

- 4533 (1988); (b) A. B. Reitz, S. O. Northey, B. E. Maryanoff, D. Liotta, and R. Monahan, III, *J. Org. Chem.*, **52**, 4191 (1987); (c) P. A. Bartlett, "Asymmetric Synthesis", ed. J. D. Morrison, Academic Press, London, Vol 3, p. 411 (1984).
6. (a) K. C. Nicolaou, *Tetrahedron*, **37**, 4097 (1981); (b) K. C. Nicolaou, R. L. Magolde, W. J. Sipio, W. E. Barnette, Z. Lysenko, and M. M. Joullie, *J. Am. Chem. Soc.*, **102**, 3784 (1980).
7. J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 734 (1976).
8. P. H. J. Carlson, T. Katsuki, V. S. Martin, and K. B. Sharpless, *J. Org. Chem.*, **46**, 3936 (1981).
9. A. I. Meyers and J. P. Lawson, *Tetrahedron Lett.*, **23**, 4883 (1982).
10. P. J. Kocienski, B. Lythgoe, and S. Ruston, *J. Chem. Soc., Perkin Trans.*, **1**, 829 (1978).
11. M. Schwarz, G. F. Graminski, and R. M. Waters, *J. Org. Chem.*, **51**, 260 (1986).
12. F. B. Gonzalez and P. A. Bartlett, *Org. Synthesis*, **64**, 175 (1986).
13. A. Toshimitsu, K. Terao, and S. Uemura, *J. Org. Chem.*, **52**, 2018 (1987).

## Dopping Effect of Fluorine Atom on the Superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$

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The normal and fluorinated high- $T_c$  superconducting materials,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$  with  $0.25 \leq x \leq 0.55$  and  $0.00 \leq y \leq 0.30$ , were synthesized to investigate the doping effect of fluorine atom on the superconductivity of Y123 and studied by X-ray diffraction analysis and electron probe microanalysis, resistivity and thermopower measurements, and polarized micro-Raman spectroscopy. The reproducible micro-Raman spectra were recorded and analyzed. The coherent assignments could be suggested for the spectra of normal and fluorinated samples. The fluorine atoms introduced were found to be substituted for oxygen in pyramidal Cu-O units rather than in Cu-O chains. The unit cell parameters were decreased upon the substitution of oxygen by fluorine atom. From the decreasing cell parameters and  $T_c$ , the increasing thermopower, and the possible assignments of the vibrational modes, it could be suggested that the doping of fluorine atom localizes the superconducting electrons in Y123.

### Introduction

The thermopower measurement has been considered to be a fine method to study the electronic properties of superconductor based on its sensitivity to the electron energy-band structure and the electron-excitation interactions. Since the experimental results as well as their interpretations differ from one to another<sup>1-9</sup>, this is true only if the obtained experimental results are comprehensive and interpreted exactly. It is well known that the oxygen content in a superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  is an important parameter to determine its superconductivity. In this point of view, it is important to study the thermopower of the new oxide superconductors as a function of the oxygen content for a exact superconducting properties.

The thermopower of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconductive ceramic samples was measured as a function of oxygen concentration based on the different baking temperatures of the samples<sup>10</sup>. Choi *et al.*<sup>10</sup> found that both the magnitude and the temperature dependence of the thermopower strongly depend on the oxygen deficiency in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

It was also found and suggested that the magnitude of the thermopower as a function of oxygen deficiency varied consistently with the change of the superconducting electron density and the magnon-drag effect should be considered

seriously for the superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

On the other hand, it is helpful in order to understand superconductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  to investigate whether the fluorine atoms are substituted for oxygen atoms in the chain Cu-O or the pyramidal Cu-O of the superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  by Raman spectroscopy. It has been reported by several workers<sup>11-16</sup> that the Cu-O vibrations in the superconducting Y123 system are consisted of Cu-O bending, chain Cu-O stretching and pyramidal Cu-O stretching based on Raman spectroscopy studies. The Raman lines at 335, 506 and 601  $\text{cm}^{-1}$  have been assigned to Cu-O bending, pyramidal Cu-O stretching and chain Cu-O stretching vibrations, respectively. The symmetric and asymmetric pyramidal Cu-O stretching vibrational modes have also been observed at 502 and 589  $\text{cm}^{-1}$  respectively in Y123 superconductors<sup>13,15</sup>.

