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References

1. M. Salmon, A. F. Diaz, A. J. Logan, M. Krounbi, and J. Bargon, *Mol. Cryst. Liq. Cryst.*, **83**, 1297 (1983).
2. (a) E. H. Song, J. K. Chon, and W. Paik, *Bull. Korean Chem. Soc.*, **9**, 43 (1988); (b) E. H. Song, J. K. Chon, and W. Paik, *ibid.*, **11**, 41 (1990).
3. K. Naoi, M. Lien, and H. Smyrl, *J. Electrochem. Soc.*, **138**, 440 (1991).
4. M. Nechtschein, F. Devreux, F. Genoud, E. Vieil, J. M. Pernaut, and E. Genies, *Synthetic Metals*, **15**, 59 (1986).
5. S. Dong, J. Dings, and R. Zhan, *J. Chem. Soc., Faraday Trans. I*, **85**, 1599 (1989).
6. W. J. Albery and C. C. Jones, *Faraday Discuss. Chem. Soc.*, **78**, 193 (1984).
7. E. M. Genies and J. M. Pernaut, *J. Electroanal. Chem.*, **191**, 111 (1985).
8. F. Devreux, F. Genoud, M. Nechtschein, and B. Villeret, *Synth. Met.*, **18**, 89 (1987).
9. F. T. A. Vork and L. J. J. Janssen, *Electrochim. Acta*, **33**, 1513 (1988).
10. J. C. Scott, P. Pfluger, M. T. Krounbi, and G. B. Street, *Phys. Rev. B*, **28**, 2140 (1983).
11. J. L. Bredas, J. C. Scott, K. Yakushi, and G. B. Street, *ibid. B*, **30**, 1023 (1984).
12. K. J. Wynne and G. B. Street, *Macromolecules*, **18**, 2361 (1985).
13. E. M. Genies, G. Bideu, and A. Diaz, *J. Electrochem. Soc.*, **149**, 101 (1983).
14. S. Asavapiriyant, G. K. Chandler, G. A. Chandler, G. A. Gunawardena, and D. Pletcher, *J. Electroanal. Chem.*, **177**, 229 (1984).

Substitutional Effects of Na in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ Oxide Superconductors

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Sodium substituted samples of $\text{Y}_{1-x}\text{Na}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ for $0.00 \leq x \leq 0.16$ were prepared and characterized by X-ray powder pattern, electrical resistivity and magnetic susceptibility measurements, Raman spectroscopy, and idometric titration. The Na substituted compounds have narrow solid solution limits where $0.00 \leq x \leq 0.16$. As the Na concentration increases, the parent orthorhombic structure tends to gradually change to tetragonal. Small changes in the superconducting transition temperature, T_c , are observed in this solid solution region. Raman spectra for the Na phases are virtually identical with that of $\text{YBa}_2\text{Cu}_3\text{O}_7$ except that the Cu(1)-O(4) stretching mode at 504 cm^{-1} and the Cu(2)-O(2,3) bending mode at 340 cm^{-1} for $x=0.16$ are slightly shifted. The hole concentrations of the sodium substituted compounds ranged from 0.31 to 0.33 per Cu site are increased with Na content. The substitution of Na^+ for Y^{3+} site appears to create oxygen vacancies in the Cu-O chains, causes structural change from orthorhombic to tetragonal, and increases hole concentration in the substituted system.

Introduction

Following the discovery of superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (hereafter YBCO) by Wu *et al.*¹, there have been a lot of research on the substitutional effects on almost all sites in the compound². These are mainly concerned with possible isolation of new high T_c superconducting phases as well as investigation of the physical properties caused by the substitutions. It has been known that substitution of Y^{3+} in YBCO by most trivalent rare earth elements has little effect on the superconducting properties³. This suggests that interactions between superconducting electrons and magnetic moments of the rare earth ions are relatively negligible even if the effective magnetic moments are changed by employing various isovalent cations⁴. In the case of the $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ compound, however, the superconductivity is severely suppressed as Pr concentration increases⁵. This anomalous

behavior in the Pr substituted YBCO is believed to be related to the mixed valent state of Pr ions (Pr^{3+} and Pr^{4+}), in which f electrons contributed by the Pr ion cause superconducting pair breaking in the Pr substituted compounds. These results prompt us to investigate the substituted YBCO system where the interlayer cation site (Y^{3+}) is replaced with other nonisovalent cations.

