

## Copper position in type-I $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$ clathrate

L. Yang<sup>a</sup>, Y. Wang<sup>a</sup>, T. Liu<sup>b</sup>, T.D. Hu<sup>b</sup>, B.X. Li<sup>c</sup>, K. Ståhl<sup>d</sup>, S.Y. Chen<sup>e</sup>, M.Y. Li<sup>f</sup>,  
P. Shen<sup>f</sup>, G.L. Lu<sup>a</sup>, Y.W. Wang<sup>a</sup>, J.Z. Jiang<sup>a,\*</sup>

<sup>a</sup>Laboratory of New-Structured Materials, Department of Materials Science and Engineering, Zhejiang University, Zheda road 38, Hangzhou 310027, PR China

<sup>b</sup>Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, PR China

<sup>c</sup>Department of Physics, Hangzhou Teacher College, Hangzhou 310012, PR China

<sup>d</sup>Department of Chemistry, Building 207, Technical University of Denmark, DK-2800 Lyngby, Denmark

<sup>e</sup>Department of Mechanical Engineering, I-Shou University, Kaohsiung, Taiwan, ROC

<sup>f</sup>Institute of Materials Science and Engineering, National Sun-Yat-sen University, Kaohsiung, Taiwan, ROC

Received 20 December 2004; received in revised form 5 March 2005; accepted 11 March 2005

Available online 8 April 2005

### Abstract

Local structure of Cu in a type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate has been investigated by synchrotron X-ray powder diffraction, Cu *K*-edge extended X-ray absorption fine spectroscopy, X-ray absorption near edge spectroscopy (XANES) and theoretical calculation. It is found that XANES spectra cannot be explained by the substitution of Cu atoms at Si16*i*, and Si24*k* positions. Our calculations show that the binding energies of the Si atom in Si16*i*, Si24*k* and Si6*c* positions are 9.000, 9.495 and 8.911 eV, respectively. Both experimental and theoretical results support that Cu atoms in the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate, as a doped element, prefer to occupy the least-binding Si, i.e., the Si6*c* sites. No structural change between 112 and 300 K was observed and the (100)-faceted cubic crystal has negligible distortion/ordering according to transmission electron microscopy.

© 2005 Elsevier Inc. All rights reserved.

PACS: 82.75.Fq; 81.05.Zx; 61.72.Tt; 61.10.Ht

Keywords: Synchrotron radiation; EXAFS; Silicides; Semiconductor; FP-LMTO

### 1. Introduction

Type-I clathrates, with space group  $Pm\bar{3}n$ , are composed of host atoms of Si or other group IV or III/V elements with guest atoms such as alkali and alkaline earth elements exhibiting many interesting properties, e.g., superconductivity [1–3], thermoelectric applications [4,5], magnetism [6] and wide band gap [7,8]. Silicon clathrates were mostly synthesized by thermal decomposition of Zintl silicides [9,10]. Recently, a high-pressure high-temperature synthesis route was developed [11]. For instance, a silicon clathrate doped

with only barium,  $\text{Ba}_8\text{Si}_{46}$ , was obtained for the first time under a pressure of 3 GPa and at 800 °C [11]. However, substituting Si atoms by noble elements, e.g., Cu, Ag, Au, clathrate structure in the BaSi system can be easily formed even in ingots prepared by arc melting furnace [12,13]. The catalytic role of noble elements for forming type-I clathrates is not well understood. Prior to solving the problem, the knowledge of the atomic structure of noble elements located in clathrates is required. Although one previous work [14], based on X-ray single crystal diffraction measurements, was reported for the system, other techniques, e.g., X-ray absorption fine spectroscopy (XAFS) technique, which are sensitive to the fine difference in local structure, are still desirable to be applied to study the atomic structure

\*Corresponding author. Fax: +86 571 8795 1171.

E-mail address: [jiangjz@zju.edu.cn](mailto:jiangjz@zju.edu.cn) (J.Z. Jiang).

of the BaCuSi system. In this work, the local structure of Cu for the prototypical type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  system was investigated by performing Cu *K*-edge extended X-ray absorption fine spectroscopy (EXAFS), X-ray absorption near edge spectroscopy (XANES) measurements and theoretical simulation.