The aim of this work is to investigate the doping effect of the fluorine atom on the superconductivity of the fluorinated Y123 system from X-ray and electron probe microanalyses, resistivity and thermopower measurements, and Raman spectroscopy.

### Experimental

$\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$  was prepared from the following mixture: 0.5000  $\text{Y}_2\text{O}_3$ , 2.000  $\text{BaCO}_3$  and 3.000  $\text{CuO}$ .  $\text{Y123O}_{7-x}\text{F}_y$

phases containing varying amounts of fluorine atoms were prepared from the following sets of mixtures: 2.950 CuO, 0.0500  $\text{CuF}_2$ , 0.5000  $\text{Y}_2\text{O}_3$  and 2.000  $\text{BaCO}_3$ ; 2.925 CuO, 0.0750  $\text{CuF}_2$ , 0.5000  $\text{Y}_2\text{O}_3$  and 2.000  $\text{BaCO}_3$ ; 2.900 CuO, 0.1000  $\text{CuF}_2$ , 0.5000  $\text{Y}_2\text{O}_3$  and 2.000  $\text{BaCO}_3$ ; and 2.850 CuO, 0.1500  $\text{CuF}_2$ , 0.5000  $\text{Y}_2\text{O}_3$  and 2.000  $\text{BaCO}_3$ . Each mixture was ball-mill-mixed, finely ground, calcined at 840 °C for 9h in air, sintered at 920 °C for 8h in air, annealed at 740 °C for 13h in air, and then cooled to room temperature in air at a cooling rate of 40 °C  $\text{h}^{-1}$ . The well-mixed powder was pressed into a pellet under 49.03 MPa and the pellet sintered at 910 °C for 14h in air and then annealed at 520 °C for 9h. After annealing, each specimen was furnace-cooled to room temperature at a cooling rate of 40 °C  $\text{h}^{-1}$ . Assuming that no hydrolysis exists and the  $\text{CuF}_2$  is stable, the expected compositions are close to  $\text{Y123O}_{6.65}\text{F}_{0.10}$ ,  $\text{Y123O}_{6.60}\text{F}_{0.15}$ ,  $\text{Y123O}_{6.55}\text{F}_{0.20}$  and  $\text{Y123O}_{6.45}\text{F}_{0.30}$ .

X-ray diffraction powder analyses were carried out on a diffractometer (Phillips, PW1710,  $\text{CuK}\alpha$ ) equipped with a curved graphite monochromator in a selected beam path. Electron probe microanalyses were performed to see if  $\text{BaCuO}_2$  microcrystals were incorporated in the larger normal and fluorinated Y123 polycrystals, since the Raman spectra lines due to this  $\text{BaCuO}_2$  impurity phase as well as the present normal and fluorinated Y123 superconductors were observed at frequencies of 630–640  $\text{cm}^{-1}$ . No  $\text{BaCuO}_2$  phase was detected by electron probe microanalyses (EPMA, JEOL JCX 333).

A specimen of about  $1.4 \times 6.0 \times 15 \text{ mm}^3$  in volume was cut from the pellet and used for resistance measurements by a standard four-probe a.c. technique. Copper wires were employed as electrical leads and were attached to the sample with conducting indium. The current used for the resistance measurements was 5–30 mA. The resolution of the voltage measurement was  $1 \times 10^{-7}\text{V}$ . The potential difference was measured with a lock-in amplifier (EG & G Co., PARC 5210) up to 10  $\mu\text{V}$  on an IBM-PC/AT and the frequency was fixed near 110Hz. The temperature was measured with a copper-constantan thermocouple. A multiplexer board (PCLD 789 MUX; Advantech Co., Ltd.) and a 14-bit A/D converter (PCL 714; Advantech Co., Ltd.) were used to convert voltage into temperature, and the error range of temperature was  $\pm 0.01^\circ\text{C}$ . The measured resistance was converted to resistivity using cell parameters. The thermopower was measured by employing the dc method. A sample with a typical volume of about  $10 \times 2 \times 0.2 \text{ mm}^3$  was mounted on two copper blocks, one of them was heated by a nichrome wire. The temperature gradient across the sample was monitored by a Chromel-Constantan thermocouple mounted independently on the copper blocks. The resistivity was measured through the low-frequency a.c. four-probe technique.