Sodium substituted compounds of the type $\text{Y}_{1-x}\text{Na}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ have been prepared by solid state reaction. Since the ionic size of monovalent Na^+ is almost identical with that of trivalent Y^{3+} , the Na^+ ion is expected to be substituted into Y^{3+} site without much effect on the structural integrity in the parent orthorhombic YBCO structure. From the structural standpoint, distortions in the sodium substituted phases might be expected to be negligible due to the small change in ionic radii. Structural distortions in the ABO_3 type perovskite structures are normally estimated by the value of toler-

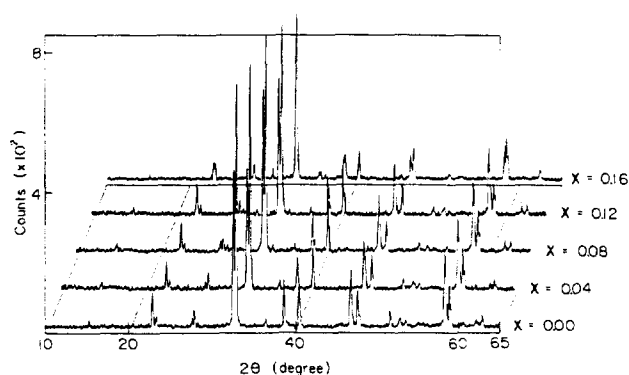


Figure 1. X-ray powder diffraction patterns for the $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$ compounds.

ance factor t given by $d_{A-O}/\sqrt{2} d_{B-O}$. Replacement of Y^{3+} with Na^+ , however, is expected to cause a significant change in the electronic environment of the CuO_2 sheets such as hole concentration and valence state of Cu ions due to the charge difference between two cations. This Na substitutional study on the interlayer cation site in YBCO is thus able to elucidate relationships between superconductivity, copper valence, and hole concentration.

In this paper we report experimental results on $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$ compounds. The sodium substituted phases were characterized by X-ray powder diffraction, electrical resistivity and magnetic susceptibility measurements, and Raman spectroscopy. In addition, hole concentrations were determined by an idometric titration method.

Experimental

Nominal compositions of $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$ ($x=0.00, 0.04, 0.08, 0.12, \text{ and } 0.16$) were prepared by solid state reactions. Stoichiometric amounts of Y_2O_3 (99.99%, Kojundo), Na_2CO_3 (99.99%, Aldrich), $Ba(NO_3)_2$ (99.98%, Aldrich), and CuO (99.99%, Kojundo) were mixed and pelletized. The samples were heated at $530^\circ C$ for 20 h before calcination to prevent $Ba(NO_3)_2$ from melting and to avoid loss of the volatile sodium. The resulting samples were reground and pelletized, which were then calcined at $900^\circ C$ for 20 h and sintered at $950^\circ C$ for 40 h under O_2 . X-ray powder diffraction of the compounds were obtained on a Rigaku diffractometer with $CuK\alpha$ radiation. The unit cell parameters were refined by the least square methods. Electrical resistivity measurements were carried out using a standard four probe method. The dc magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design). The oxygen contents and hole concentrations were determined by an idometric titration technique⁷. Raman spectra were obtained at room temperature using a SPEX-1403 double grating spectrometer and photon counting electronics. The polished samples were scanned at 0.5 cm^{-1} step with a time duration of 3 s.

