

## Electronic structure and superconducting gap of silicon clathrate $\text{Ba}_8\text{Si}_{46}$ studied with ultrahigh-resolution photoemission spectroscopy

T. Yokoya,<sup>1</sup> A. Fukushima,<sup>1</sup> T. Kiss,<sup>1</sup> K. Kobayashi,<sup>2</sup> S. Shin,<sup>1,2</sup> K. Moriguchi,<sup>3</sup> A. Shintani,<sup>3</sup> H. Fukuoka,<sup>4</sup> and S. Yamanaka<sup>4,5</sup>

<sup>1</sup>*Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan*

<sup>2</sup>*The Institute of Physical and Chemical Research (RIKEN), Sayo-gun, Hyogo 679-5143, Japan*

<sup>3</sup>*Electronics Engineering Laboratories, Sumitomo Metal Industries, Ltd., 1-8 Fusochi, Amagasaki, Hyogo 660-0891, Japan*

<sup>4</sup>*Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan*

<sup>5</sup>*CREST, Japan Science and Technology Corporation (JST), Kawaguchi 332-0012, Japan*

(Received 20 April 2001; published 1 October 2001)

We study the electronic structure and superconducting transition of silicon clathrate  $\text{Ba}_8\text{Si}_{46}$  ( $T_c = 8$  K) using photoemission spectroscopy. We observe a narrow band at the Fermi level ( $E_F$ ), whose width ( $\sim 0.3$  eV) is substantially smaller than that of band structure calculations ( $\sim 1.5$  eV). Ultrahigh-resolution measurements show a superconducting gap at 5.4 K [ $2\Delta(0)/k_B T_c = 3.51$ ]. Fine structures associated with phonons are observed within 70 meV of  $E_F$ . These results characterize  $\text{Ba}_8\text{Si}_{46}$  as a weak-coupling superconductor most probably driven by phonon.

DOI: 10.1103/PhysRevB.64.172504

PACS number(s): 74.25.Jb, 74.70.Wz, 79.60.-i

Silicon clathrate  $\text{Na}_8\text{Si}_{46}$  has been known as a nonsuperconducting metal down to 2 K for more than thirty years.<sup>1</sup> The crystal structure consists of  $\text{Si}_{20}$  and  $\text{Si}_{24}$  cages sharing their pentagonal faces with each other, with Na atoms occupying these cages (see Fig. 1). Though the silicon clathrate is reminiscent of the electron-doped  $\text{C}_{60}$ , the intercage bonding makes the clathrate different from the doped  $\text{C}_{60}$ , where individual  $\text{C}_{60}$  molecules essentially influence its physical properties: Clathrates are covalent crystals, while fullerides are molecular crystals. Motivated by the discovery of the superconductivity in the doped  $\text{C}_{60}$  compounds with the highest transition temperature ( $T_c$ ) exceeding 30 K (Ref. 2) and expectation of higher  $T_c$  even in the silicon clathrates because of expected higher Debye temperatures originating in the rigid  $sp^3$  Si-Si covalent bonding, Yamanaka *et al.* succeeded in synthesizing superconducting  $\text{Na}_2\text{Ba}_6\text{Si}_{46}$  with  $T_c$  of 4 K (Ref. 3). A remarkable point of this success is that this is a superconductor with  $sp^3$  Si-Si covalent bonding, implying a possibility of occurring superconductivity in the other cubic-silicon-like  $sp^3$  materials. This, along with their physically and industrially interesting properties,<sup>4-6</sup> has brought about renewed attention, and has stimulated experimental and theoretical studies.

Comparative band structure calculations<sup>7</sup> of  $\text{Si}_{46}$  and  $\text{Na}_2\text{Ba}_6\text{Si}_{46}$  show that the density of states (DOS) of the conduction band in  $\text{Na}_2\text{Ba}_6\text{Si}_{46}$  is strongly modified compared to that of pristine  $\text{Si}_{46}$  due to strong hybridization between  $\text{Si}_{46}$  and Ba states. This modification produces a sharp peak at the Fermi level ( $E_F$ ), which is thought to play a crucial role for the superconductivity because of the very high DOS at  $E_F$ . Nuclear magnetic resonance (NMR) studies have experimentally confirmed that the existence of the strong hybridization<sup>8-10</sup> together with partial ionization of Na and Ba in  $\text{Na}_x\text{Ba}_y\text{Si}_{46}$  (Ref. 8), but also discussed somewhat lower DOS at  $E_F$  compared to the value from the calculations.<sup>7</sup> Raman spectroscopy has been performed<sup>11,12</sup>