## 2. Experimental

Alloy ingot with a composition of  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  was prepared by arc melting pure elements of 99.99% copper, 99.9% barium and 99.9999% silicon in a purified argon atmosphere. The as-prepared sample was examined by synchrotron X-ray powder diffraction with Rietveld refinement. X-ray powder diffraction data were collected at beamline I711 at the MAX II synchrotron in Lund, Sweden, using a Huber G670 imaging plate Guinier camera between  $8^\circ$  and  $100^\circ$  in steps of  $0.005^\circ$  in  $2\theta$ . The Rietveld refinement program is a local variation of the LHMP1 program [15], using the pseudo-Voigt profile function and Chebyshev polynomial background fitting. The compact polycrystals were also pulverized by an alumina mortar and pestle, and then collected on copper grids overlaid with a carbon-coated film for transmission electron microscopic (TEM) study using a JEOL 3010 instrument at 300 keV and a beam current of 60 pA/cm<sup>2</sup>.

X-ray absorption fine spectroscopy measurements were carried out in transmission at 112, 132, 172, 212, and 300 K at the 1W1B beamline of Beijing Synchrotron Radiation Facility operating at 60–100 mA and 2.2 GeV. The high-order harmonic content was suppressed by detuning the two crystals by about 30% of the maximum intensity in a Si (111) double-crystal monochromator. The samples were ground into fine powder and taped on the Scotch tape. The tape was folded in order to access the optimal jump at the absorption edge. A cryogenic set up was used working at temperature range between liquid nitrogen and ambient temperature. WINXAS program was used for data analysis, which follows a typical data-analyzing process. The EXAFS oscillations were multiplied by a scaling factor  $k^2$ , where  $k$  ranged from 2.5 to  $13.5 \text{ \AA}^{-1}$ . The first shell (at about 2.5 Å) of coordination at the Fourier transformation was filtered and fitted using the theoretical phase-shift and backscattering amplitude. The coordination number was fixed to 4. XANES calculations of clusters were carried out using FEFF8 programs, a real-space full multiple-scattering approach using self-consistent potential. Various clusters around a central Cu atom (containing 5 atoms up to about 2.5 Å for three Si sites, 9 atoms up to about 3.7 Å for three Si sites, 23 atoms for Si6*c* site, 22 atoms for Si24*k* site, or 21 atoms for Si16*i* site up to about 4.6 Å, and 31 atoms for Si6*c* site, 32 atoms for Si24*k* site, or 33 atoms for Si16*i* site up to

about 5.5 Å) were constructed for the self-consistent field (SCF) potential calculation. The XANES spectra were calculated using the Hedin–Lundqvist self-energy with an energy dispersion of 0.5 eV to account for the core hole lifetime and the instrumental broadening effects. The full multiple scattering (FMS) calculations were used for all the clusters. The muffin-tin (MT) radii were automatically overlapped up to 1.15 (by default) to reduce the effects of discontinuities between adjacent regions of muffin-tin potentials. Furthermore, binding energies at three Si16*i*, Si24*k*, Si6*c* positions with clusters of about 70 atoms were calculated using the FP-LMTO method, which is a self-consistent implementation of the Kohn–Sham equations in the local-density approximation [16]. In this method, space is divided into two parts: non-overlapping MT spheres centered at the nuclei and the remaining interstitial region. The electron wave functions are expanded in terms of MT orbitals. The LMTO's are augmented Hankel functions only inside the MT spheres [17]. This method has been successfully used to investigate the structures of the silicon clusters and properties of the silicon crystal [18].

## 3. Results and discussion

TEM lattice image (Fig. 1a) indicated the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate has a cubic structure with well-developed (100) surface. The inset electron diffraction pattern indicated a lattice constant of about 1.02 nm with negligible tetragonal or hexagonal distortion. The reconstructed image, i.e., inverse Fourier transform (Fig. 1b), shows Si cagelike lattice analogous to the simulated lattice image of  $\text{Na}_8\text{Si}_{46}$  clathrate [19] in accord with Cu substitution for specific Si atoms. The absence of superlattice diffraction spots (Fig. 1a) indicated that there is negligible substitutional order. Fig. 2 shows observed and difference X-ray powder diffraction profiles for the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate at 323 K. A structure with space group of  $Pm\bar{3}n$  and  $Z = 1$  was found to be the most promising indexing scheme. Tiny residual pure silicon was found while some weak peaks located at low angles were also detected and attributed to an as yet unidentified phase. Results for the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate obtained from structure refinements are summarized in Table 1. In the type-I  $\text{Ba}_8\text{Si}_{46}$  clathrate [2,11], 46 Si atoms in its simple cubic primitive unit cell are located at three distinct Wyckoff symmetry sites marked as Si6*c*, Si16*i* and Si24*k*. The crystal structure is open since it is obtained by packing two ‘small’ Si<sub>20</sub>-atom cages and six ‘large’ Si<sub>24</sub>-atom cages together. The two non-framework symmetry sites marked Ba2*a* and Ba6*d*, are the centers of the ‘small cage’ (pentagonal dodecahedron) and the ‘large cage’ (tetraikadecahedron), respectively. During the Rietveld refinement for the  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate, a few atomic

