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Electron Density Distribution of $Tl_2Ba_2Ca_2Cu_3O_{10}$

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Abstract The synthesis method of $Tl_2Ba_2Ca_2Cu_3O_{10}$ and the electron density distribution from precise XRD data have been studied. A quantitative and qualitative analysis of the electron density distribution in $Tl_2Ba_2Ca_2Cu_3O_{10}$ has been made using the maximum entropy method(MEM).

Key words MEM, Tl-system superconductor

Introduction

The great leader Comrade **Kim Jong Il** said.

"Scientists and technicians should work to overcome by their own efforts the problems which require an urgent solution for the development of the national economy of our country, and to introduce the scientific and technical successes of developed countries in accordance with its specific reality."("**KIM JONG IL** SELECTED WORKS" Vol. 10 P. 195～196**)**

In this paper we have considered the synthesis and the electron density distribution of Tl-system superconductor high-T_c phase($Tl_2Ba_2Ca_2Cu_3O_{10}$).

The position of atoms is clearly shown and this is closely with SEM for Tl-system high superconductor. And electron density distribution of coaxial circle is shown in the position of Ca atom. It is because of substitution effect of Tl and Ca.

1. Theoretical Consideration

The electronic structure of many material has been studied by many researchers[7－10], and these studies have provided enhanced knowledge about the bonding in these materials.

Recently, the maximum entropy method(MEM) has provided a thrust in the calculation of electron density distribution as this method is proved to be unbiased and more accurate when compared with the conventional Fourier synthesis.

MEM does not suffer seriously from termination errors and the requirement of the structural model to be very nearly the same as the true one is not needed.

The probabilistic approach was formulated by Colins [11] to analyze the structure factor in order to Calculate the electron density at the i^{th} pixel by increasing the entropy iteratively, where the entropy is defined as

$$S = -\sum \rho'(r_i)\ln[\rho'(r_i)/\rho'_0(r_i)]$$

where $\rho'(r_i)$ and $\rho'_0(r_i)$ are normalized electron densities of the present and previous iteration cycles, and are defined as,

$$\rho'(r_i) = \rho(r_i) \Big/ \sum \rho(r_i)$$
$$\rho'_0(r_i) = \rho_0(r_i) \Big/ \sum \rho_0(r_i) .$$

A weak constraint is introduced as

$$C = (1/N) \sum [F_{obs}(k) - F_{cal}(k)]^2 \Big/ \sum \sigma(k)^2$$

which is expected to be unity under minimum iterations. Here N, $F_{obs}(k)$, $F_{cal}(k)$ and $\sigma(k)$ are the number of available reflections, observed and calculated structure factors and standard deviations of the observations respectively.

Maximizing the entropy is done with help of a Lagrange function $G(\lambda)$, defined as

$$G(\lambda) = S - (\lambda/2)C$$

where λ is the unknown Lagrange multiplier and when $\partial G(\lambda)/\partial \rho'(r_i) = 0$ resulting in the electron density given by

$$\rho(r_i) = \rho_0(r_i) \exp\{(\lambda \rho_{\text{num}}/N) \cdot \sum 1/\sigma(k)^2 \cdot |F_{obs}(k) - F_{cal}(k)| \exp(-2\beta \pi j k r)\} .$$

where, ρ_{num} is the number of electrons in the unit cell. When $F_{obs}(k)$, $\sigma(k)$ and λ are given, one can obtain $\rho(r_i)$ which will be the desired electron density distribution $\rho_{\text{MEM}}(r_i)$ when $C = 1$.

Calculation algorithm to obtain electron density distribution is shown in Fig 1.