and compared with calculations<sup>13-15</sup> in order to study the phonon modes. Recently, neutron scattering studies reported that the phonon density of states of  $\text{Si}_{46}$  is found to extend up to  $\sim 70$  meV (Ref. 16). However, so far, to our best knowledge, no photoemission (PE) study reporting the electronic structure of the valence band and superconducting gap of superconducting silicon clathrates is known, except for an x-ray photoemission<sup>17</sup> which measured the valence band of nonsuperconducting  $\text{Si}_{34}$  type clathrate samples. The reason is because bulk superconducting samples for PE measurements are not available till now. Fortunately, more recently, high-pressure synthesis enables us to make bulk  $\text{Ba}_8\text{Si}_{46}$  having  $T_c$  of 8 K (Ref. 18), giving us an opportunity to perform PE spectroscopy on this compound.

In this Brief Report, we report experimental electronic structures of  $\text{Ba}_8\text{Si}_{46}$ . The PE spectra of the valence band region show several features up to 14 eV binding energy. We also find a sharp peak at  $E_F$ , which is expected to be a crucial factor for the superconductivity from band structure

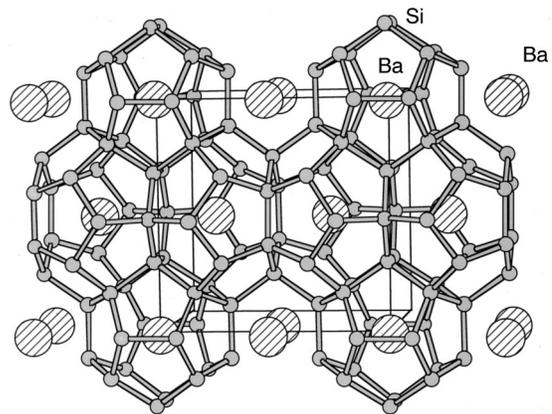


FIG. 1. Schematic structure model of  $\text{Ba}_8\text{Si}_{46}$ . Ba atoms occupy all of the silicon cages.

calculations.<sup>7,19</sup> But the observed bandwidth ( $\sim 0.3$  eV) of the peak at  $E_F$  is narrower than the calculated bandwidth ( $\sim 1.5$  eV), suggestive of a deviation from one electron approximation. Furthermore, we observe a clear opening of a superconducting gap below  $T_c$  with the gap size of 1.3 meV, which corresponds to a reduced gap size of  $2\Delta(0)/k_B T_c = 3.51$ . We also observe fine structures up to  $\sim 70$  meV in superconducting spectrum, whose energy is nearly equivalent to the highest phonon energy for  $\text{Na}_8\text{Si}_{46}$  clathrate.<sup>16</sup> These results for the superconducting state classify  $\text{Ba}_8\text{Si}_{46}$  into a weak-coupling superconductor most probably mediated by phonon. These experimental results provide direct information on the electronic structure and superconducting transition of the silicon clathrate superconductor.

$\text{Ba}_8\text{Si}_{46}$  samples were prepared using a high-pressure synthesis as described in the literature.<sup>18</sup>  $\text{Ba}_8\text{Si}_{46}$  made by the same procedure has shown superconductivity below 8 K for both resistivity and susceptibility measurements.<sup>18</sup>

PE measurements were performed on a spectrometer built using a GAMMADATA-SCIENTA SES2002 electron analyzer and a high-flux discharging lamp with a toroidal grating monochromator. The total energy resolutions (analyzer and light) for total valence band measurements using the  $\text{He I}\alpha$  (21.218 eV) and  $\text{He II}\alpha$  (40.814 eV) resonance lines were set to 70 and 100 meV, respectively, while that for  $E_F$  region was set to 8 meV. Ultrahigh-resolution measurement very close to  $E_F$  for a superconducting gap was done with 2.4 meV resolution. The sample temperatures were measured using a silicon-diode sensor mounted just close to it. The base pressure of the spectrometer was better than  $5 \times 10^{-11}$  Torr. Samples were fractured *in situ* to obtain clean surfaces and all the measurements were done within 3 h after the fractures. We did not see any spectral changes within the time interval, indicating the observed spectra are reflecting intrinsic electronic structures. Temperature dependent spectral changes were confirmed by cycling temperature across  $T_c$ .  $E_F$  of samples was referenced to that of a gold film evaporated onto the sample substrate and its accuracy is estimated to be better than  $\pm 0.05$  meV.

