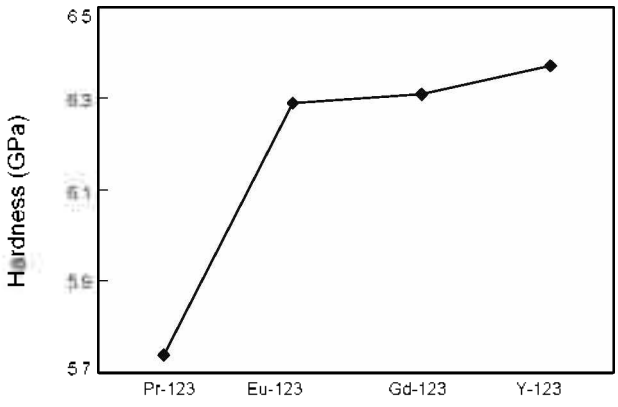

Figure 2. Tendencies of hardness (H_v) changing along the rare earth sequence.

Table 1. Chemical bond parameters and calculated hardness of Y-123 crystals, where d^{μ} is bond length, f_c^{μ} is covalency, v_b^{μ} is bond volume, N_e^{μ} is valence electron density of type μ bond, H_v^{μ} is hardness of type μ bond, H_{av} and $H_{v\,expt}$ are calculated average value and experimental microhardness, respectively.

bond	d^{μ}(Å)	f_c^{μ}	v_b^{μ}(Å^3)	N_e^{μ}	H_v^{μ}	H_{av} (GPa)	$H_{v\,expt}$ (GPa)[21]
BaO(1)	2.741	0.037	5.194	0.128	2.32	6.37	6.0
BaO(2)	2.982	0.024	6.687	0.15	2.06		
BaO(3)	2.959	0.037	6.534	0.153	2.16		
BaO(4)	2.876	0.036	5.999	0.111	1.87		
YO(2)	2.409	0.036	3.525	0.426	7.10		
YO(3)	2.385	0.035	3.421	0.438	7.41		
Cu(1)O(4)	1.942	0.462	1.587	1.68	50.25		
Cu(1)O(1)	1.846	0.35	1.847	1.805	52.31		
Cu(2)O(1)	2.289	0.221	3.061	0.653	13.36		
Cu(2)O(2)	1.929	0.29	1.811	0.828	25.97		
Cu(2)O(3)	1.961	0.289	1.902	0.798	24.30		

Table 2. Chemical bond parameters and calculated hardness of of Eu-123 crystals, where d^{μ} is bond length, f_c^{μ} is covalency, v_b^{μ} is bond volume, N_e^{μ} is valence electron density of type μ bond, H_v^{μ} is hardness of type μ bond, H_{av} and $H_{v\,expt}$ are calculated average value and experimental microhardness, respectively.

bond	d^{μ}(Å)	f_c^{μ}	v_b^{μ}(Å^3)	N_e^{μ}	H_v^{μ}	H_{av}(GPa)
BaO(1)	2.749	0.041	5.260	0.127	2.30	6.29
BaO(2)	2.898	0.026	6.163	0.162	2.33	
BaO(3)	2.975	0.025	6.667	0.15	2.07	
BaO(4)	2.866	0.038	5.961	0.112	1.90	
EuO(2)	2.509	0.037	3.999	0.375	5.91	
EuO(3)	2.406	0.037	3.527	0.425	7.12	
Cu(1)O(4)	1.949	0.476	1.875	1.422	45.31	
Cu(1)O(1)	1.85	0.352	1.603	2.079	57.31	
Cu(2)O(1)	2.259	0.222	2.919	0.685	14.27	
Cu(2)O(2)	1.926	0.294	1.809	0.829	26.22	
Cu(2)O(3)	1.971	0.297	1.939	0.774	23.74	

Table 3. Chemical bond parameters and calculated hardness of of Pr-123 crystals, where d^{μ} is bond length, f_c^{μ} is covalency, v_b^{μ} is bond volume, N_e^{μ} is valence electron density of type μ bond, H_v^{μ} is hardness of type μ bond, H_{av} and $H_{v\,expt}$ are calculated average value and experimental microhardness, respectively.