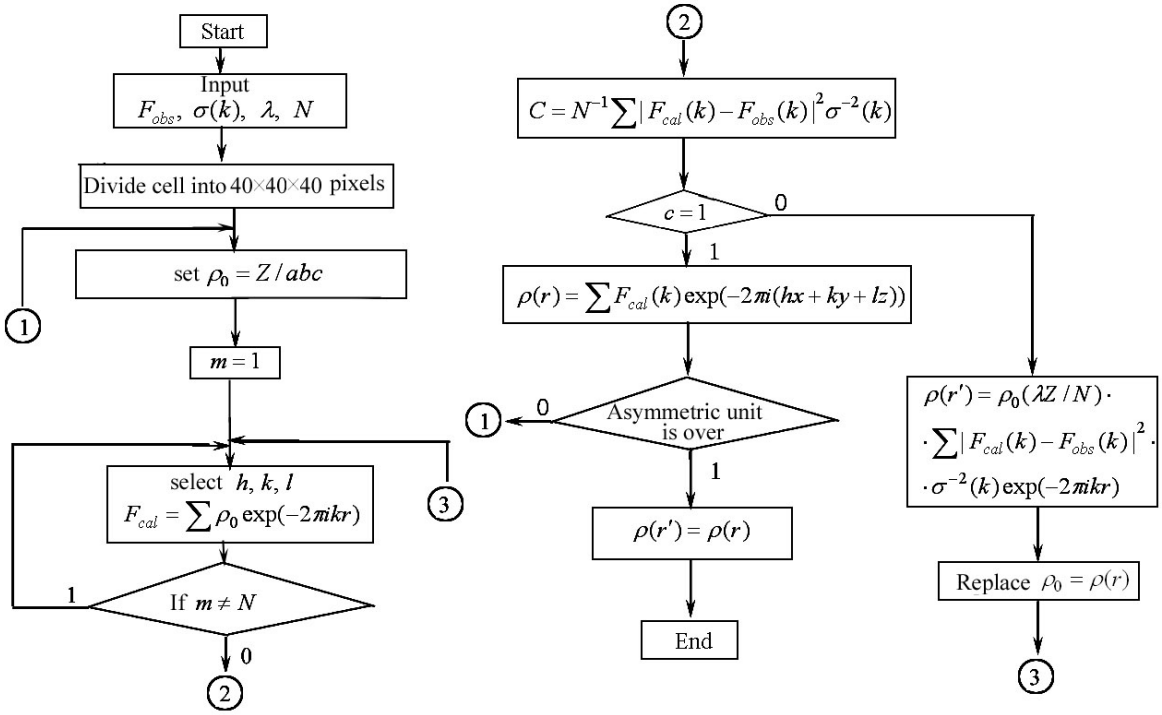

Fig. 1. Calculation algorithm

2. The Synthesis of $Tl_2Ba_2Ca_2Cu_3O_{10}$ Superconductor

The synthesis of Tl-system superconductor and the effects of sintering conditions on its formation has been studied by many researchers [1－7].

The starting materials except Tl_2O_3 with a composition of Ba∶Ca∶Cu=2∶2∶3 were prepared by mixing and grinding $BaCO_3$(purity 99.9%), $CaCO_3$(purity 99.9%), CuO(purity 99.9%).

Then the starting materials were pressed and sintered at 890℃ several times, thus obtained Ba-Ca-Cu oxide.

And the starting materials with a composition of Tl∶Ba∶Ca∶Cu=2∶2∶2∶3 were prepared by mixing and grinding Ba-Ca-Cu oxide and Tl_2O_3, obtained the sample 10mm in diameter, 1～2mm in thickness by pressing $(1.5～2)\cdot10^8$Pa.

This was put on Al_2O_3 plate and kept in a pipe of stainless steel, and sintered in oxygen of 2L/min at 880℃ for 5～10min.

The T-onset of the sample was 110K, it's critical electric current was $3\cdot10^7 A/m^2$ in liquid nitrogen temperature.

Measurement condition is as follows.

X-ray tube: target-Cu, voltage－35kV, current－20mA, scanning: scan mode－CONTI, scan speed － 2.000deg/min, full scale － 2.0kcps, Data processing condition: smoothing points － 7, background subtraction－YES, $K\alpha_1$, $K\alpha_2$ separation－YES.

X-ray diffraction pattern for the $Tl_2Ba_2Ca_2Cu_3O_{10}$ sample and 37 peaks that background subtraction are concealed and $K\alpha_1$, $K\alpha_2$ are separated are shown in Fig. 2 and table.