Figure 2 shows valence band PE spectra of superconducting  $\text{Ba}_8\text{Si}_{46}$  obtained at 5.4 K using  $\text{He I}\alpha$  and  $\text{He II}\alpha$ . The valence band spectrum measured with  $\text{He II}\alpha$  shows a peak at  $E_F$  and several features as shown by vertical lines. Corresponding structures are seen in  $\text{He I}\alpha$  spectrum, though the accessible energy region of  $\text{He I}\alpha$  spectrum is smaller than that of  $\text{He II}\alpha$  due to the smaller photon energy. In Fig. 2, we also show the total DOS obtained from the first principles calculations using local density approximation (LDA) (Ref. 19), incorporating a matrix element effect as well as resolution and lifetime broadening as a Gaussian with full width at half maximum (FWHM) of 0.5 eV. As shown with thin dotted lines, the experimentally observed features beyond 2 eV can be related to those in the calculated DOS. However, well-separated three prominent structures which can be assigned to Si  $3s$ , Si  $3s-p$ , and Si  $3p$  like states of the  $\text{Si}_{46}$  framework in the calculations do not clearly appear in the experimental spectrum. This indicates that the Ba atom influences the  $\text{Si}_{46}$  cage more than the expectation from band

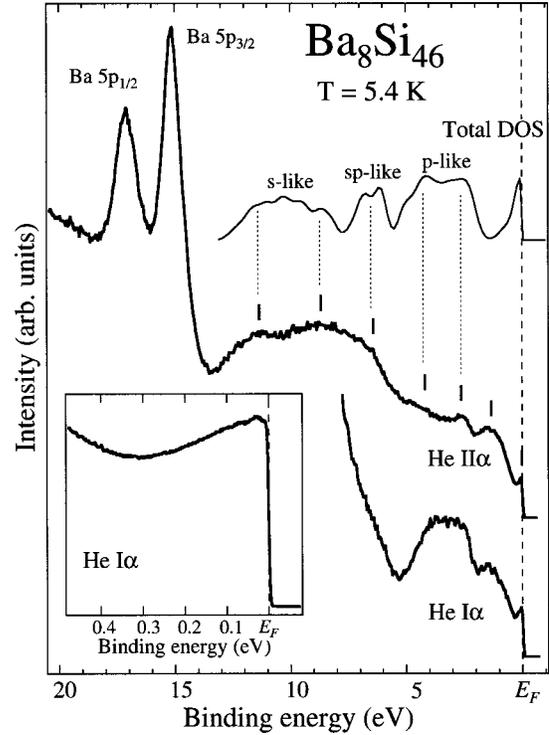


FIG. 2. Valence band PE spectra of  $\text{Ba}_8\text{Si}_{46}$  measured  $\text{He I}\alpha$  and  $\text{He II}\alpha$  resonance lines at 5.4 K (thick lines), together with the total DOS calculated by first principle LDA calculations (Ref. 19) including matrix element effects and broadened with a Gaussian with FWHM of 0.5 eV (thin line). The inset shows high-resolution (8 meV) spectra near  $E_F$  of  $\text{Ba}_8\text{Si}_{46}$ .

calculations, supporting the NMR study which confirmed the existence of strong hybridization in  $\text{Na}_x\text{Ba}_y\text{Si}_{46}$ .<sup>8</sup>

