ON THE NATURE OF TWO-DIMENSIONAL SHORT-RANGE ORDERING IN $YBa_2Cu_3O_{7-\delta}$

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The unit cell doubling of $YBa_2Cu_3O_{7-\delta}$ was observed in a number of diffraction studies. As far as the crystals studied were oxygen deficient ($\delta>0.2$) the observed diffuse superstructure peaks were attributed to the oxygen-vacancy ordering. In our previous paper /1/ the two-dimensional diffuse X-ray scattering on a single crystal with $\delta=0.05$ was explained by the ordering of copper and oxygen valencies. Nevertheless we were not able to exclude that the observed effects were due to oxygen-vacancy ordering in the part of the crystal volume of $\sim 10^{-3}$. Now /2/ we give an additional evidence of the electronic origin of the observed ordering.

The measurements of the diffuse scattering intensity were carried out on the $YBa_2Cu_3O_{7-\delta}$ plate-like monocrystal of $3\times3\times0.007\ mm^3$ having more than 87% of the superconducting phase and $T_c=92K$ ($\Delta T_c<0.02K$). The X-ray radiation of $\lambda_{Mo}=0.71$ Å was monochromatized by pyrolytic graphite. The unit cell parameters and twin system were similar to that known from literature.

The regular network of very weak diffuse spots observed on the mono-Laue photograph indicates that these spots result from the relspace objects extended in [001] direction (rods) and the unit cell is doubled in [010] or [100] direction. (Because of the twinning it is not possible to shoose between them.) From the width of the diffuse peaks the correlation lengths were found to be $r_l\cong25$ Å along the doubled edge and $r_t\cong50$ Å in the perpendicular direction.

Using the diffractometer some of the rods were scanned along l and their intensities were found to be modulated with a period of $l=2.65$ (fig. 1). This modulation has to be described by the structure factor with items like $\cos^2(2\pi lZ_1)$ where $Z_1=0.19$ or $[1+\cos(2\pi lZ_2)]^2$ where $Z_2=0.38$. As far as $Z_1\cong Z_{Ba}=0.189$, $Z_2\cong Z_{O2}\cong Z_{O1}=0.378$ all the atoms in one block between two Cu2 planes (fig. 2) should be considered in the structure factor calculations. In other words the diffuse scattering is caused by the two-dimensional short-range ordering in each block, with the nearest blocks being uncorrelated.

The intensities of 45 superstructure rods (i. e. h=n, k=n/2, or h=n/2, k=n) at l=0 were measured up to $\sin\Theta/\lambda=1$ Å^{-1}. These intensities were discribed by structure factors including a contribution of the oxygen-vacancy ordering and a possible displacements x_i, y_i of the ordered atoms from their mean positions

$$A_1=-f_O[\cos(\pi h)+2\pi(hx_{O4}+2ky_{O4})\sin(\pi k)], \tag{1}$$

$$B_1=-f_O[\sin(\pi k)+2\pi(hx_{O5}+2ky_{O5})\cos(\pi h)]. \tag{2}$$

the contribution of the valency ordering of copper and oxygen

$$A_2=p_{Cu1}\Delta f_{Cu1}+2p_{Cu2}\Delta f_{Cu2}+2p_{O1}\Delta f_{O1}+2p_{O2}\Delta f_{O2}\cos(\pi h), \tag{3}$$

$$B_2=(2p_{O3}\Delta f_{O3}+p_{O4}\Delta f_{O4})\sin(\pi k). \tag{4}$$

where the differential atomic factor $\Delta f_i(q=\sin\Theta/\lambda)=f_i(q)-f_i,\ (q)$ (fig. 2) and $-1\leqslant p_i\leqslant1$, and also the contribution of the atomic displacements x_i, y_i taking place in both these cases

$$\begin{aligned}A_3=&-8\pi f_{Ba}(hx^a_{Ba}+2ky^a_{Ba})\cos(\pi h)\cdot\sin(\pi k)-8\pi^2 f_{Cu}[h^2(x^p_{Cu1}x^a_{Cu1}+2x^p_{Cu2}x^a_{Cu2})+\\&+4k^2(y^p_{Cu1}y^a_{Cu1}+2y^p_{Cu2}y^a_{Cu2})+2hk(x^p_{Cu1}y^a_{Cu1}+x^a_{Cu1}y^p_{Cu1}+2x^p_{Cu2}y^a_{Cu2}+\\&+2x^a_{Cu2}y^p_{Cu2})]-4\pi f_O[h(2x^a_{O3}+x^a_{O4})+2k(2y^a_{O3}+y^a_{O4})]\sin(\pi k),\end{aligned} \tag{5}$$

$$\begin{aligned}B_3=&-16\pi^2 f_{Ba}[h^2x^p_{Ba}x^a_{Ba}+4k^2y^p_{Ba}y^a_{Ba}+2hk(x^p_{Ba}y^a_{Ba}+x^a_{Ba}y^p_{Ba})]\cos(\pi h)\sin(\pi k)+\\&+4\pi f_{Cu}[h(x^a_{Cu1}+2x^a_{Cu2})+2k(y^a_{Cu1}+2y^a_{Cu2})]+\\&+8\pi f_O[hx^a_1+2ky^a_{O1}+(hx^a_{O2}+2ky^a_{O2})\cos(\pi k)].\end{aligned} \tag{6}$$

