E17-94-299

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APICAL OXYGEN ANHARMONICITY AND FERROELECTRICITY IN $YBa_2Cu_3O_7$

Submitted to Proceedings of the International Workshop
«Anharmonic Properties of High-T_c Cuprates»,
Bled, Slovenia, September 1—6, 1994

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1994

1 INTRODUCTION

A major role for the superconductivity in $YBa_2Cu_3O_7$ has been ascribed by several authors (see e.g. [1, 2]) to the apical oxygen atoms denoted usually as O4. In particular, the debate on possible lattice instability associated with the apical oxygen O4 in $YBa_2Cu_3O_7$ keeps still on.

Temperature dependent EXAFS studies [3, 4, 5] show a split position i.e., a double-well potential for the O4 motion. High temperature Raman measurements [6, 7] indicate significant softening and broadening of the O4 derived A_g mode characteristic of anharmonicity. This mode exhibits in addition an anomalous isotope effect i.e. upon substitution of ^{18}O for ^{16}O its frequency shift has been found to be weaker than in the harmonic theory urging the authors to conclude on anharmonicity of this mode [8].

The nuclear pair-distribution analyses of the elastic and inelastic neutron scattering data [9] for Ti and La-based cuprates clearly indicate a split position for the apical atoms,too whereas the Rietveld refinements do not show any noticeable anomaly [10]. We remind that the latter method gives the long range structure while the former one probes the local structure.

Theoretically it has been demonstrated that a strong electron-phonon coupling brings about an effective double-well potential for the infrared (IR) active mode involving the in-phase vibration of O4 atoms [11]. First principles LDA calculations [12], [13] predict a single-well potential, but an asymmetric one with considerable cubic term, for O4. Furthermore a tunneling model related to O4 vibration has been assumed to account for the linear specific heat term at low temperatures [14].

On the other hand, other authors stress that a double-well potential can not be reconciled with Raman as well as IR measurements [15]. However, a growing body of experimental evidence for strong electron-lattice coupling with promi-

nent participation of O4 can not be doubted calling likewise for a theoretical diversity.

Therefore it would be of great interest to look for a model which would interpolate between a single-well potential and a double-well one depending on certain external factors. In our opinion, a good candidate is offered by an asymmetric double-well potential.

It has been proposed [16] that the O4 atom can fluctuate between two inequivalent positions created by the asymmetric interaction of O4 with the two nearest-neighbour copper atoms along the c-axis (chain Cu1 and plane Cu2) whereby one of the positions is supposed to be a metastable one . The reason for the interaction asymmetry is believed to be the different oxygen coordination of these copper atoms. Given the energy difference between these two positions is considerably larger than kT one may expect that the metastable position is not occupied and the atom remains largely in the stable position behaving itself like in a single-well potential. However, if in the course of measurements the atom is excited by heating up and/or by means of other excitations (e.g. photons in EXAFS) it could be activated to overcome the barrier or tunnel through it towards the metastable position setting up the double-well character of the potential.

Here we formulate a two-sublattice model Hamiltonian which we treat in the molecular field approximation(MFA). We then present the results and a discussion of the consequences for thermodynamics arising if one assumes such an asymmetric double-well potential for the O4 atom. The paper is organized as follows: next Section explains the proposed model, in the last Section we present our results and discuss related experiments.

2 Model

We start by formulating a two-sublattice pseudo-spin model described by the following Hamiltonian (in the absence of external fields)

$$H = -\frac{1}{2}\sum_{ij}\left[J_{ij}(S_{i1}^{z}S_{j1}^{z} + S_{i2}^{z}S_{j2}^{z}) + 2K_{ij}S_{i1}^{z}S_{j2}^{z}\right] -$$

$$-\Omega\sum_{j}(S_{j1}^{x} + S_{j2}^{x}) - \Delta\sum_{j}(S_{j2}^{z} - S_{j1}^{z}), \qquad (1)$$