Furthermore, we find there is a substantial discrepancy between the present results and calculations especially for the electronic states within 2 eV below  $E_F$ . Besides a peak at  $E_F$ , we observe a broad hump at 1.5 eV in the observed spectrum, no representative structure of which we see in the calculation. The observed result is reminiscent of that reported for metal-insulator transition systems like  $\text{V}_2\text{O}_3$ .<sup>20</sup> As for the peak at  $E_F$ , the intensity seems smaller compared to the intensity of the bands at 2–6 eV, while those are similar in the calculation. Further, the width of the peak at  $E_F$  is smaller than that of the calculated one, as shown in the inset of Fig. 2. We see that the peak shows a width of  $\sim 0.3$  eV with fine structures near  $E_F$  (we will discuss this later), while the calculated peak has a width of  $\sim 1.5$  eV. These results indicate that the LDA calculation is not enough for describing the electronic structure of Si clathrate, implying importance of electron correlations which may be expected from the flat bands due to its large unit cell, as in the  $\text{C}_{60}$  crystals.<sup>2</sup> However, in order to address the electron correlation in the silicon clathrates, further studies including resistivity, specific heat, and de Haas–van Alphen measurements will be necessary.

In  $\text{He II}\alpha$  spectrum, we can observe Ba  $5p_{1/2}$  and  $5p_{3/2}$  shallow core levels at 17.1 and 15.1 eV binding energies, respectively. The energy position of the Ba  $5p_{3/2}$  is 15.1 eV

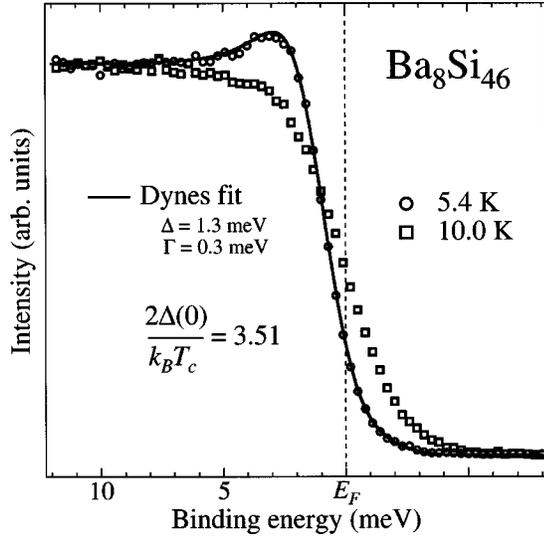


FIG. 3. Ultrahigh-resolution PE spectra of  $\text{Ba}_8\text{Si}_{46}$  measured at 5.4 K (superconducting state, open circles) and 10.0 K (normal state, open squares) using an energy resolution of 2.4 meV. A curve superimposed on the superconducting spectrum is the result of a numerical calculation using the Dynes function with  $\Delta=1.3$  meV and  $\Gamma=0.3$  meV.

and found to have a shift of 0.6 eV compared to that of a Ba metal (14.6 eV) (Ref. 21). This value is similar to the shift of  $5p_{3/2}$  reported for BaS (0.53 eV) but slightly smaller than that of BaO (0.86 eV) (Ref. 22), in which Ba atoms are believed to take a divalent state. This observation agrees with the NMR measurements<sup>8</sup> reporting that the Ba atoms are partially ionized, indicating a covalent-like bonding of Ba atoms and  $\text{Si}_{46}$  cages.

To study the superconducting electronic structure of  $\text{Ba}_8\text{Si}_{46}$ , we further performed ultrahigh-resolution measurements. In Fig. 3, we show the results measured at 5.4 K (superconducting state, open circles) and 10.0 K (normal state, open squares) normalized with area under the curve from 12 to  $-8$  meV. The normal state spectrum has a leading edge whose midpoint is nearly located at  $E_F$ . In contrast, the superconducting-state spectrum exhibits a spectacular redistribution of the spectral intensity from at and above  $E_F$  to higher binding energy, forming a new peak around 3 meV. This is a direct measurement of the superconducting gap of silicon clathrates. To obtain the magnitude of the superconducting gap, we have done numerical simulations using the Dynes function,<sup>23</sup> assuming a constant normal-state DOS and using the energy resolution of 2.4 meV. We superimpose a result using  $\Delta=1.3$  meV and  $\Gamma=0.3$  meV (curve), which well reproduces the superconducting spectrum as shown in Fig. 3. From the known temperature dependence of the superconducting gap for both weak- and strong-coupling superconductors,<sup>24</sup> we estimate the gap value at 0 K and obtain a reduced gap,  $2\Delta(0)/k_B T_c=3.51$ . This classifies  $\text{Ba}_8\text{Si}_{46}$  into a weak-coupling superconductor. We note that this value is similar to those obtained for  $\text{K}_3\text{C}_{60}$  and  $\text{Rb}_3\text{C}_{60}$  (3.53) using photoemission spectroscopy.<sup>25</sup>