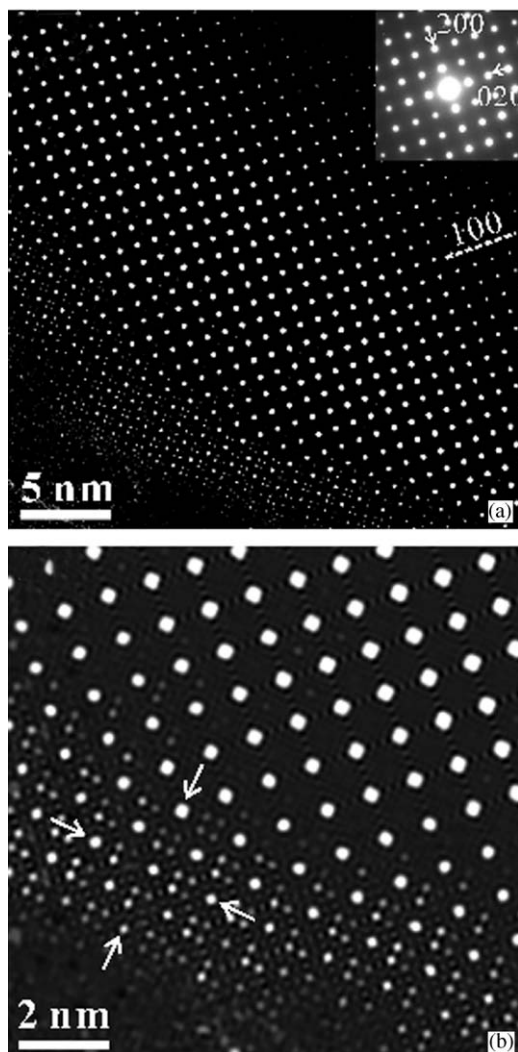


Fig. 1. TEM of the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate. (a) Lattice image with inset electron diffraction pattern showing well-developed (100) surface and negligible distortion. (b) The reconstructed image shows Si cage-like lattice (arrows), analogous to the simulated lattice image of  $\text{Na}_8\text{Si}_{46}$  clathrate [19].

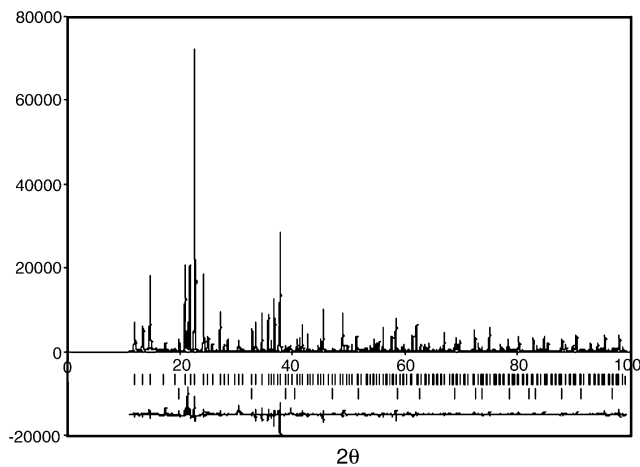


Fig. 2. Observed and difference X-ray powder diffraction profiles for the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate at 323 K.

arrangements were tested, e.g., (1) Cu atoms substitute  $\text{Ba}_{2a}$  or  $\text{Ba}_{6d}$  sites, which do not work at all. (2) Cu atoms substitute  $\text{Si}_{16i}$  or  $\text{Si}_{24k}$ . It seems that the XRD pattern could be fitted, but with a larger  $R$ -value as compared to the scheme that Cu atoms substitute  $\text{Si}_{6c}$ , as shown in Fig. 2.

It is well known that XAFS technique is sensitive to the fine difference in local structure. Thus, we further apply this technique to directly study the local structure of Cu atoms by performing Cu  $K$ -edge XAFS measurements. If Cu atoms substituted  $\text{Si}_{16i}$  or  $\text{Si}_{24k}$ , the nearest neighbor coordination number and elements of the Cu atom were 3Si and 1Cu while 4Si for the substitution of  $\text{Si}_{6c}$ . Fig. 3a show the normalized experimental EXAFS spectra measured at the Cu- $K$  edge of  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  at 112 and 172 K and the corresponding FTs are shown in Fig. 3b. No significant structural change for the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate was detected between 112 and 300 K, except that the oscillating amplitude of EXAFS was weakened due to the thermal effect.