bond	d^{μ}(Å)	f_c^{μ}	v_b^{μ}(Å^3)	N_e^{μ}	H_v^{μ}	H_{av}(GPa)
BaO(1)	2.776	0.039	5.417	0.123	2.19	5.74
BaO(2)	3.006	0.025	6.878	0.146	1.98	
BaO(3)	2.943	0.025	6.454	0.155	2.17	
BaO(4)	2.893	0.038	6.131	0.109	1.82	
PrO(2)	2.456	0.037	3.751	0.4	6.50	
PrO(3)	2.476	0.037	3.843	0.391	6.27	
Cu(1)O(4)	1.965	0.461	1.921	1.617	47.52	
Cu(1)O(1)	2.893	0.368	6.131	1.74	17.12	
Cu(2)O(1)	2.255	0.222	2.903	0.689	14.39	
Cu(2)O(2)	1.964	0.296	1.918	0.782	24.08	
Cu(2)O(3)	1.979	0.298	1.962	0.765	23.35	

Table 4. Chemical bond parameters and calculated hardness of of Gd-123 crystals, where d^{μ} is bond length, f_c^{μ} is covalency, v_b^{μ} is bond volume, N_e^{μ} is valence electron density of type μ bond, H_v^{μ} is hardness of type μ bond, H_{av} and $H_{v\,expt}$ are calculated average value and experimental microhardness, respectively.

bond	d^{μ}(Å)	f_c^{μ}	v_b^{μ}(Å^3)	N_e^{μ}	H_v^{μ}	H_{av}(GPa)
BaO(1)	2.744	0.039	5.231	0.127	2.30	6.31
BaO(2)	2.92	0.025	6.304	0.158	2.25	
BaO(3)	2.936	0.025	6.408	0.156	2.20	
BaO(4)	2.865	0.038	5.954	0.112	1.90	
GdO(2)	2.485	0.037	3.885	0.385	6.15	
GdO(3)	2.433	0.037	3.647	0.41	6.76	
Cu(1)O(4)	1.947	0.475	1.869	1.422	45.38	
Cu(1)O(1)	1.884	0.357	1.693	1.974	53.23	
Cu(2)O(1)	2.211	0.22	2.737	0.729	15.65	
Cu(2)O(2)	1.929	0.295	1.817	0.823	26.02	
Cu(2)O(3)	1.964	0.296	1.918	0.78	24.04	

4, we find that the Ba-O and RE-O types of bond have a lower covalent character and the Cu-O types of bond have more covalent character. The can be understood by the electronegativity. Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used. Ba, Re and Cu are assigned the value of 0.9, ~1.0 and 1.9, respectively. The higher the element electronegativity, the greater the ionicity of its oxide. The calculated hardness of Y-123 is in good agreement with the available experimental one. Fig. 2 shows the tendencies of hardness (Hv) changing along the rare earth elements sequence. It is obvious that the tendencies are monotone increasing, that is to say, the hardness values increase as the unit cell volume of the rare earth superconductor decrease. The tendencies also is relative to the ionic radius of rare earths ions. The ionic radius of Pr, Eu, Gd and Y are 1.013, 0.947, 0.938 and 0.9 Å, respectively. The larger the ionic radius of rare earths ions, the lower the hardness of superconductors. According theory,[12] bond density or electronic density, bond length and degree of covalent bonding are three determinative factors for the hardness of a crystal. From Table 1-4 it can be seen that the larger the ionicity, the smaller the hardness of the pseudobinary crystals. BaO bonds are almost purely ionic, thus the pseudobinary crystals BaO(1), BaO(2), BaO(3), and BaO(4) have the smallest hardness values. In contrast, Cu(1)O(4) and Cu(1)O(1) have the smaller ionicity, thus their hardness are higher. The ionicity of ReO bonds are close to that of BaO bonds, the smaller bond length result in a higher hardness than one of the BaO bonds. Furthermore, the effect of the bond density or electronic density on hardness is significant. They is a direct proportional relation. The data of Eu-123 are plotted in Fig. 3.

In order to understand further its properties, the calculation of the total energy on the compound was carried out in the framework of density functional theory (DFT) with the Material

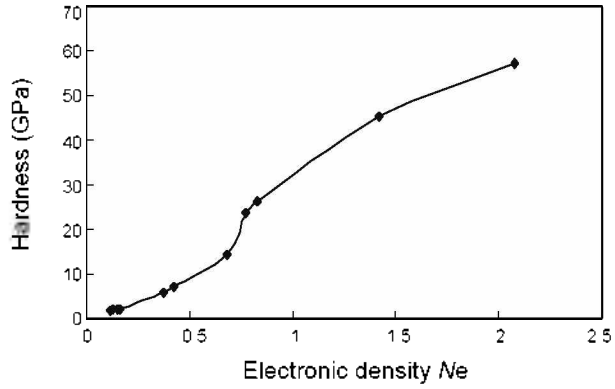

Figure 3. Electronic density N_e and hardness of the pseudobinary crystals in Eu-123.