Lastly, we turn to the structures near  $E_F$  but in slightly wider regions as shown in Fig. 4. First we emphasize that the

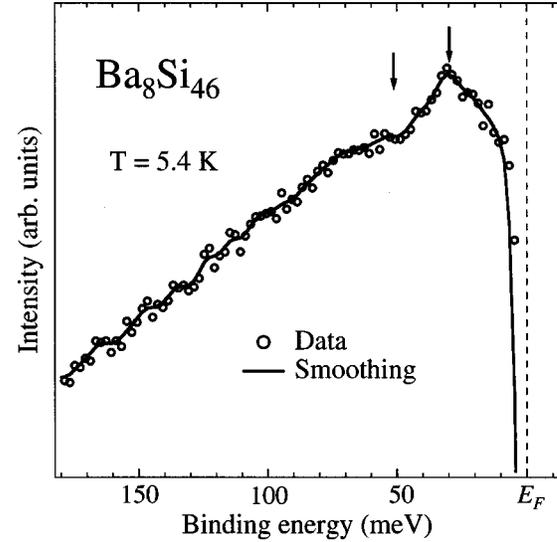


FIG. 4. High-resolution PE spectrum of  $\text{Ba}_8\text{Si}_{46}$  using an energy resolution of 8 meV (open circles) together with a smoothing curve demonstrating existence of fine structures. Arrows are representing the positions of a weak dip ( $\sim 50$  meV) and a maximum ( $\sim 30$  meV) in the intensity.

spectrum is for the superconducting state, though it does not show the superconducting condensation peak due to a lower resolution (8 meV) and a larger step size (2 meV) compared to the energy scale of the superconducting gap. As one can see, the intensity has a maximum at 30 meV and broad shoulder around 70 meV. Consequently, we observe a weak dip around 50 meV and intensity suppression close to  $E_F$ . We find that the energy positions of the dip and the maximum relate very well to the peak and dip positions in the phonon spectrum of  $\text{Na}_8\text{Si}_{46}$  (Ref. 16), respectively, indicating that the electrons are coupled with phonons in the superconducting state. We observe similar spectral shape even for normal state, consistent to the Raman scattering measurement reporting importance of electron-phonon coupling for the normal state.<sup>11</sup> These results suggest the superconductivity of silicon clathrate is most probably driven by phonon.

In conclusion, we have studied the electronic structure and superconducting transition of the silicon clathrate superconductor,  $\text{Ba}_8\text{Si}_{46}$ , using PE spectroscopy. We observed a peak at  $E_F$  for superconducting  $\text{Ba}_8\text{Si}_{46}$ , suggesting that the peak at  $E_F$  is a necessary feature to get superconductivity for this different type of superconductor. From the ultrahigh-resolution PE spectroscopy, we observe a reduced gap of 3.51 as well as phonon-induced features. These indicate the superconductivity of the silicon clathrate classified as a weak-coupling one most probably mediated by phonon. These experimental results provide important information on the electronic structure and the mechanism for this superconductor with the unique structure.

We would like to thank Dr. A. Chainani for valuable and stimulating discussion. This work was supported by grants from the Ministry of Education, Culture and Science of Japan. T.K. thanks JSPS for financial support.