Fig. 4 shows XANES spectra of  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  at 112 and 172 K. The features of A, B, C, D and E are marked. According to the Rietveld results, we know that Cu atoms can only sit at Si sites. Following simulation schemes were thus pursued. (1) Convergence for various cluster sizes when Cu atoms substitute three different Si sites. We found for all three sites, simulated XANES spectra converge above clusters containing about 20–23 atoms. One example is shown in Fig. 4a for the  $\text{Si}_{6c}$  site. The main peaks appearing in the spectra are marked as A, B, C, D and E. Peaks A and B show up for cluster size of 5, Peaks C and D show up for cluster size of 9, E shows for 23. (2) Cu concentration dependence of XANES spectra when Cu atoms substitute three different Si sites. For the  $\text{Si}_{24k}$  site in the type-I clathrate, there are 24 Si atoms. We compare the XANES spectra for four arrangements: (A) Cu atoms substitute all 24  $\text{Si}_{24k}$  sites, (B) only Si and Ba atoms are in the first five shells (at about 5.5 Å), (C) one Cu atom sits in the first shell (at about 2.5 Å) and the rest are Si and Ba, and (D) one Cu atom sits in both the first (at about 2.5 Å) and third shell (at about 4.0 Å) and the rest are Si and Ba. Surprisingly, we found the simulated XANES spectra are very similar for the four arrangements. This result indicates that XANES spectra are sensitive to the location of Cu atoms in Si sites rather than the concentration. (3) Simulation of XANES spectra for the substitution of three different Si sites, as shown in Fig. 4b. It is clear that spectra for  $\text{Si}_{16i}$  and  $\text{Si}_{24k}$  are far from the experimental curve while the  $\text{Si}_{6c}$  gives the best match, which is consistent with results reported from the X-ray single crystal diffraction measurements in the system [14].

From a crystallographic point of view, the  $\text{Si}_{6c}$  sites have the highest symmetry in the three Si sites. They are

Table 1  
Structural data for the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate at 323 K

$a$ (Å)	Ba1	Ba2	Si16i	Si24k	Si6c	Cu	$\rho$ (g/cm <sup>3</sup> )	$R$
10.3236(1)	0, 0, 0	0.25, 0.5, 0	0.1844(2), 0.1844(2), 0.1844(2)	0, 0.3099, 0.1192	0.25, 0, 0.5	0.25, 0, 0.5	3.808	$R_B = 6.65$
	$g = 0.042(1)$	$g = 0.125$	$g = 0.333$	$g = 0.5$	$g = 0.047(1)$	$g = 0.078(1)$		$R_p = 17.51$
	$B = 0.53(3)\text{Å}^2$	$B = 2.19(3)\text{Å}^2$	$B = 1.19(7)\text{Å}^2$	$B = 0.63(5)\text{Å}^2$	$B = 0.64(7)\text{Å}^2$	$B = 0.64(7)\text{Å}^2$		$R_{wp} = 20.07$

Numbers in parentheses are estimated standard deviations in the last decimal places quoted.  $g$  is the occupancy factors and  $B$  is the equivalent isotropic temperature factor coefficient.

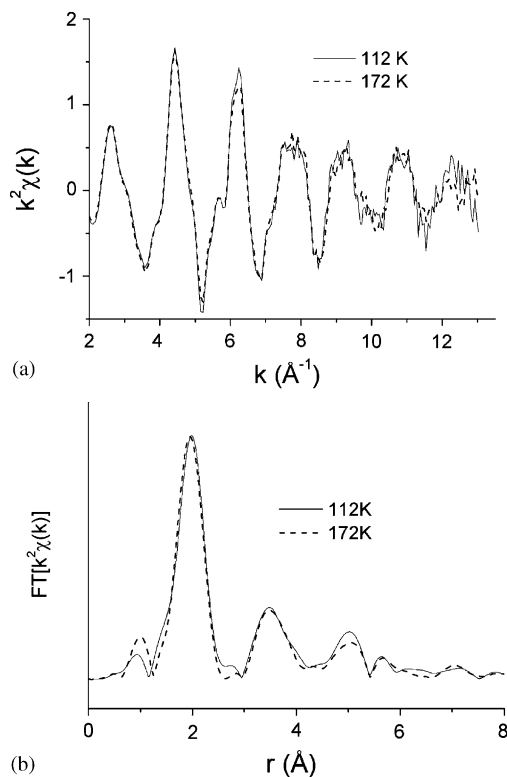


Fig. 3. (a) Experimental  $k^2 \cdot \chi(k)$  spectra measured at the Cu- $K$  edge of the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate at 112 and 172 K and (b) the corresponding FT's spectra. 1st peak: Cu–Si at about 2 Å, 2nd peak: Cu–Si and Cu–Cu at about 3.5 Å.