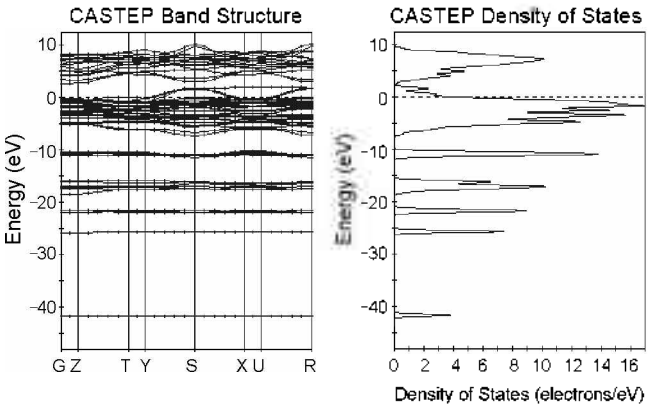

Figure 4. Band structure and DOS of Y-123.

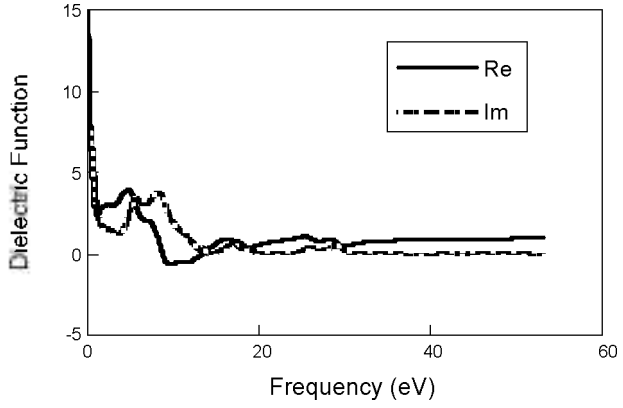

Figure 5. Dielectric function of Y-123.

Studio.[22] The interactions between the ions and the electrons are described by using Ultrasoft Vanderbilt pseudopotential and the electron-electron interaction is treated within the GGA approximation. The calculations were performed using an energy cut-off of 300 eV for the plane wave basis set and converged with respect to the k-point integration. The Brillouin zone is sampled on a 5 × 5 × 2 Monkhorst-Pack k-point mesh. The calculated of the energy band structure and density of state of Y-123 are plotted in Fig. 4, indicating that it seems to be metallic. In fact, owing to the strong electronic correlations, it is a magnetic insulator.[23,24]

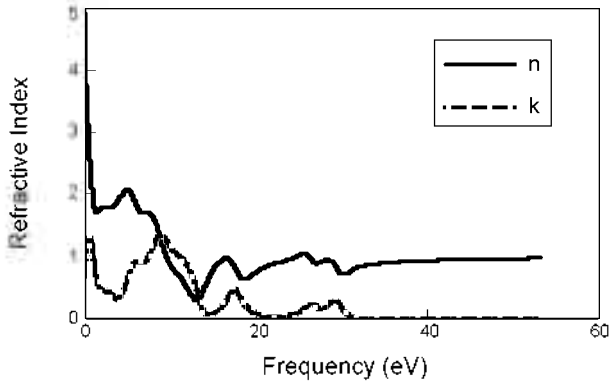

Figure 6. Refractive index of Y-123.

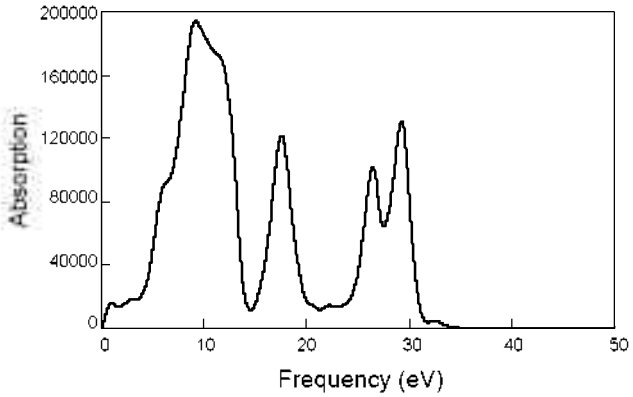

Figure 7. Absorption coefficient of Y-123.