where the indices 1 and 2 refer to the two sublattices, J_{ij} and K_{ij} are the effective interaction constants among O4 atoms in the same and different sublattices, respectively and i, j denote the sites. Ω is the tunneling frequency in the one-particle double-well potential and Δ is the asymmetry parameter. The lattice model is shown in Fig.(1). We assume that in the fully oxygenated $YBa_2Cu_3O_7$ superconducting compound the stable position is closer to the Cu2-O2,O3 plane. This assertion is made in accordance with the fact that the Cu2-O4 bond length experiences an abrupt decrease upon doping into the superconducting phase [17]. Since the basal plane bearing the one-dimensional Cu1-O1 chains is the inversion plane of the elementary cell, the two asymmetric double-well potentials for the two O4 ions on either sides of the inversion plane (along the c-axis) form mirror images of each other as depicted in Fig. 1. Note that the abscissa represents the c-axis of the elementary cell, i.e. perpendicular to the Cu-O planes. For the sake of clearness we denote the oxygen sublattice, which has the deeper minimum on the left side by 1, the respective oxygen atom by O4(1) and correspondingly the sublattice with the deeper well on the right side by 2, the oxygen atom by O4(2). It is interesting to point out that the two-sublattice model with asymmetric double-well potential was applied long time ago in the study of ferroelectricity in the Rochelle salts [18]. It is noteworthy that depending on the magnitude of Δ the potential can

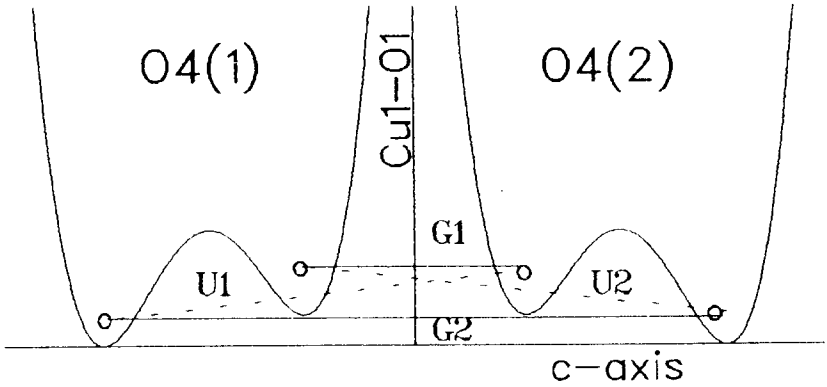

Figure 1: The potentials for the two O4 atoms along the c-axis and the atom displacements corresponding to the IR (U1,U2 configurations) and Raman (G1,G2 configurations) modes (dashed and solid lines, respectively, see also text).

change from a symmetric double-well to a quasi-single-well form. The pseudo-spin operator S^z_{in} is assumed to equal $-1/2$ if the O4 atom is in the left well and $+1/2$ if it is in the right well. The S^x_{in} operator describes the tunneling of the O4 atoms between two wells.

To consider thermodynamical properties of the model we have to calculate the free energy. For this purpose we employ the Bogoliubov variational principle and introduce a trial Hamiltonian H_0 which describes a system of non-interacting pseudo-spins in the MFA:

$$H_0 = -\sum_{i,n=1,2} h^z_n S^z_{in} - \sum_{i,n=1,2} \Omega S^x_{in}, \tag{2}$$

where $n = 1,2$ is the sublattice index. Then for the true free energy of the model (1) we have the following estimation from above:

$$F = -T \ln \mathrm{Tr}(e^{-\frac{H}{kT}}) \leq F_1 = F_0 + < H - H_0 >_0, \tag{3}$$

where

$$< A >_0 = \frac{\mathrm{Tr}(Ae^{-\frac{H_0}{kT}})}{\mathrm{Tr}(e^{-\frac{H_0}{kT}})}. \tag{4}$$

and

$$F_0 = -T(\ln 2\cosh\frac{h_1}{kT} + \ln 2\cosh\frac{h_2}{kT}) \tag{5}$$

is the exact free energy of our trial system with molecular fields $h_n = \sqrt{(\Omega^2 + (h_n^z)^2)}$.