Results and Discussion

The $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$ ($0.00 \leq x \leq 0.16$) compounds were characterized by various physicochemical techniques. Figure 1 displays X-ray powder diffraction (XRD) patterns of the

Table 1. Lattice Parameters and Unit Cell Volumes for $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$. All Peaks are Indexed with an Orthorhombic Cell

x	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	Volume(\AA^3)
0.00	3.813	3.879	11.653	172.365
0.04	3.824	3.896	11.707	174.437
0.08	3.825	3.893	11.708	174.323
0.12	3.826	3.894	11.712	174.489
0.16	3.864	3.891	11.674	175.543

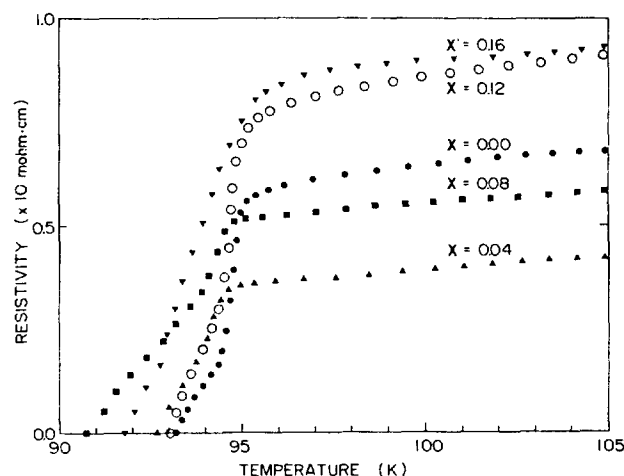


Figure 2. Resistivity as a function of temperature in the $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$ systems.

compounds. XRD patterns of the sodium phases are almost identical with that of YBCO, in which all the major peaks correspond to those of the parent YBCO compound. Earlier reports on the sodium substituted YBCO compound reveal that Na can substitute Y in YBCO compound up to $x=0.5$ ⁸. However, our careful studies on the sodium substitution for Y in YBCO compound suggest that the sodium substituted phases have a narrow solid solution range of $0.00 \leq x \leq 0.16$. Beyond $x=0.16$, $BaCuO_2$ is formed as a major impurity which was identified in the XRD patterns and Raman spectra. This might be attributed to the large difference in the charge states of Na^+ and Y^{3+} . This charge difference appears to make it difficult to form a complete range of solid solutions even though the size constraint should enable Na^+ to substitute into Y^{3+} site.

As Na concentration increases, the (103) and (013) peaks separated in YBCO ($x=0.00$) at $2\theta=32.56$ and 32.85 , respectively, are merging to one peak. Similarly other peaks having (hkl) and (khl) peaks show a tendency to overlap with Na contents, indicating that structural strain is gradually reduced in the Na substituted YBCO compounds. This might be due to substitution of lower valent Na^+ for trivalent Y^{3+} , which would cause anion vacancy in the system and result in the deficiency in the oxygen sites. The lattice parameters and cell volumes calculated from the XRD data are shown in Table 1, where the peaks are indexed with an orthorhombic cell. The c axes of the sodium phases are elongated compared with that of YBCO. Similar changes in lattice constants are observed in oxygen deficient YBCO, where the parent

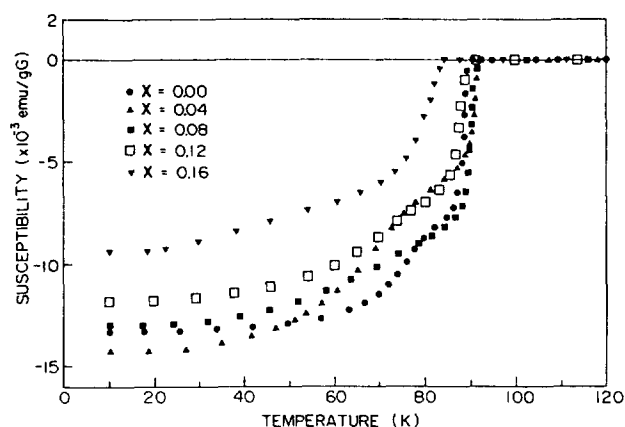


Figure 3. Magnetic susceptibility vs. temperature for the $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$ compounds.