Gilman[25] has studied mechanical hardness, chemical hardness, and optical hardness in detail. He found that the three types of hardness are directly related to one another through the electronic structures. Optical hardness is associated with the electronic polarizability which determines the refractive index. CASTEP can calculate the optical properties of solids that are due to electronic transitions. When performing calculations of optical properties it is common to evaluate the complex dielectric constant and then express other properties in terms of it. The complex dielectric constant is shown in Fig. 5. In general, the difference in the propagation of an electromagnetic wave through vacuum and some other material can be described by a complex refractive index. $N = n + ik$. The result of refractive index is shown in Fig. 6. In vacuum N is real, and equal to unity. For transparent materials it is purely real, the imaginary part being related to the absorption coefficient by: $\eta = 2\,k\omega/c$. The absorption coefficient indicates the fraction of energy lost by the wave when it passes through a unit thickness of the material. It is derived by considering the rate of production of Joule heat in the sample. The result of absorption coefficient is shown in Fig. 7.

Conclusion

In conclusion, the chemical bond parameters of Y-123, Eu-123, Pr-123 and Gd-123 compounds have calculated using the

chemical bond theory of complex crystals. Their hardness have been predicted by the chemical bond definition of hardness. The calculated results indicate that the covalency of the Cu-O types of bond is greater that that of the Ba-O and Re-O types of bond. And the hardness values increase as the unit cell volume of the rare earth superconductor structures decrease.

References

1. Ikuta, H.; Oka, T.; Mizutani, U. *Oyo Buturi*. **1999**, *68*, 403.
2. Gou , H. Y.; Hou , L.; Zhang , J. W.; Gao, F. M. *Appl. Phys. Lett.* **2008**, *92*, 241901.
3. Gou , H. Y.; Hou, L.; Zhang , J. W.; Wang, Z. B.; Gao, L. H.; Gao, F. M. *Appl. Phys. Lett.* **2007**, *90*, 191905.
4. Tse, J. S.; Klug, D. D.; Gao, F. *Phys. Rev. B* **2006**, *73*, 140102.
5. Gou, H.; Hou, L.; Zhang, J.; Li, H.; Sun, G. F.; Gao, F. M. *Appl. Phys. Lett.* **2006**, *88*, 221904.
6. Gou, H. Y.; Hou, L.; Zhang, J. W.; Sun, G. F.; Gao, L. H.; Gao, F. M. *Appl. Phys. Lett.* **2006**, *89*, 141910.
7. Gou, H. Y.; Hou, L.; Zhang, J. W.; Sun, G. F.; Gao, L. H.; Gao, F. M. *Phys. Status Solidi B* **2008**, *245*, 58.
8. Zhang, S. Y.; Gao, F. M.; Wu, C. X. *Journal of Alloys and Compounds* **1998**, *275-277*, 835.
9. Gao, F. M.; Li, D. C.; Zhang, S. Y. J. *Phys. Condens. Matter.* **2003**, *15*, 5079.
10. Wu, Z.; Meng, Q.; Zhang, S. *Physical Review B* **1998**, *58*, 958.
11. Xue, D.; Zhang, S. *Appl. Phys. Lett.* **1997**, *70*, 943.
12. Gao, F. M. *Physical Review* B **2004**, *69*, 094113.
13. Gao, F. M.; Xu, R.; Liu, K. *Physical Review B* **2005**, *71*, 052103.
14. Gao, F. M.; Hou, L.; He, Y. H. *Journal of Physical Chemistry B* **2004**, *108*, 13069.
15. Gao, F. M.; Qin, X. J.; Wang, L. Q.; He, Y. H.; Sun, G. F.; Hou, L.; Wang, W. Y. *Journal of Physical Chemistry B* **2005**, *109*, 14892.
16. Phillips, J. C. *Rev. Mod. Phys.* **1970**, *42*, 317.
17. Levine, B. F. *J. Chem. Phys.* **1973**, *59*, 1463.
18. Gao, F. M.; Zhang, S. Y. *Journal of Physics and Chemistry of Solids* **1997**, *58*, 1991.
19. Gao, F. M. *Journal of Physics: Condensed Matter* **2003**, *15*, L637.
20. Gao, F. M.; Zhang, S. Y. *Journal of the Chinese Rare Earth Society* **1993**, *11*, 186.
21. Yoshino, Y.; Iwabuch, A.; Noto, K.; Sakai, N.; Murakami, M. *Physica C* **2001**, *357-360*, 796.
22. Material studio 2.2, 2002.
23. Yamani, Z.; Akhavan, M. *Phys. Rev. B* **1997**, *56*, 7894.
24. Kim, H. T. *Physica C* **2000**, *341-348*, 259.
25. Gilman, J. J. *Mat. Res. Innovat.* **1997**, *1*, 71.