



Resonant Inelastic X-ray Scattering Spectra of BP Calculated by the Tight-Binding Method

Hiroharu YORIKAWA*

Graduate School of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya 321-8585, Japan

(Received April 6, 2010; accepted June 24, 2010; published August 10, 2010)

The resonant inelastic soft-x-ray scattering (RIXS) spectra of boron phosphide (BP) crystal have been calculated by using the tight-binding (TB) approximation and compared with spectra obtained experimentally by Agui *et al.* It is shown that typical features observed in the experimental spectra of B *K* and P *L*_{2,3} emissions are well reproduced by the calculations based on the TB approximation with *spd* basis. The dependence of main peaks of both the spectra on the excitation energy is explained in terms of the band structure.

KEYWORDS: resonant inelastic soft-x-ray scattering, x-ray emission spectroscopy, boron phosphide, electronic structure, tight-binding approximation

DOI: [10.1143/JPSJ.79.084712](https://doi.org/10.1143/JPSJ.79.084712)

1. Introduction

Resonant inelastic soft-x-ray scattering (RIXS) spectra involve rich information about the electronic band structure in condensed matter compared to an ordinary x-ray emission spectrum (XES),^{1,2)} because information on both conduction and valence bands is reflected on the spectra. The technique of the RIXS has been applied to many materials.^{3–18)} Good agreement between theory and experiment has been reported for the *K* spectra of carbon materials, diamond and graphite.^{3–8)} However, unfortunately there has been insufficient theoretical investigation of RIXS spectra of other materials. Boron phosphide (BP) is one of such materials. The RIXS spectra of BP were measured by Agui *et al.*¹⁴⁾ and reported in this journal about ten years ago. They succeeded in interpreting their experimental results in terms of mapping of the electronic band structure. The electronic band structure of BP has been investigated by means of a variety of methods such as the total-energy pseudopotential method,^{19,20)} the empirical tight-binding (TB) method,²¹⁾ the TB linear muffin-tin orbital (TB-LMTO) method,²²⁾ and the full-potential linearized augmented plane wave (FLAPW) method.¹⁵⁾ Lin *et al.* not only performed the FLAPW calculations, but also observed B *K* RIXS spectra to compare them with *p* partial density of states (*p*-PDOS).

In the present study, we attempt to calculate the RIXS spectra of BP, since there is no report of its calculated RIXS spectra although Agui *et al.*¹⁴⁾ observed both B *K* (B 1*s*) and P *L*_{2,3} (P 2*p*) spectra. It is interesting to examine whether the experimental results can be reproduced by the TB calculations. The TB method for the band structure calculation is suitable for calculating RIXS spectra because it is required to perform the Brillouin zone integration for each of incident energies, except that it has a limitation for the conduction band with a high energy.

2. Calculations

RIXS is a scattering process of incident photons by electrons in solids. In this process electrons absorb and emit photons with conserving crystal momentum. The expression for RIXS spectrum of B 1*s* is given by the following:

$$S(E, E_{\text{ex}}) \propto E^3 \sum_{n \in v} \sum_{m \in c} \int_{\text{BZ}} |M_{c,1s}(\mathbf{k})|^2 |M_{1s,v}(\mathbf{k})|^2 \times \delta(E_m(\mathbf{k}) - E_{1s} - E_{\text{ex}}) \delta(E_n(\mathbf{k}) - E_{1s} - E) d\mathbf{k}. \quad (1)$$

This expression was used by Johnson and Ma⁴⁾ to calculate the RIXS spectrum for diamond. The notations *m* and *n* in eq. (1) are band indices for conduction and valence bands, respectively; *E*_{1*s*} is the binding energy of 1*s* core level; *E*_{ex} and *E* are the energies of incident and emitted photons, respectively; and *M*_{*c*,1*s*}(**k**) and *M*_{1*s*,*v*}(**k**) are matrix elements of electric-dipole transitions for absorption and emission processes. The *S*(*E*, *E*_{ex}) can be regarded as a restricted joint density of states (*r*-JDOS) multiplied by *E*³.⁴⁾

