Rietveld Analysis of the Superconducting $Na_xH_yC_{60}$

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The room temperature structure of a superconducting phase of $Na_xH_yC_{60}$ was determined from the analysis of its powder X-ray diffraction pattern by the Rietveld method. The space group is $Fm\bar{3}m$, with Z=4, and the refined cell parameter a is 14.406(1) Å. Na^+ ions in the octahedral and tetrahedral interstitial sites are off-centered. From their occupancies, the composition x is estimated at 3.6.

Na_3C_{60} does not reveal superconductivity (SC) although it has the electronic structure similar to those of K_3C_{60} and Rb_3C_{60} superconductors.[1-3] The peculiarity originates in the inherent phase-instability of Na_3C_{60}, where a small Na^+ ion is contained in a large octahedral interstitial site. In order to get the stability, we have tried to introduce spacers into the vacancies around Na^+ ions. We succeeded in obtaining a nitrogen-included sodium-C_{60} superconductor. It was prepared by the reaction between C_{60} and sodium azide (NaN_3).[4] Superconductivity was also observed for hydrogen-included $Na_xH_yC_{60}$, which was prepared by the reaction of C_{60} with sodium hydride. The $Na_xH_yC_{60}$ compound crystallizes in a single face-centered-cubic (f.c.c.) phase with a cell constant a=14.356(3) Å and shows an onset superconducting transition temperature T_c of 15 K.[5] Here we report the crystal structure of the compound, which is helpful for understanding of superconducting behaviors of an Na-H-C_{60} ternary system.

The X-ray powder diffraction data were measured for a superconducting sample (volume fraction V_{SC}=65%) with a nominal composition $(NaH)_4C_{60}$ at room temperature. The X-ray data were collected on a Mac Science powder X-ray diffractometer MXP^3 with a graphite monochromatized CuK α radiation using a step width of 0.01°.[5] The Rietveld refinement by the RIETAN94 program[7-8] was carried out. Most reflections can be indexed on an f.c.c. lattice, so that a model structure has been assumed to belong to the space group $Fm\bar{3}m$, with Z=4, referring to the structure of K_3C_{60}.[2] A few weak reflections which can be explained in terms of a primitive tetragonal lattice has been observed for the sample. We consider that the sample consists of an f.c.c. phase, containing a minority tetragonal phase. After the refinement, the best fit was obtained for a mixture of these two phases, as shown in Figure 1. The best indices are weighted pattern R-factor R_{wp} =8.60%, integrated intensity R-factor R_I =10.96%, structure factor R-factor R_F =8.66% and goodness of fit S=3.94. The refined cubic cell constant a is 14.406(1) Å and the space group is $Fm\bar{3}m$, since the assumption of $Fm\bar{3}$ has led to significantly large R factors. On the other hand, the cell constants of the tetragonal phase are a=10.153(3) Å and c=14.336(3) Å. When the cell is transformed using the axes along the face diagonal directions in the ab square, new a and b axes are both 14.358 Å long, and the transformed lattice is very close to a cubic cell. We regard the cubic phase as superconducting phase, so it will be discussed below.

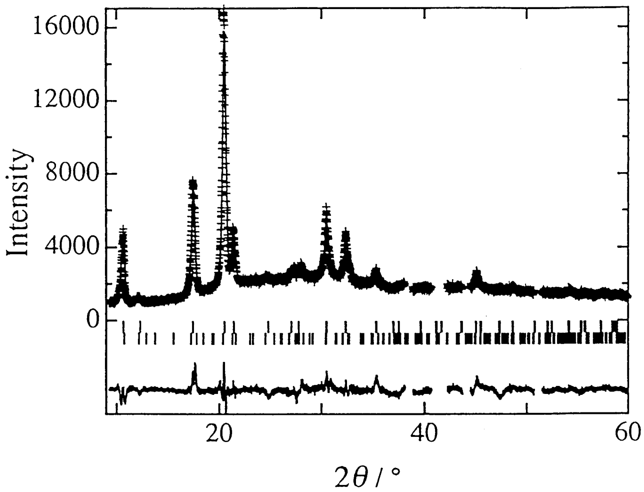

Figure 1. Rietveld refinement fit pattern (solid line) for the observed powder X-ray diffraction pattern (crosses) of a sample with a nominal composition $(NaH)_4C_{60}$ and V_{sc}=65%. The vertical lines indicate the allowed positions for the cubic phase (upper) and for the tetragonal phase (lower). The differences between the observed and calculated intensities are shown at bottom in the same scale.