Polarized Raman spectra of selected micro-crystals extracted from sintered samples were recorded at room temperature on a Dilor micro-Raman spectrometer (Omars 89) equipped with a photo-diode array multichannel detector and an ion argon laser source (Spectra-Physics 164) emitting a line at 514.5 nm.

## Results and Discussion

The typical powder X-ray diffraction patterns of the nor-

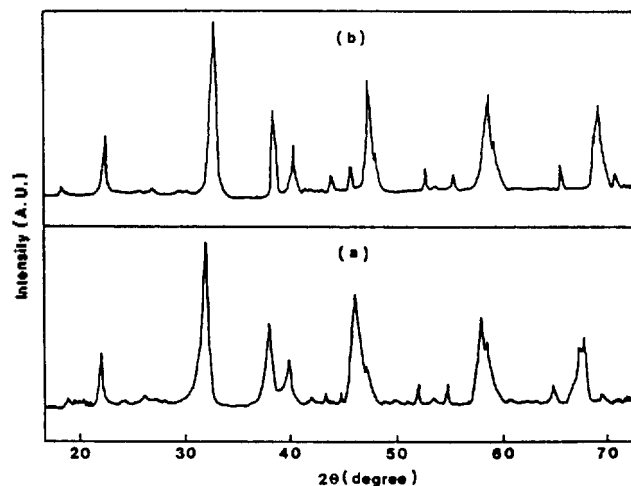


Figure 1. X-ray diffraction patterns of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ (a) and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.45}\text{F}_{0.30}$ (b) superconductors.

Table 1. Unit Cell Parameters for the Normal and Fluorinated  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$  Superconductors with Orthorhombic Symmetry

$x$	$y$	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$
0.25	0.00	3.855	3.895	11.77
0.55	0.30	3.800	3.840	11.62
0.45	0.20	3.820	3.860	11.68
0.40	0.15	3.830	3.870	11.71
0.35	0.10	3.840	3.880	11.74

mal and fluorinated Y123 samples are shown in Figure 1. Based on X-ray diffraction patterns and electron probe microanalysis, the present normal and fluorinated Y123 samples are all identified as essentially a single phase with the layered perovskite structure. The phase of the sample was found to be an orthorhombic and oxygen deficient perovskite with a chemical composition of  $0.25 \leq x \leq 0.55$  determined from redox titration<sup>17</sup>. The X-ray powder diffraction data of the sample were successfully indexed on the basis of an orthorhombic symmetry with the cell parameters listed in Table 1. The cell parameters indicate that the present compounds are typical perovskite-type, showing the length of the  $c$  axis is approximately three times as long as that of the  $a$  or  $b$  axis. The substitution of oxygen atom by fluorine atom decreases the unit cell parameters as considered from the difference in ionic radii. The unit cell volume ( $V_m$ ) decreases with increase in fluorine atom amount in the fluorinated Y123 superconductor, as shown in Figure 2.