In the calculation of P 2*p* spectra, we have to take into account of the following: *E*_{1*s*} in eq. (1) is replaced by the binding energy of 2*p*_{3/2} or 2*p*_{1/2}, and the fact that the initial state for transitions changes from 2*p*_{3/2} to both 2*p*_{3/2} and 2*p*_{1/2} levels, which are separated from each other by 0.87 eV²³⁾ due to the spin-orbit interactions, as the excitation energy *E*_{ex} increases. In the actual calculations, the *δ*-line in eq. (1) for absorption or emission was replaced by a Gaussian curve broadened with a FWHM of *Γ*_a or *Γ*_e, respectively. The value of *Γ*_a was set to 0.3 eV for B 1*s* and P 2*s* spectra, while that of *Γ*_e to 2.0 eV for the B 1*s* and to 1.6 eV for the P 2*p*.

We note that experimentally observed RIXS spectra are not necessarily represented by the expression in eq. (1) alone, because they also contain the component which arises from processes not obeying momentum conservation. The breakdown of the momentum conservation is due to the relaxation processes such as the electron-phonon and electron-electron interactions which destroy the temporal coherence between the absorption and emission processes in RIXS.²⁾ The experimental RIXS spectrum is expressed as

$$S_{\text{total}}(E, E_{\text{ex}}) = \alpha S(E, E_{\text{ex}}) + (1 - \alpha) S_{\text{XES}}(E), \quad (2)$$

where the first term is the coherent component described by eq. (1) and the second the incoherent component given by the XES spectrum, *α* (coherent fraction) being a phenomenological parameter. The *α* is usually estimated from experimental data or by comparing eq. (2) with experimental

*E-mail: yorikawa@cc.utsunomiya-u.ac.jp

Table I. Tight-binding parameters (in units of eV) of BP crystal. An sp^3d^2 basis model, where only two d -states $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ are included, is employed, because the other three states play a role similar to p -states.²⁴⁾ The subscripts a and c of orbitals (s , p , and d) stand for B and P atoms, respectively. These parameters are determined so as to reproduce the electronic band structures obtained from the first-principles pseudopotential calculation²⁵⁾ and the experimental energy gap of 2.1 eV. The electronic band structure calculated by using these parameters is illustrated in Fig. 4.

B self-energy	$E_s^{(a)}$	$E_p^{(a)}$	$E_d^{(a)}$	
	-2.2719	2.5149	16.2991	
P self-energy	$E_s^{(c)}$	$E_p^{(c)}$	$E_d^{(c)}$	
	-4.8624	4.8501	12.3931	
1st nearest-neighbor interactions				
$s_a s_c \sigma$	$s_a p_c \sigma$	$s_a d_c \sigma$	$p_a p_c \sigma$	$p_a p_c \pi$
-2.2095	2.8229	-2.1669	4.8221	-1.8342
$p_a d_c \sigma$	$p_a d_c \pi$	$d_a d_c \sigma$	$d_a d_c \pi$	$d_a d_c \delta$
5.4941	2.4432	3.7746	-0.2368	-0.8435
$s_c p_a \sigma$	$s_c d_a \sigma$	$p_c d_a \sigma$	$p_c d_a \pi$	
4.3105	5.4771	-4.4062	-3.4876	
2nd nearest-neighbor interactions				
$s_a s_a \sigma$	$s_a p_a \sigma$	$s_a d_a \sigma$	$p_a p_a \sigma$	$p_a p_a \pi$
0.6036	-0.3757	-0.2332	0.2254	0.0316
$p_a d_a \sigma$	$p_a d_a \pi$	$d_a d_a \sigma$	$d_a d_a \pi$	$d_a d_a \delta$
-0.3599	-0.1061	0.5738	-0.0305	-0.6763
$s_c s_c \sigma$	$s_c p_c \sigma$	$s_c d_c \sigma$	$p_c p_c \sigma$	$p_c p_c \pi$
-0.6033	0.6142	1.1571	0.3458	-0.6986
$p_c d_c \sigma$	$p_c d_c \pi$	$d_c d_c \sigma$	$d_c d_c \pi$	$d_c d_c \delta$
-0.0304	-0.1004	0.7364	0.3319	-0.2234