not located at the strongly bonded  $\text{Si}_{20}$  cage and have thus more space available. We further calculated binding energies for three Si16i, Si24k, and Si6c positions using the FP-LMTO method. All atomic coordination data were taken from type-I  $\text{Ba}_8\text{Si}_{46}$  [2,11]. Our calculations show that the binding energies of the Si atom in Si16i, Si24k, and Si6c positions are 9.000, 9.495 and 8.911 eV, respectively. The lowest binding energy is the Si6c position. We believe that the Si6c atom with the lowest binding energy is most likely replaced by other metal atom. This might be the reason that Cu atoms in the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate, as a doped element, prefer the Si6c sites, as experimentally observed here. In addition, calculations of binding energies in the ternary  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate, in which Cu atoms randomly substituted Si atoms, are still desirable.

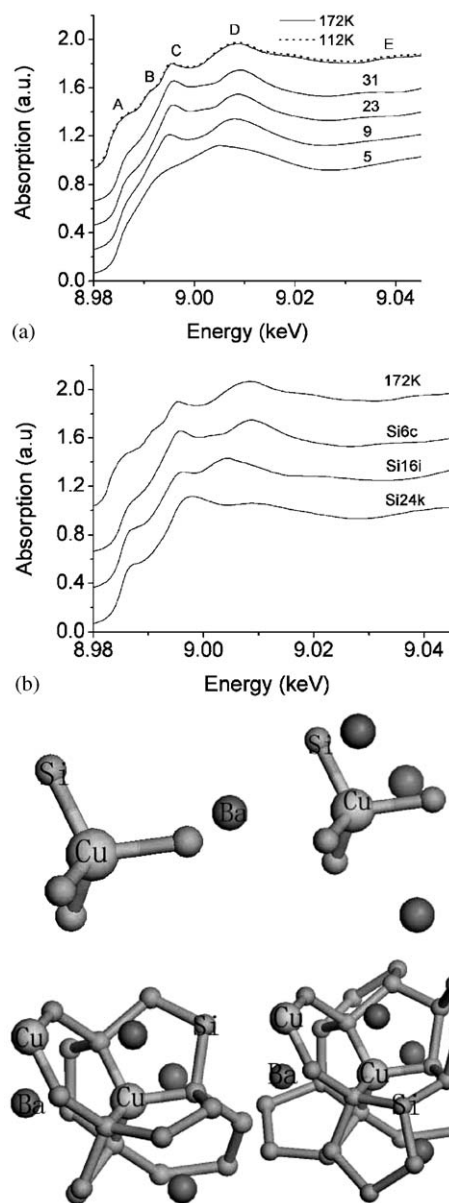


Fig. 4. (a) XANES spectra of the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate at 112 and 172 K together with multiple scattering calculations of Cu  $K$ -edge XANES for the substitution of Cu atom at Si6c site of various clusters around Cu: 5, 9, 23 and 31 atoms. The features of A, B, C, D and E are marked. (b) Multiple scattering calculations of Cu  $K$ -edge XANES for the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate at three Si6c, Si16i, and Si24k crystallographic sites for clusters of 23, 22, 21, respectively, centered by Cu. For comparison, the experimental data at 112 and 172 K are also presented. (c) The Cu centered clusters for the substitution of Cu atom at Si6c site: 5, 9, 23 and 31 atoms.

#### 4. Conclusions

In conclusion, local structure of Cu in type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate has been investigated by synchrotron X-ray powder diffraction, Cu *K*-edge EXAFS, XANES and theoretical calculation. It is experimentally found that XANES spectra cannot be explained by the substitution of Cu atoms at Si16*i* and Si24*k* positions. Our calculations show that the lowest binding energy of Si atom is in fact at the Si6*c* position. Both experimental and theoretical results support that doped Cu atoms in the type-I  $\text{Ba}_8\text{Cu}_4\text{Si}_{42}$  clathrate, as a doped element, prefer the Si6*c* sites without structural change between 112 and 300 K.