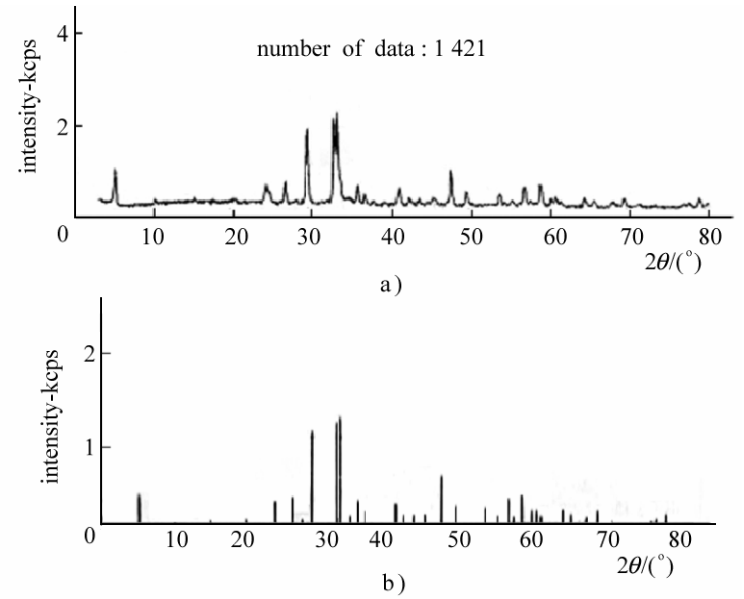

Fig. 2. X-ray diffraction pattern

a) before removal of background subtraction,

b) separating of $K\alpha_1$, $K\alpha_2$ after removal of background subtraction

Table. X-ray diffraction data

No.	2θ/(°)	d_{hkl}/Å	I/I_0	FWHM/(°)	Intensity/kcps
1	78.758	12.141	9	0.255	0.110
2	77.295	12.334	4	0.182	0.051
3	76.644	12.422	2	0.095	0.028
4	71.117	13.245	3	0.000	0.033
5	69.166	13.570	12	0.431	0.145
6	67.649	13.837	7	0.431	0.145
7	65.373	14.263	9	0.501	0.111
8	64.235	14.488	13	0.292	0.157
9	61.200	15.131	7	0.296	0.092
10	60.604	15.266	12	0.314	0.153
11	59.954	15.416	12	0.303	0.151
12	58.653	15.726	27	0.378	0.337
13	57.407	16.038	7	0.434	0.087
14	56.648	16.234	25	0.356	0.306
15	55.077	16.660	7	0.384	0.092
16	53.451	17.128	15	0.393	0.181
17	49.333	18.457	17	0.366	0.208
18	47.382	19.170	44	0.328	0.540
19	45.106	20.083	10	0.667	0.118
20	43.426	20.820	8	0.196	0.102
21	42.125	21.432	8	0.418	0.101
22	40.879	22.057	20	0.404	0.244
23	38.928	23.116	3	0.191	0.036
24	37.628	23.884	4	0.443	0.051
25	36.544	24.568	12	0.333	0.149
26	35.623	25.181	22	0.335	0.275
27	34.593	25.907	8	0.795	0.099
28	33.076	27.060	100	0.369	1.231
29	32.696	27.365	95	0.335	1.170
30	29.282	30.473	88	0.320	1.079
31	27.873	31.981	5	0.503	0.056
32	26.519	33.583	26	0.298	0.320
33	24.080	36.926	22	0.683	0.274
34	20.178	43.969	5	1.048	0.062
35	15.030	58.893	5	5.527	0.060
36	10.153	87.046	5	0.437	0.060
37	5.114	172.665	29	0.304	0.351

3. Result and Analysis

I_i, intensity of the i^{th} diffraction peak is defined as,

$$I_i = S\sum_k |F_k|^2 m_k L(\theta_k)$$

where k is number of the diffraction peak for I_i, S is scale factor, F_k is crystal structure factor, m_k is multiple number and $L(\theta_k)$ is Lorentz factor.