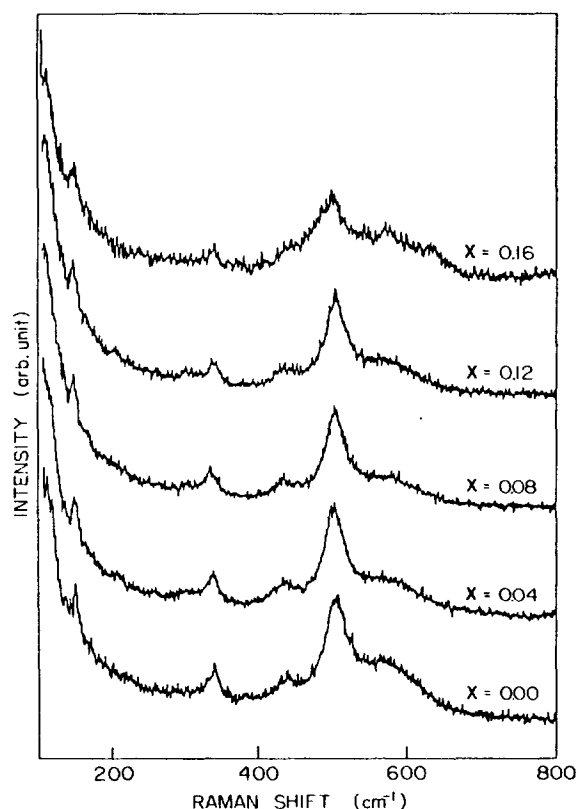


Figure 4. Raman spectra of the $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$ phases.

orthorhombic structure changes to tetragonal with decreasing oxygen content in the Cu-O chain site⁹. In the Na substituted system, the oxygen vacant sites would be created by the substitution of lower valent Na^+ for trivalent Y^{3+} site in order to preserve charge balance in the host structure.

Figure 2 displays resistivity plots as a function of temperature for the $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$. Resistivity data show that the superconducting transition temperatures of the sodium compounds appear not to be affected by Na dopants. Resistivity measurements, however, are not able to tell the volume fraction of the superconducting phase. The magnetic susceptibility data versus temperature shown in Figure 3 clearly demonstrate the decreasing fraction of the superconducting

Table 2. Frequencies in cm^{-1} of Raman Vibrational Modes in $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$

x	Raman shifts (cm^{-1})				
0.00	504	438	340	150	115
0.04	504	438	339	150	115
0.08	504	435	339	150	115
0.12	503	438	340	150	114
0.16	498	445	340	150	115

phase with Na contents, where the samples were measured at a constant applied field of 20 Oe. Degrees of flux expulsion and T_c are gradually decreased as Na concentration increases. Especially for the $x=0.16$ sample, T_c and volume fraction of superconducting phase was severely depressed. This might be associated with the abrupt change in structure which resulted from oxygen vacancies on the Cu-O chain site. This behavior in the degradation of superconductivity in the sodium phases is similar with that observed in oxygen deficient YBCO, in which T_c is depressed with decreasing oxygen content¹⁰.

Raman spectra for the Na substituted samples shown in Figure 4 give similar patterns with that of YBCO. Most of the peak positions in the sodium phases shown in Table 2 are pretty close to those of the YBCO bands. In the case of the $x=0.16$ sample, however, the 504 cm^{-1} mode which is assigned as axial motion of Cu(1)-O(4) in the Cu-O chain shifts to slightly lower frequency while the bending mode of the Cu(2)-O(2,3) in the CuO_2 layer at 438 cm^{-1} moves to higher frequency. These behaviors in Raman modes for the Na substituted compounds are similar to the trends observed in Raman spectra of the oxygen deficient YBCO^{11,12}. These results are also consistent with the XRD data of the sodium compounds. However, the Raman spectra of the rare earth substituted compounds are different from that of the sodium compound, in which the Raman modes at 504 and 340 cm^{-1} in YBCO are mostly affected by the substitution for Y site¹³. These results indicate that substitution by the Na^+ ion primarily affects oxygens on the Cu-O chain site which are not directly coordinated with the interlayer cation site. If the Na substituents affect the CuO_2 layers, the behaviours of the Raman modes will be similar with those of the fluorine substituted YBCO compound in which fluorine atoms exclusively substituted into the oxygens of the CuO_2 layers¹⁴.