From the electron probe microanalysis, it was found that the homogeneous backscattered electron intensities showed no compositional zoning and the X-ray image of Y atom indicated homogeneous Y-distribution in the normal and fluorinated Y123 superconductors. However, very small dips appeared in the middle of the line profile for the normal Y123 sample and in the corner of the fluorinated Y123, indicating the rough surfaces of the specimens. In order to identify the dips, magnified portions of the Y-distributions for both normal and fluorinated samples were analyzed and gave identical results. No compositional variation was detected from the quantitative analysis, showing that no microcrystal im-

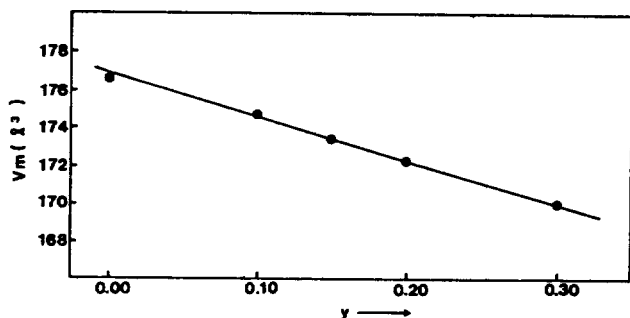


Figure 2. The unit cell volume ( $V_m$ ) vs. fluorine atom contents for the fluorinated Y123 superconductors.

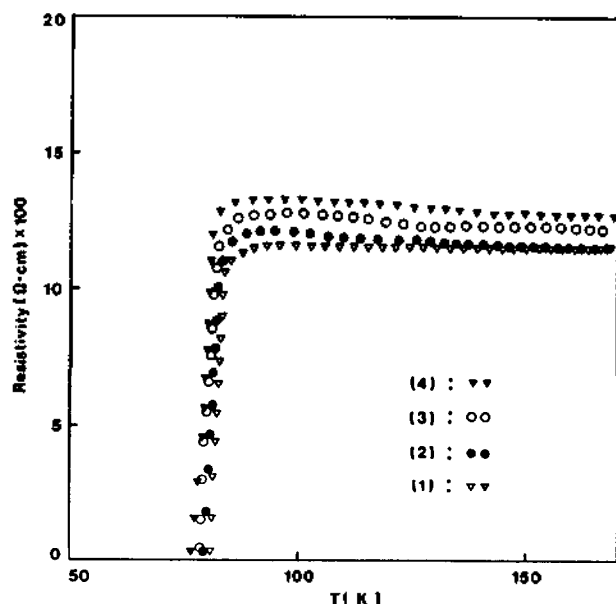


Figure 3. Resistivity vs. temperature (K) for various samples: (1)  $x = 0.25, y = 0$ ; (2)  $x = 0.35, y = 0.10$ ; (3)  $x = 0.45, y = 0.20$  and (4)  $x = 0.55, y = 0.30$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$ .

purities such as  $\text{BaCuO}_2$  exist in the present  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$  superconductors.

The typical resistivities for the normal and fluorinated Y123 are shown in Figure 3. The zero-resistivity critical temperatures decrease with increase in the amount of fluorine atoms. This implies that the higher electro-negativity of fluorine atom than that of oxygen atom localizes the superconducting electrons and drops the charge carrier mobility. This phenomenon was also observed in the thermopower measurements.

As can be seen in Figure 4, the thermopower at 273K is positive for the fluorinated Y123 and increases with increasing fluorine atom amount. Based on the localization of superconducting electrons, the electron concentration and mobility should be reduced for  $0.35 \leq x \leq 0.55$  and  $0.00 \leq y \leq 0.30$  in the normal and fluorinated  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$ . According to the simple theory and the sign of the measured thermopower, the major charge carrier of the present superconductor is an electron, since the thermopower of conductor is approximately inverse proportional to the carrier concentration. It is satisfied that the positive thermopower of the fluorinated Y123 increases along with the amount of fluorine

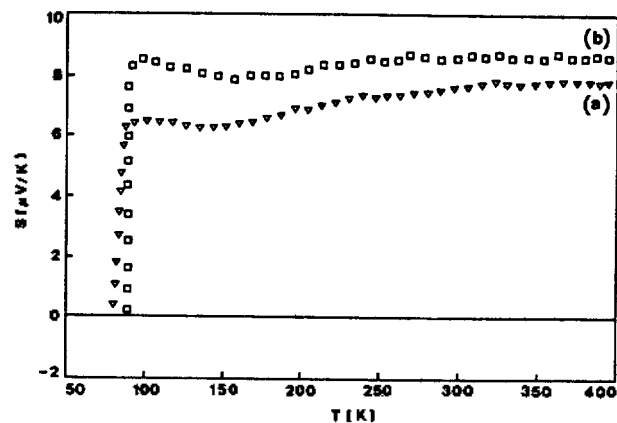


Figure 4. Temperature dependence of the thermopower of fluorinated Y123 superconductors: (a)  $x = 0.35, y = 0.10$ ; (b)  $x = 0.40, y = 0.15$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$ .