In the cubic phase, the space group $Fm\bar{3}m$ indicates the C_{60} molecules are orientatioally disordered. If Na^+ ions in octahedral (O) and tetrahedral (T) sites are assumed to be positioned at the center of each site, they give negaive displacement parameters. Therefore, they are expected to be off-centered. Na^+ ions in an O-site are located on the $32f(x,x,x)$ coordinate and eight possible positions due to the symmetry of the f.c.c. system are found at eight corners of a cube. After the refinement with isotropic displacement parameters, the best coordinate for an Na^+ ion in an O-site is (0.445,0.445,0.445) and the refined occupancy is 0.20. The calculated number of Na^+ ions in the O-site, 1.6, indicates that one or two Na^+ ions can be placed on the corners of the cube. On the other hand, an Na^+ ion in a T-site is found at the $96k(x,x,z)$ position. The refined coordinate (0.22,0.22,0.28) gives four equivalent positions in the T-site, which correspond to four corners of a tetrahedron. The occupancy of 0.25 is the best value for this sample and one Na^+ ion is expected to exist in each T-site. The composition x in $Na_xH_yC_{60}$ can be estimated at 3.6, which is close to the initial composition of 4.

The structure of $Na_xH_yC_{60}$ is shown in Figure 2(a). Figure 2(b) represents the possible positions for Na^+ ions in a unit cell. An Na^+ ion in an O-site is positioned at a corner of a cube, 1.37 Å apart from its center. An edge of the cube d_1 is 1.58 Å long, a face diagonal d_2 2.24 Å and a body diagonal d_3 2.74 Å. Thus the vacancy is found to be large enough to accommodate an $H^{-\delta}$ (hydride ion). An Na^+ ion in a T-site is located at 0.75 Å (d_4) from the center of a tetrahedron, whose edge is 1.22 Å (d_5) long. The Na^+ ion in the T-site faces to the center of a six-membered

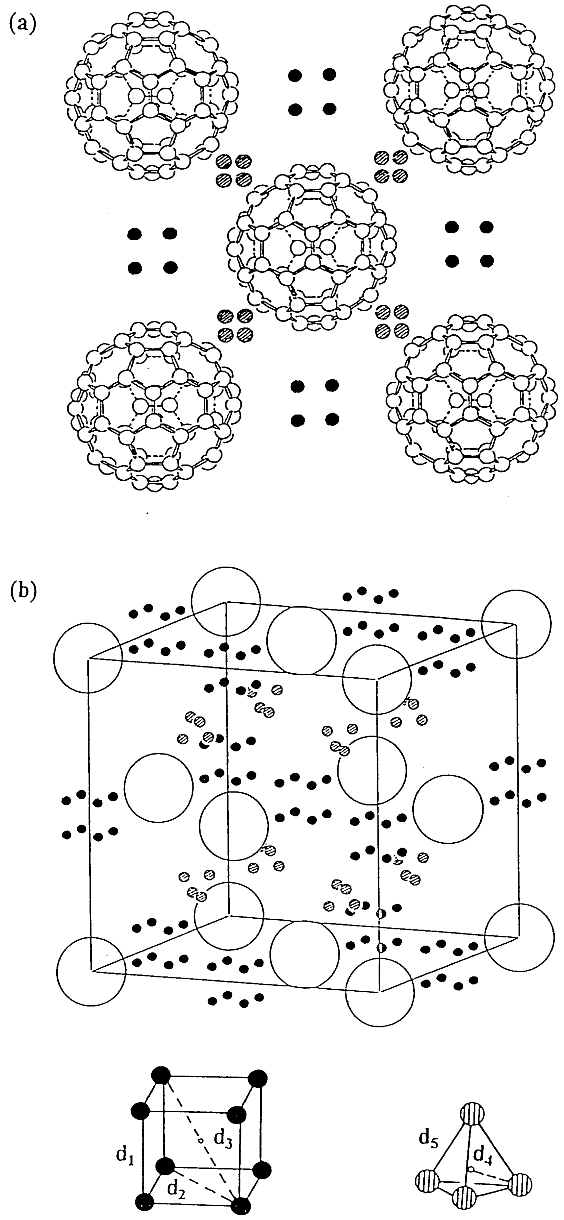

Figure 2. (a) Crystal structure of Na$_x$H$_y$C$_{60}$ in the space group $Fm\bar{3}m$. Open circles show C atoms, full circles Na$^+$ ions in O-sites, and slashed-marked circles those in T-sites. (b) Possible positions for Na$^+$ ions in a unit cell. Open circles show C$_{60}$ molecules.

ring of a neighboring C$_{60}$ molecule and the shortest distance between the Na$^+$ ion and a carbon atom in the ring is 3.02 Å. The off-centered location of Na$^+$ in the T-site may be induced by motion of the Na$^+$ ion or an occlusion of an H$^{-\delta}$ ion.

Taking into account of the room-temperature cell constant, the T_c value for Na$_x$H$_y$C$_{60}$ deviates far from the lines drawn on the basis of McMillan's theory for M$_3$C$_{60}$($Fm\bar{3}m$) and Na$_2$MC$_{60}$($Pa\bar{3}$) superconductors reported by Yildrim *et al.*[6] We are interested in the structure of this compound at low temperature, since the temperature dependences of spin susceptibility and ESR linewidth suggest an occurrence of a phase transition below *ca.* 250 K.[9] A structure analysis of the compound at low temperature is now in progress.

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