#### Acknowledgments

The authors would like to thank BSRF in Beijing, NSRL in Hefei, SPring8 and KEK in Japan, MAXlab in Sweden, and HASYLAB in Germany for use of the synchrotron radiation facilities. Financial support from the National Natural Science Foundation of China (Grants Nos. 50341032 and 50425102), National Excellent Doctoral Dissertation (Grant No. 200320) and Zhejiang University is gratefully acknowledged.

#### References

- [1] H. Kawaji, H.O. Horie, S. Yamanaka, M. Ishikawa, *Phys. Rev. Lett.* 74 (1995) 1427.
- [2] S. Yamanaka, E. Enishi, H. Fukuoka, M. Ishikawa, *Inorg. Chem.* 39 (2000) 56.
- [3] M.J. Teraoka, Y. Moritomo, S. Yamanaka, *Nat. Mater.* 2 (2003) 653.
- [4] J.L. Cohn, G.S. Nolas, V. Fessatidis, T.H. Metcalf, G.A. Slack, *Phys. Rev. Lett.* 82 (1999) 779.
- [5] J.S. Tse, K. Uehara, R. Rousseau, A. Ker, C.I. Ratcliffe, M.A. White, G. Mackay, *Phys. Rev. Lett.* 85 (2000) 114.
- [6] D. Connetable, V. Timoshevskii, E. Artacho, X. Blasé, *Phys. Rev. Lett.* 87 (2001) 206,405.
- [7] J. Gryko, P.F. McMillan, R.F. Marzke, G.K. Ramachandran, D. Patton, S.K. Deb, O.F. Sankey, *Phys. Rev. B* 62 (2000) R7707.
- [8] G.B. Adams, M.O. Keeffe, A.A. Demkov, O.F. Sankey, Y.M. Huang, *Phys. Rev. B* 49 (1994) 8048.
- [9] G.K. Ramachandran, P.F. McMillan, J. Diefenbacher, J. Gryko, J.J. Dong, O.F. Sankey, *Phys. Rev. B* 60 (1999) 12,294.
- [10] G.K. Ramachandran, P.F. McMillan, J.J. Dong, O.F. Sankey, *J. Solid State Chem.* 154 (2000) 626.
- [11] E. Reny, S. Yamanaka, C. Cros, M. Pouchard, *Chem. Commun.* (2000) 2505.
- [12] R.F.W. Herrmann, K. Tanigaki, T. Kawaguchi, S. Kuroshima, H. Suematsu, *Chem. Phys. Lett.* 283 (1998) 29.
- [13] Y. Nozue, G. Hosaka, E. Enishi, S. Yamanaka, *Mol. Cryst. Liq. Cryst.* 341 (2000) 509.
- [14] G. Cordier, P. Woll, *J. Less-Common Met.* 169 (1991) 291.
- [15] J.Z. Jiang, R. Lin, K. Nielsen, S. Mørup, D.G. Rickerby, R. Clasen, *Phys. Rev. B* 55 (1997) 14,830.
- [16] M. Methfessel, M.V. Schilfgaarde, *Int. J. Mod. Phys. B* 7 (1993) 262; M. Methfessel, M.V. Schilfgaarde, *Phys. Rev. B* 48 (1993) 4937; M. Methfessel, *Phys. Rev. B* 38 (1988) 1537; M. Methfessel, C.O. Rodriguez, O.K. Andersen, *Phys. Rev. B* 40 (1989) 2009.
- [17] K. Andersen, *Phys. Rev. B* 12 (1975) 3060; O.K. Andersen, R.G. Woolley, *Mol. Phys.* 26 (1975) 905; M. Springborg, O.K. Andersen, *J. Chem. Phys.* 87 (1975) 7125.
- [18] B.X. Li, P.L. Cao, *Phys. Rev. B* 62 (2000) 15,788; B.X. Li, P.L. Cao, *Phys. Rev. A* 62 (2000) 023,201; B.X. Li, P.L. Cao, D.L. Que, *Phys. Rev. B* 61 (2000) 1685; B.X. Li, P.L. Cao, R.Q. Zhang, S.T. Lee, *Phys. Rev. B* 65 (2002) 125,305.
- [19] P. Mélinon, P. Keghelian, A. Perez, B. Champagnon, Y. Guyot, L. Saviot, E. Reny, C. Cros, M. Pouchard, A.J. Dianoux, *Phys. Rev. B* 59 (1999) 10,099.