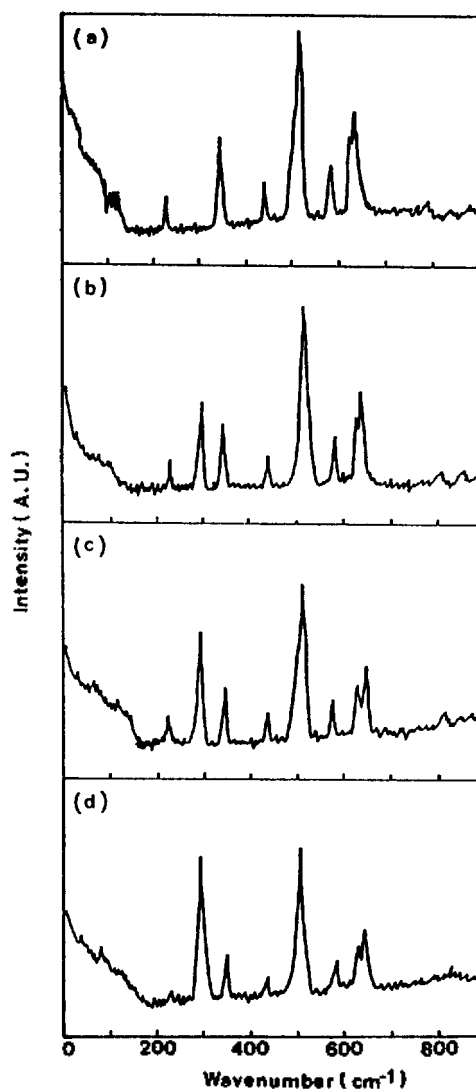


Figure 5. Typical Raman spectra of microcrystals of the normal and fluorinated Y123 superconductors obtained at room temperature: (a)  $x = 0.33, y = 0$ ; (b)  $x = 0.43, y = 0.10$ ; (c)  $x = 0.53, y = 0.20$  and (d)  $x = 0.55, y = 0.30$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$ . (a), (b) and (c): data from ref. (16).

**Table 2.** Comparison of Raman Band Frequencies of the Normal and Fluorinated Y123 Superconductors: (a)  $x = 0.33$ ,  $y = 0$ ; (b)  $x = 0.43$ ,  $y = 0.10$ ; (c)  $x = 0.53$ ,  $y = 0.20$  and (d)  $x = 0.55$ ,  $y = 0.30$  in  $YBa_2Cu_3O_{7-x}F_y$ ; (a), (b) and (c): data from ref. (16)

(a)	(b)	(c)	(d)	Mode assignments
220	220	220	220	
—	298	298	298	pyramidal F-Cu-O stretching
337	337	337	337	Cu-O bending
445	445	445	445	
501	501	501	501	pyramidal Cu-O stretching
582	582	582	582	
623	623	623	623	
637	637	637	637	Cu-O chain stretching

atom. The large magnitude of thermopower implies that the superconductivity of the fluorinated Y123 is not metallic, but by the activated carriers. This is also consistent with the temperature dependence of resistivity shown in Figure 3.