data. As the excitation energy E_{ex} increases, α approaches zero and $S_{\text{total}}(E, E_{\text{ex}})$ is reduced to $S_{\text{XES}}(E)$, since the decay process becomes slow enough for the relaxation to be complete.

To obtain the electronic band structure of the zinc-blende BP crystal, we used two sets of the TB parameters. One is Ferhat *et al.*'s sp basis set, which is based on the three-centered scheme,²¹⁾ and the other is our set based on sp^3d^2 basis, which has been obtained for the present work. It is listed in Table I. We included the d basis, expecting that d character plays an important contribution to the conduction band. Both the sets take into account of the interactions up to the second nearest neighbors.

3. Results and Discussion

Agui *et al.* presented thirteen experimental spectra in ref. 14: eleven RIXS spectra and two so-called x-ray emission spectra. They labeled B 1s spectra by Roman numerals and P 2p spectra by Arabic numerals, in ascending order of the excitation energy, i.e., I to VI, and VII(XES) for B 1s, while 1 to 5, and 6(XES) for P 2p. Our calculated results are presented in Figs. 1–3, where the same labels as in ref. 14 are used so that our spectra correspond to data of Agui *et al.* The values of the excitation energy we used in the calculations are: 0.1, 1.8, 2.4, 5.8, 7.3 eV for B 1s RIXS spectra I to V; and 1.0, 1.8, 3.2, 5.7, 10.8 eV for P 2p RIXS spectra 1 to 5. These energies are measured from the bottom of the conduction band. We notice that Agui *et al.*'s spectrum VI of B 1s obtained with E_{ex} greater than about

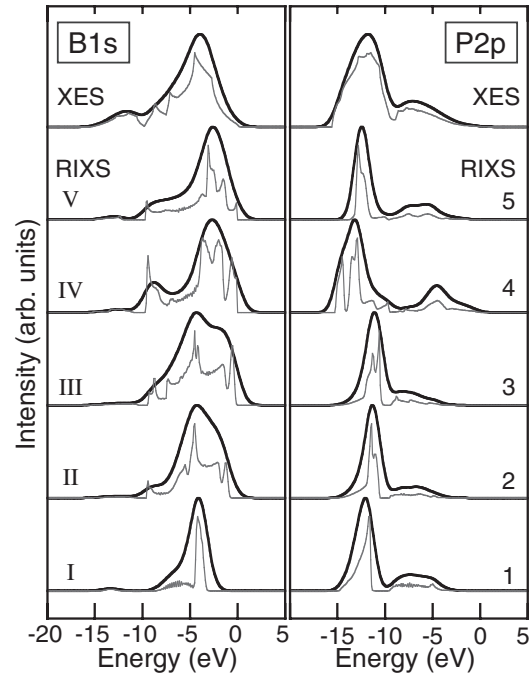


Fig. 1. Calculated coherent components for five excitation energies. They were obtained from the TB calculations with sp basis. Thick curves include the Gaussian broadening (see text for detail), while thin curves indicate r -JDOS's. In the top the XES's are also shown by thick curves, along with B p -PDOS and P s -PDOS drawn by the thin lines. The origin of the abscissa axis is taken at the valence band top.