Crystal structure factor is defined as

$$F_k = \sum_j g_j f_j T_j \cos(2\pi(hx_j rky_j + lz_j))$$

where j is atom number of a cell, g_j is occupation rate, f_j is atom scattering factor, T_j is temperature factor, and x_j, y_j, z_j are atom coordinates.

And atom scattering factor with two Gaus function is defined as,

$$f = A\exp(-a\sin^2\theta/\lambda^2) + (Z-A)\exp(-b\sin^2\theta/\lambda^2).$$

Lattice constant are $a = b = 0.38502\text{nm}$, $c = 3.5572\text{nm}$ respectively, electron density of initial state is given as $\rho_0 = (81\times2 + 56\times2 + 20\times2 + 29\times3 + 10\times8)/a\cdot b\cdot c$.

Electron density distribution in different section is shown in Fig. 3.

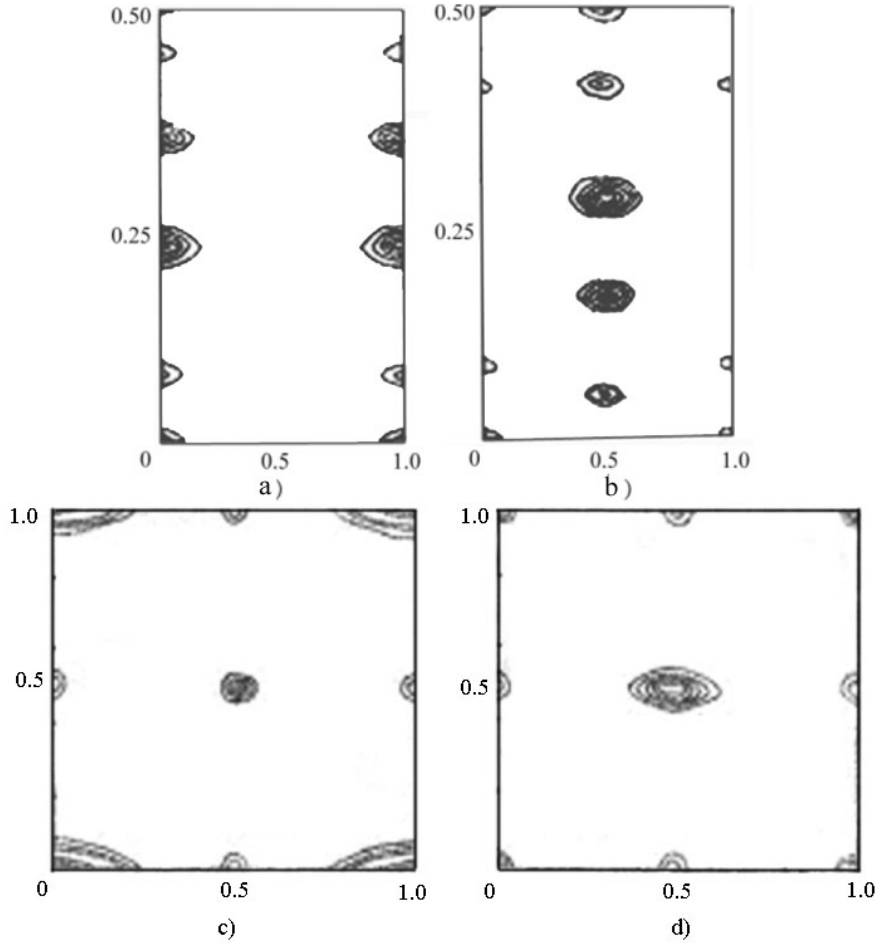

Fig. 3. Electron density distribution
a) (101) surface, b) (121) surface, c) (110) surface, d) (112) surface

As shown in Fig. 3, the position of atoms is clearly shown and this is closely with SEM for Tl-system high superconductor. And electron density distribution of coaxial circle is shown in the position of Ca atom. It is because of substitution effect of Tl and Ca[6].

In future, quantitative analysis on this will be further discussed.

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