- <sup>1</sup>J. S. Kasper, P. Hagenmuller, M. Pouchard, and C. Cros, *Science* **150**, 1713 (1965); C. Cros, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.* **2**, 570 (1970).
- <sup>2</sup>For review, see O. Gunnarsson, *Rev. Mod. Phys.* **69**, 575 (1994).
- <sup>3</sup>H. Kawaji, H. Horie, S. Yamanaka, and M. Ishikawa, *Phys. Rev. Lett.* **74**, 1427 (1995); S. Yamanaka, H. Horie, H. Nakano, and M. Ishikawa, *Fullerene Sci. Technol.* **3**, 21 (1995).
- <sup>4</sup>J. L. Cohn, G. S. Nolas, V. Fessatidis, T. H. Metcalf, and G. A. Slack, *Phys. Rev. Lett.* **82**, 779 (1999); J. S. Tse, K. Uehara, R. Rousseau, A. Ker, C. I. Ratcliffe, M. A. White, and G. MacKay, *ibid.* **85**, 114 (2000).
- <sup>5</sup>A. San-Miguel, P. Kéghélian, X. Blase, P. Mélinon, A. Perez, J. P. Itié, A. Polian, E. Reny, C. Cros, and M. Pouchard, *Phys. Rev. Lett.* **83**, 5290 (1999).
- <sup>6</sup>T. Kawaguchi, K. Tanigaki, and M. Yasukawa, *Phys. Rev. Lett.* **85**, 3189 (2000).
- <sup>7</sup>S. Saito and A. Oshiyama, *Phys. Rev. B* **51**, 2628 (1995).
- <sup>8</sup>F. Shimizu, Y. Maniwa, K. Kume, H. Kawaji, S. Yamanaka, and M. Ishikawa, *Phys. Rev. B* **54**, 13 242 (1996).
- <sup>9</sup>J. Gryko, P. F. McMillan, R. F. Marzke, A. P. Dodokin, A. A. Demkov, and O. F. Sankey, *Phys. Rev. B* **57**, 4172 (1998).
- <sup>10</sup>G. K. Ramachandran, P. F. McMillan, J. Diefenbacher, J. Gryko, J. Dong, and O. F. Sankey, *Phys. Rev. B* **60**, 12 294 (1999).
- <sup>11</sup>S. L. Fang, L. Grigorian, P. C. Eklund, G. Dresselhaus, M. S. Dresselhaus, H. Kawaji, and S. Yamanaka, *Phys. Rev. B* **57**, 7686 (1998).
- <sup>12</sup>Y. Guyot, B. Champagnon, E. Reny, C. Cros, M. Pouchard, P. Mélinon, A. Perez, and I. Gregora, *Phys. Rev. B* **57**, R9475 (1998).
- <sup>13</sup>R. Alben, D. Weaire, J. E. Smith, Jr., and M. H. Brodsky, *Phys. Rev. B* **11**, 2271 (1975).
- <sup>14</sup>D. Kahn and J. P. Lu, *Phys. Rev. B* **56**, 13 898 (1997).
- <sup>15</sup>M. Menon, E. Richter, and K. R. Subbaswamy, *Phys. Rev. B* **56**, 12 290 (1997).
- <sup>16</sup>P. Mélinon, P. Kéghélian, A. Perez, B. Champagnon, Y. Guyot, L. Saviot, E. Reny, C. Cros, M. Pouchard, and A. J. Dianoux, *Phys. Rev. B* **59**, 10 099 (1999).
- <sup>17</sup>P. Mélinon, P. Kéghélian, X. Blase, J. Le Brusca, A. Perez, E. Reny, C. Cros, and M. Pouchard, *Phys. Rev. B* **58**, 12 590 (1998).
- <sup>18</sup>S. Yamanaka, E. Enishi, H. Fukuoka, and M. Yasukawa, *Inorg. Chem.* **39**, 56 (2000).
- <sup>19</sup>K. Moriguchi, M. Yonemura, A. Shintani, and S. Yamanaka, *Phys. Rev. B* **61**, 9859 (2000).
- <sup>20</sup>For review, see M. Imada, A. Fujimori, and Y. Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998).
- <sup>21</sup>S. Hüfner, *Photoelectron Spectroscopy*, Springer Series in Solid State Sciences Vol. 82 (Springer-Verlag, Berlin, Heidelberg, 1995).
- <sup>22</sup>J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, in *Handbook of X-ray Photoelectron Spectroscopy*, edited by J. Chastain and R. C. King, Jr. (Physical Electronics, Inc., Eden Prairie, MN, 1995).
- <sup>23</sup>R. C. Dynes, V. Narayanamurti, and J. P. Garno, *Phys. Rev. Lett.* **41**, 1509 (1965).
- <sup>24</sup>D. J. Scalapino, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Vol. 1, Sec. IV.
- <sup>25</sup>R. Hesper, L. H. Tjeng, A. Heeres, and G. A. Sawatzky, *Phys. Rev. Lett.* **85**, 1970 (2000).