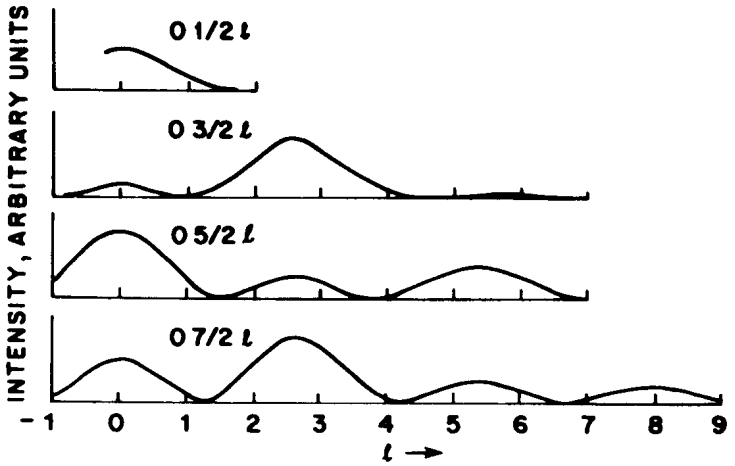

Fig. 1.

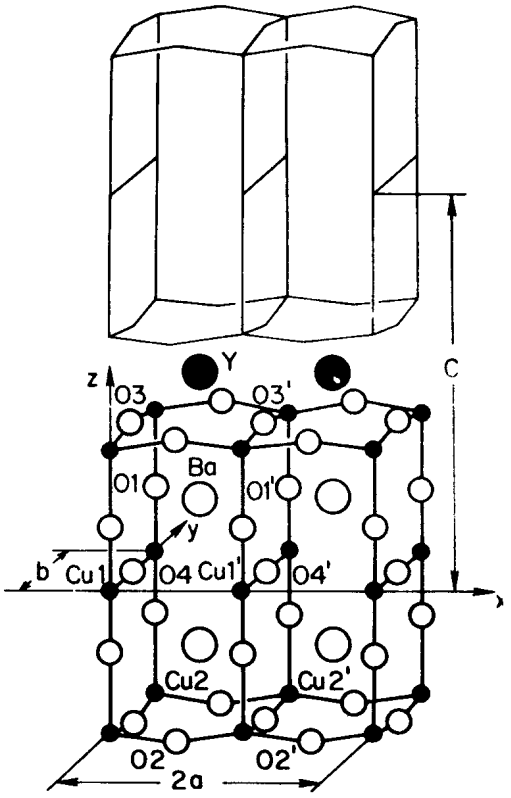

Fig. 2

where instead of x_i, y_i parallel and antiparallel components $x_i^p=(x_i+x_{i'})/2$, $x_i^a=(x_i-x_{i'})/2$, $y_i^p=(y_i+y_{i'})/2$, $y_i^a=(y_i-y_{i'})/2$ are used. The equations (1—6) were written in assumption that the b-edge is doubled. If the a-edge is doubled (1—6) are still valid but f_i, Δf_i, x_i, y_i should be renamed. For the general case

$$A = P\cdot A_1+A_2+A_3 . \tag{7}$$

$$B=P\cdot B_1+B_2+B_3 . \tag{8}$$

where P=1 are 0 if there is or there is no oxygen-vacancy ordering. Using (1—8) to fit the observed intensities corrected for the absorption, polarization, and the relspace volume participating in the scattering we have defined the parameter of (1—6). The best result, $\cdots^2=4.8$, was for $p_{Cu1}=$ $=0.96(12)$, $p_{Cu2}=0$, $p_{O1}=-1$, $p_{O2}=-0.06(26)$, $p_{O3}=0$, $p_{O4}=0.76(34)$ $y^a_{Ba}=-0.00013(1)$, $y^a_{Cu1}+2y^a_{Cu2}=0.00008(1)$. The value of the other parameters was less than their standard deviations. The final result is that the diffuse scattering is due to valency ordering and accompanying atom displacements. The diffuse peak intensities for small h and k when the atom displacement contribution is negligible are caused by difference of one electron between O1+Cu1+2Cu2 and O1Δ+Cu1'+ +2Cu2'.

The temperature measurements were carried out in the range $85\leqslant T(K)\leqslant 300$. The peak intensity as well as the correlation lengths r_t and r_l were found to be temperature independent. This surprising result indicates that the observed ordering should be a quantum effect if it is, indeed, valency ordering.

REFERENCES

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