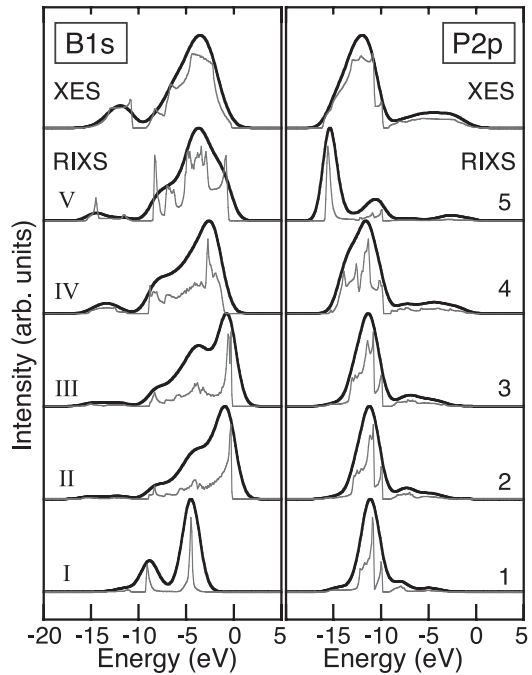


Fig. 2. Calculated coherent components for five excitation energies. They were obtained from the TB calculations with spd basis. Thick curves include the Gaussian broadening (see text for detail), while thin curves indicate r -JDOS's. In the top the XES's are also shown by thick curves, along with B p -PDOS and P ($s + d$)-PDOS depicted by the thin lines. The origin of the abscissa axis is taken at the valence band top.

10 eV from the conduction bottom is omitted, since the TB approximation can not be valid for such a high-energy conduction band.

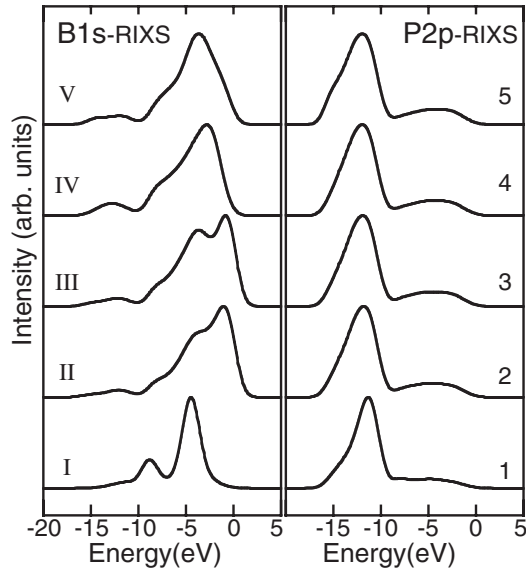


Fig. 3. The spectra obtained from eq. (2) by using the value of α estimated from the experimental data.

The RIXS spectra calculated by using two TB parameter sets are shown in Figs. 1 and 2 along with XES. From both the results we see similarity in some points and also dissimilarity. Let us compare these calculated results with the experiment¹⁴ to consider which TB parameter set is appropriate for describing the experiment. For B 1s spectra, RIXS spectrum I and XES in Fig. 1 are more similar to the experimental spectra than those in Fig. 2, but there is a crucial difference between them. This difference is the dependence of the peak position on the excitation energy E_{ex} . It is observed experimentally that the peak position varies with E_{ex} : It shifts to the high energy side with the increasing E_{ex} and then goes back to the low energy side approaching to the position of XES. This typical behavior is reproduced by the TB calculations with *spd* basis, as shown in Fig. 2. Furthermore, we like to point out that the experimental spectrum of B 1s obtained by Lin *et al.* (see Fig. 7 in ref. 15) with the excitation energy of 193.0 eV (which corresponds to $E_{\text{ex}} \simeq 3.0$ eV measured from the conduction bottom) is close to our spectrum IV in Fig. 2. From the above it is found that the experimental spectra of B 1s RXIS almost are made from the coherent component, in other words the fraction of the coherent component is high.