Oxygen contents and hole concentration in the Na substituted compounds were determined by an idometric titration. For the $x=0.16$ sample, the idometric titration was not carried out due to the presence of little amount of impurity phases. As expected from the XRD and Raman results, the oxygen contents are decreased with Na contents. Figure 5 shows the result of oxygen contents and hole concentrations as a function of Na contents. The hole concentration of the whole system was calculated by using sodium and oxygen contents¹⁵. As Na concentration increases, the oxygen content is gradually decreased and the hole concentration is increased reversely. Oxygen defects in the Cu-O chain site would thus increase holes in the Na substituted system. However, it is not clear yet whether the extra holes are located on

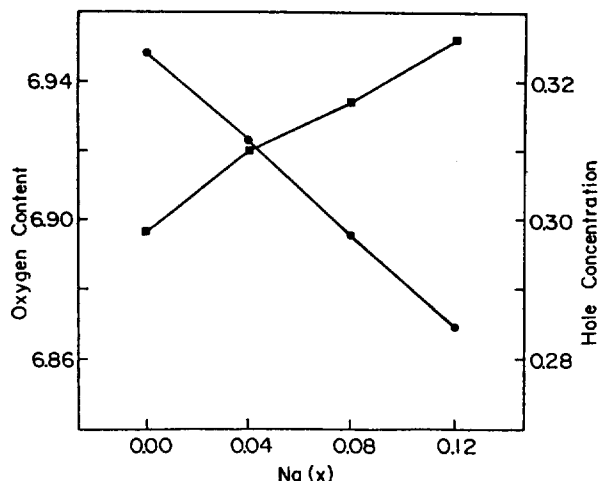


Figure 5. Oxygen content (●) and hole concentration (■) vs. Na content for $Y_{1-x}Na_xBa_2Cu_3O_{7-y}$ compounds. Errors associated with measured oxygen contents are estimated to be ± 0.01 .

the Cu-O chains or the CuO_2 sheets. The location and concentration of mobile holes are important to understand the relationship between hole contents and superconductivity. Shafer *et al.* reported that T_c was largely influenced by concentration of the mobile CuO_2 sheets¹³. However, we did not determine the mobile hole concentration at this moment.

Summary

Effects of Na substitution for Y in YBCO have been investigated. We have found that monovalent sodium can be substituted into yttrium site up to $x=0.16$ without much changing superconducting properties in the parent YBCO. This result is different from that of the rare earth substituted YBCO compounds where the trivalent rare earth elements completely substituted the yttrium site in YBCO compound. Substitution by lower valent Na^+ would create oxygen vacancies and produce holes in the Na substituted system. On the basis of the XRD and Raman spectral data, the oxygen vacant sites will be Cu-O chains which are not directly bonded to the Na atom. Our experimental results suggest that replacement of Y^{3+} with Na^+ affects electronic environments mainly in non-bonded Cu-O chains and causes little effects on adjacent CuO_2 sheets.

Currently we are carrying out Hall measurement to determine the mobile hole concentrations and performing Rietveld analysis to obtain in plane Cu-O bond length which are believed to be correlated with T_c ¹⁶. Both data will give a clue to understand the relationship between hole concentration, in plane Cu-O bond, and T_c in the Na substituted system.