Figure 5 shows typical Raman spectra of micro-crystals of ( $x = 0.33$ ,  $y = 0$ ), ( $x = 0.43$ ,  $y = 0.10$ ), ( $x = 0.53$ ,  $y = 0.20$ ), and ( $x = 0.55$ ,  $y = 0.30$ ) in  $YBa_2Cu_3O_{7-x}F_y$  superconductors. As shown in Table 2, all of the Raman band frequencies are the same, irrespective of the amount of fluorine atom. A new Raman band at  $298\text{ cm}^{-1}$ , however, appears in the fluorinated superconductors, tentatively assigning to pyramidal F-Cu-O stretching. The intensity of the  $298\text{ cm}^{-1}$  band increases with increase in fluorine atom amount. This increase of  $298\text{ cm}^{-1}$  band intensity reduces the intensities of the other bands, relatively with the increasing fluorine atom concentration. Based on these phenomena, the fluorine atom substitutes for an oxygen atom in the pyramidal Cu-O units rather than in the Cu-O chains, since the Cu-O vibrations in the Cu-O chains occur at frequencies higher than  $298\text{ cm}^{-1}$ . For the normal Y123, the Cu-O chain stretching vibration takes place at  $623\text{ cm}^{-1}$ , but the pyramidal Cu-O stretching does at  $501\text{ cm}^{-1}$  (13-16,18).

It is concluded that the fluorine atom substituted for an oxygen atom in the pyramidal Cu-O units from Raman data (Figure 5) localizes the superconducting electrons and results in reductions of the mobility and carrier concentration from resistivity and thermopower data (Figures 3 and 4), indicating the decreasing  $T_c$  and increasing thermopower as the fluorine atom amount increases.

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## References

1. A. P. Goncalves, I. C. Santos, E. B. Lopes, R. T. Henriques, M. Almeida, and M. D. Figueiredo, *Phys. Rev.*, **B37**, 7476 (1988).
2. N. Mitra, J. Trefny, M. Young, and B. Yarar, *Phys. Rev.*, **B36**, 5581 (1987).
3. H. J. Tordahl and A. Mawdsley, *Phys. Rev.*, **B35**, 8881 (1987).
4. C. Uher and A. B. Kaiser, *Phys. Rev.*, **B36**, 5680 (1987).
5. M. F. Hundley, A. Zettl, A. Stacy, and M. C. Cohen, *Phys. Rev.*, **B35**, 8800 (1987).
6. R. C. Yu, M. J. Naughton, X. Yan, P. M. Chaikin, F. Holtzberg, R. L. Greene, J. Stuart, and P. Davis, *Phys. Rev.*, **B37**, 7963 (1988).
7. T. Chen, C. J. McEwan, L. E. Wegner, and E. M. Logothetis, *Phys. Rev.*, **B35**, 7124 (1987).
8. R. C. Budhani, Sin-Mo H. Tzeng, and R. F. Bunshah, *Phys. Rev.*, **B36**, 8873 (1987).
9. C. Uher, A. B. Kaiser, E. Gmelin, and L. Walz, *Phys. Rev.*, **B36**, 5676 (1987).
10. W. N. Kang, K. C. Cho, Y. M. Kim, and Mu-Yong Choi, *Phys. Rev.*, **B39**, 2763 (1989).
11. R. M. Macfarlane, H. Rosen, and H. Seki, *Solid State Commun.*, **63**, 831 (1987).
12. R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.*, **58**, 2340 (1987).
13. Y. Dai, J. J. Swinnea, H. Steinfink, J. B. Goodenough, and A. Campion, *J. Am. Chem. Soc.*, **109**, 5291 (1987).
14. H. Rosen, E. M. Engler, T. C. Strand, V. Y. Lee, and D. Bethune, *Phys. Rev.*, **B36**, 726 (1987).
15. Z. Iqbal, S. W. Steinhauser, A. Bose, N. Cipollini, and H. Eckhardt, *Phys. Rev.*, **B36**, 2283 (1987).
16. S. K. Cho, D. Kim, J. S. Choi, and K. H. Kim, *J. Phys. Chem. Solids*, **51**, 113 (1990).
17. D. C. Harris, M. E. Hills, and T. A. Hewston, *J. Chem. Ed.*, **64**, 847 (1987).
18. P. B. Kirby, M. R. Harrison, W. G. Freeman, I. Samuel, and M. J. Haines, *Phys. Rev.*, **B36**, 8315 (1987).