Next we compare the calculated P 2p spectra with experimental ones, which consist of a prominent peak with a structure at the high energy side. The prominent peak has been attributed to the emission from the critical point L by Agui *et al.* No noticeable change in the spectral shape was observed experimentally, even if the excitation energy varied. This means a low coherent fraction. As a matter of fact, we have estimated the value of α from the experimental data of Agui *et al.* by seeking the maximum value of α satisfying $S_{\text{total}}(E, E_{\text{ex}}) - (1 - \alpha)S_{\text{XES}}(E) \geq 0$ over the whole spectral range [see eq. (2)], after normalizing each of the experimental spectra. The obtained value of α is about 40, 10, and 5% for P 2p spectra 1, 2, and 3–5, respectively, contrary to 70–80% for B 1s spectra. The spectrum 1 in Fig. 2 can be directly compared with the experimental

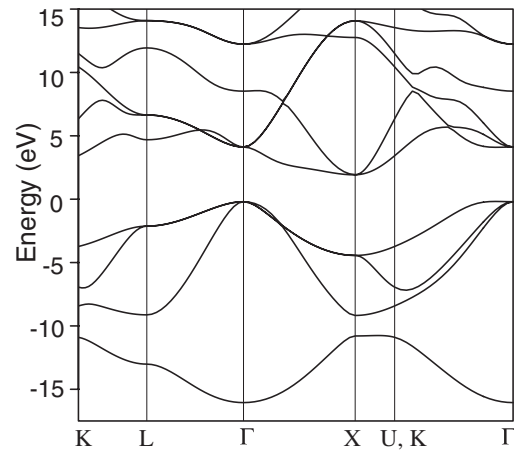


Fig. 4. Electronic band structure of BP obtained by using the *spd* basis whose TB parameters are listed in Table I.

spectrum with a relatively high value of α . We found that the two small peaks in the structure at the high energy side of the prominent peak are separated from it by 3.5 and 6.4 eV, respectively, in good agreement with experimental results of 3.7 and 7.4 eV. As seen from Fig. 2, the energy position of the prominent peak was calculated to be -11.8 eV, which well agrees with the experimental result of -11.9 ($= 116 - 130 + 2.1$) eV read from Fig. 1 in ref. 14.

In Fig. 3, we show the spectra obtained from eq. (2) by using $S(E, E_{\text{ex}})$ and $S_{\text{XES}}(E)$ in Fig. 2 and the value of α estimated from the experimental data above. We consider that the spectra in Fig. 3 generally agree with the experimental measurements of Agui *et al.*, although there are some points that are not completely reproduced.

Here we mention the limitation of TB calculations for the conduction bands with high energies. We have confirmed that the TB approximation deviates from the first-principles pseudopotential calculation²⁵ in the high energy bands lying around 10 eV above the conduction bottom (see Fig. 4). Such a deviation appears in the spectra 4 and 5 in Fig. 1 and in the spectrum 5 in Fig. 2 as the shift of the main peak, but it is smeared by the incoherent component in the case of a low coherent fraction as seen in the spectrum 5 in Fig. 3.

Finally, we consider the behavior of the prominent peaks of B 1s and P 2p spectra when the excitation energy E_{ex} varies. We first discuss the shift of the main peak of B 1s spectra. This peak has been assigned to the critical point K by Agui *et al.* As shown in Fig. 4, the zinc-blende BP crystal has the indirect gap of Γ -X type, being similar to diamond, and the width of the valence band is about 16 eV. PDOS's in Fig. 5 shows that the lower half of the valence band is mainly made from P 3s and B 2p while the upper half is mainly made from B 2p and P 3p. This upper part of the valence band contributes to the K emission spectrum of B, while the lower part does to the $L_{2,3}$ emission spectrum of P. When 1s core electrons are excited to the region of the conduction bottom, wave vectors selected in the emission are those which lie near the X point. For this reason, the prominent peak is formed at about -4.5 eV, which is seen in the spectrum I in Fig. 2. When the excitation energy is increased up to about 2 eV from the conduction band bottom, wave vectors around the Γ point, which corresponds to the