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References

1. M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R.

- L. Meng, L. Gao, Z. L. Huang, Y. Q. Want, and C. W. Chu, *Phys. Rev. Lett.*, **58**, 908 (1987).
- (a) S. Ram and K. A. Narayan, *Phys. Rev. B*, **42**, 8628 (1990); (b) H. Shakad, J. Faber Jr, B. W. Veal, R. L. Hitterman, and A. P. Pauldas, *Solid State Commun.*, **75**, 445 (1990); (c) J. B. Parise and E. M. McCarron III, *J. Solid State Chem.*, **83**, 188 (1989).
- (a) E. M. Engler, V. Y. Lee, A. I. Nazzari, R. B. Beyers, G. Lim, P. M. Grant, S. S. P. Parkin, M. L. Ramirez, J. E. Vasquez, and R. J. Savory, *J. Am. Chem. Soc.*, **109**, 2848 (1987); (b) Z. Fish, J. D. Thomson, E. Zirngiebl, J. L. Smith, and S. W. Cheong, *Solid State Commun.*, **62**, 743 (1987); (c) H. Hosoya, S. Shamoto, M. Onoda, and M. Sato, *Jpn. J. Appl. Phys.*, **26**, L325 (1987).
- J. T. Markert, Y. Dalichaouch, and M. B. Maple, in *Physical Properties of High Temperature Superconductors*; Ginsberg, D. M., ed; World Scientific Publishing Co.: Singapore, 1989; pp 265-339.
- (a) I. Yang, A. G. Schrott, and C. C. Tsuei, *Phys. Rev. B*, **41**, 8921 (1990); (b) A. Kebede, C. S. Jee, J. Schwegler, J. E. Crow, T. Mihalisin, G. H. Myer, R. E. Salmon, P. Schlottmann, M. V. Kuric, S. H. Bloom, and R. P. Guertin, *Phys. Rev. B*, **40**, 4453 (1989); (c) C. Jee, A. Kebede, D. Nichols, J. E. Crow, T. Mihalisin, G. H. Myer, L. Perez, R. E. Salomon, and P. Schlottmann, *Solid State Commun.*, **69**, 379 (1989).
- (a) N. Ramadass, *Mater. Sci. & Eng.*, **36**, 231 (1978); (b) A. Manthiram, X. X. Tang, and J. B. Goodenough, *Phys. Rev. B*, **42**, 138 (1990); (c) H. Oestereicher, *J. Solid State Chem.*, **76**, 229 (1988).
- J. H. Choy, S. Y. Choi, S. H. Byeon, S. H. Chun, S. T. Hong, D. Y. Jung, W. Y. Choe, and Y. W. Park, *Bull. Korean Chem. Soc.*, **9**, 289 (1988).
- (a) Y. Dalichaouch, M. S. Torikachvili, E. A. Early, B. W. Lee, C. L. Seaman, K. N. Yang, H. Zhou, and M. B. Maple, *Solid State Commun.*, **65**, 1001 (1988); (b) A. Fartash and H. Oestereicher, *ibid.*, **66**, 39 (1988).
- J. D. Jorgensen, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, H. Claus, and W. K. Kwok *Phys. Rev. B*, **41**, 1863 (1990).
- (a) J. M. Tarascon, W. R. Mckinnon, L. H. Greene, G.W. Hull, and E. M. Vogel, *Phys. Rev. B*, **36**, 226 (1987); (b) R. J. Cava, B. L. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, *Nature*, **329**, 423 (1987).
- J. R. Ferraro and V. A. Maroni, *Appl. Spec.*, **44**, 351 (1990).
- (a) F. E. Bates, *Phys. Rev. B*, **39**, 322 (1989); (b) R. M. Macfarlane, H. J. Rosen, E. M. Engler, R. D. Jacowitz, and V. Y. Lee, *Phys. Rev. B*, **38**, 284 (1988).
- H. J. Rosen, R. M. Macfarlane, E. M. Engler, V. Y. Lee, and R. D. Jacowitz, *Phys. Rev. B*, **38**, 2460 (1988).
- S. K. Cho, D. Kim, J. S. Choi, and K. H. Kim, *J. Phys. Chem. Solids*, **51**, 113 (1990).
- (a) M. W. Shafer, T. Penny, and B. L. Olson, *Phys. Rev. B*, **36**, 4047 (1987); (b) M. W. Shafer, T. Penny, B. L. Olson, R. L. Greene, and R. H. Koch, *Phys. Rev. B*, **39**, 2914 (1989).
- M.-H. Whangbo and C. C. Torardi, *Acc. Chem. Res.*, **24**, 127 (1991).