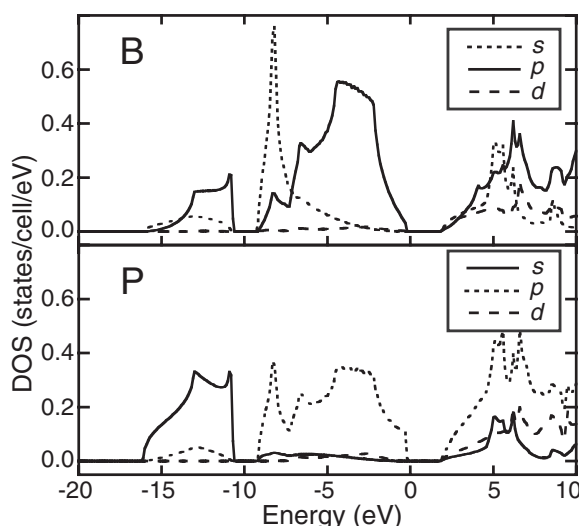


Fig. 5. Partial DOS's of BP obtained by using the *spd* basis whose TB parameters are listed in Table I.

top in the valence band, are selected. Thus the prominent peak appears close to 0 eV as seen in the spectrum II in Fig. 2. For the higher excitation energy the contribution of the wave vectors around the Γ point becomes less, but those elsewhere do more effectively. Hence the peak position moves to the low energy side. Such a peak shift has been observed in diamond.⁴⁾

Next concern is the prominent peak of the P $2p$ spectrum. This peak arises from either of the critical points X , Γ , and L , as seen from the lower part in the valence band ranging from -16 to -11 eV in Fig. 4. This band consists dominantly of P $3s$ states as seen in Fig. 5. It is expected that the position of the prominent peak shifts from -11 to -16 eV when the excitation energy increases from the conduction band bottom to about 2 eV above it. However, the lowest-energy states in the conduction band at the Γ point does not contain P $3s$ or P $3d$ component. Namely, the transition to this states is forbidden. Therefore, as the E_{ex} is increased, the critical point in the conduction band, which takes part in the transitions from the $2p$ core, changes from X to L , so that the main peak of the P $2p$ spectrum will shift from -11.0 to -13.0 eV. In practice this shift does not clearly appear, because such a slight shift is smeared by the superposition of the two P $2p$ components arising from the transitions from $2p_{3/2}$ and $2p_{1/2}$ core levels separated from each other by about 1 eV.

It is found that the nature of the wavefunction at the Γ point affects the behavior of the main peaks of B $1s$ and P $2p$ spectra when the excitation energy varies.

4. Conclusion

We have calculated the RIXS spectra of BP crystal by using the TB approximation and compared them to the experimental results reported in this journal by Agui *et al.*¹⁴⁾ We have used two TB parameter sets, paying our attention to the following characteristics: The energy position of the

main peak of the B $1s$ spectra changes with the variation of the excitation energy, and that of the main peak of the P $2p$ spectra does not change even if the excitation energy varies. We have shown that these experimental observations are consistent with the TB calculations with *spd* basis and that states around the Γ point in the lowest conduction band plays a critical role in the dependence of the main peaks of B $1s$ and P $2p$ spectra upon the excitation energy.

Acknowledgement

The author wishes to thank Professor Shinji Muramatsu for his helpful suggestions and critical reading of the manuscript.

- 1) *Proc. Int. Workshop RIXS, Walberberg, Germany, 1996*, Appl. Phys. A **65** (1997) No. 2.
- 2) Y. Ma: *Phys. Rev. B* **49** (1994) 5799.
- 3) Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P. D. Johnson, J.-E. Rubensson, T. Boske, W. Eberhardt, and S. D. Kevan: *Phys. Rev. Lett.* **69** (1992) 2598.
- 4) P. D. Johnson and Y. Ma: *Phys. Rev. B* **49** (1994) 5024.
- 5) P. Skytt, P. Glans, D. C. Mancini, J.-H. Guo, N. Wassdahl, J. Nordgren, and Y. Ma: *Phys. Rev. B* **50** (1994) 10457.
- 6) J. A. Carlisle, E. L. Shirley, E. A. Hudson, L. J. Terminello, T. A. Callcott, J. J. Jia, D. L. Ederer, R. C. C. Perera, and F. J. Himpsel: *Phys. Rev. Lett.* **74** (1995) 1234.
- 7) M. van Veenendaal and P. Carra: *Phys. Rev. Lett.* **78** (1997) 2839.
- 8) J. A. Carlisle, E. L. Shirley, L. J. Terminello, J. J. Jia, T. A. Callcott, D. L. Ederer, R. C. C. Perera, and F. J. Himpsel: *Phys. Rev. B* **59** (1999) 7433.
- 9) J.-E. Rubensson, D. Mueller, R. Shuker, D. L. Ederer, C. H. Zhang, J. Jia, and T. A. Callcott: *Phys. Rev. Lett.* **64** (1990) 1047.
- 10) K. E. Miyano, D. L. Ederer, T. A. Callcott, W. L. O'Brien, J. J. Jis, L. Zhou, Q.-Y. Dong, Y. Ma, J. C. Woicik, and D. R. Mueller: *Phys. Rev. B* **48** (1993) 1918.
- 11) S. Eisebitt, J. Lüning, J.-E. Rubensson, A. Settels, P. H. Dederichs, W. Eberhardt, S. N. Patitsas, and T. Tiedje: *J. Electron Spectrosc. Relat. Phenom.* **93** (1998) 245.
- 12) S. Shin, A. Agui, M. Watanabe, M. Fujisawa, Y. Tezuka, and T. Ishii: *Phys. Rev. B* **53** (1996) 15660.
- 13) J. Lüning, J.-E. Rubensson, C. Ellmers, S. Eisebitt, and W. Eberhardt: *Phys. Rev. B* **56** (1997) 13147.
- 14) A. Agui, S. Shin, and Y. Kumashoro: *J. Phys. Soc. Jpn.* **68** (1999) 166.
- 15) L. Lin, G. T. Woods, and T. A. Callcott: *Phys. Rev. B* **63** (2001) 235107.
- 16) G. P. Zhang, G. P. Chang, T. A. Callcott, D. L. Ederer, W. N. Kang, E.-M. Choi, H.-J. Kim, and S.-I. Lee: *Phys. Rev. B* **67** (2003) 174519.
- 17) A. V. Sokolov, E. Z. Kurmaev, S. Leitch, A. Moewes, J. Kortus, L. D. Finkelstein, N. A. Skorikov, C. Xiao, and A. Hirose: *J. Phys.: Condens. Matter* **15** (2003) 2081.
- 18) S. Eisebitt, A. Karl, W. Eberhardt, J. E. Fischer, C. Sathe, A. Agui, and J. Nordgren: *Appl. Phys. A* **67** (1998) 89.
- 19) R. M. Wentzcovitch, K. J. Chang, and M. L. Cohen: *Phys. Rev. B* **34** (1986) 1071.
- 20) P. Rodríguez-Hernández, M. González-Díaz, and A. Muñoz: *Phys. Rev. B* **51** (1995) 14705.
- 21) M. Ferhat, A. Zaoui, M. Certier, and H. Aourag: *Physica B* **252** (1998) 229.
- 22) B. N. Onwuagba: *Solid State Commun.* **89** (1994) 289.
- 23) M. Taniguchi, S. Suga, M. Seki, S. Asaoka, H. Kanzaki, Y. Akahama, S. Endo, and S. Narita: *Phys. Rev. B* **30** (1984) 4555.
- 24) G. D. Sanders and Y. C. Chang: *Phys. Rev. B* **45** (1992) 9202.
- 25) A. Masago, K. Shirai, and H. Katayama-Yoshida: *Phys. Rev. B* **73** (2006) 104102; H. Fujita, K. Shirai, and H. Katayama-Yoshida: *Inst. Phys. Conf. Ser.* **170** (2001) 617.