The condition of stationarity i.e.,

$$\frac{\delta F}{\delta h_n^z} = 0$$

yields now the following coupled nonlinear equations for the average value of the pseudo-spin $< S_{in}^{\alpha} >$ at site i in the sublattice n

$$< S_{in}^z >= \frac{1}{2}\frac{h_n^z}{h_n}\tanh\frac{h_n}{2kT}. \tag{6}$$

In the same manner, requiring

$$\frac{\delta F}{\delta < S_{in}^{\alpha} >} = 0$$

we obtain for the components of the molecular field in the two different sublattices

$$h_1^z = J < S_1^z > + K < S_2^z > -\Delta,$$

$$h_2^z = J < S_2^z > + K < S_1^z > +\Delta. \tag{7}$$

Here $K = \sum_j K_{ij}$ and $J = \sum_j J_{ij}$.

Using (1) - (7) one arrives at the following expression for the free energy F_1 in (3)

$$F_1 = \frac{J}{2}(< S_1^z >^2 + < S_2^z >^2) + K < S_1^z >< S_2^z > -$$

$$T(\ln 2\cosh\frac{h_1}{kT} + \ln 2\cosh\frac{h_2}{kT}), \tag{8}$$

The temperature dependences of the sublattice polarizations are given now by the solutions of the two coupled equations (6).

3 Results and Discussion

We have iteratively solved the coupled nonlinear equations for the sublattice polarizations (6) taking into account the Eqs. 7. Since we are concerned with the thermodynamics for simplicity the tunneling term can be safely neglected without losing any physics, i.e. we set $\Omega = 0$. We have choosen the model parameters such that T_1 is approximately 90 K (i.e. T_c of $YBa_2Cu_3O_7$) whereby we fixed $\Delta = 33$ meV. In Fig. 2 the sublattice polarizations *vs.* temperature are shown for a few selected sets of K and J represented by the

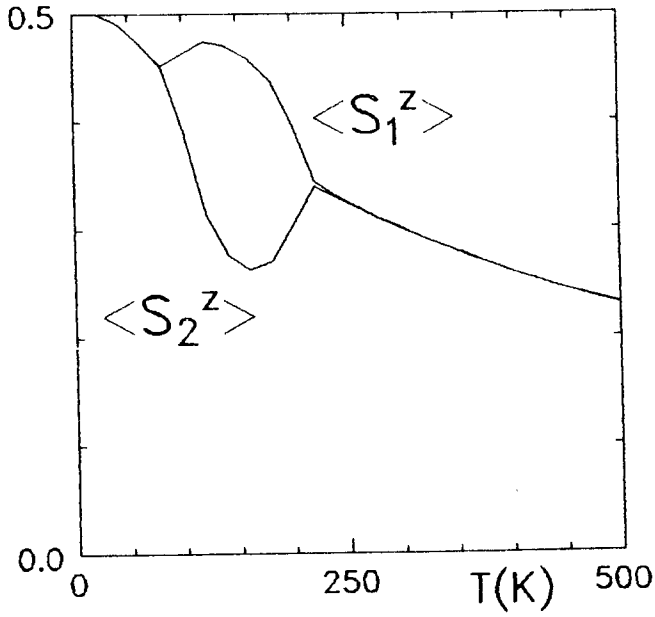

Figure 2: The temperature dependence of the sublattice polarizations.

dimensionless parameter $\alpha = (J + K)/\Delta$. As one sees the polarizations in the two sublattices are equal in magnitude, but opposite in sign except for a temperature region between T_1 and T_2. Outside of this region

$$< S_1^z > = - < S_2^z >$$

and the net polarization defined by

$$\sigma = < S_1^z > + < S_2^z > \tag{9}$$

is zero as shown in Fig. 3 although $< S_i^z > \neq 0$. For $T_1 < T < T_2$ a spontaneous polarization takes place i.e. σ becomes nonzero on approaching T_1=90K from the low temperature side or T_2=230K from the high-temperature side. It means that in this temperature range the free energy has its minimum for a ferroelectric state i.e. when O4(1) is localized in the deeper (or higher) well

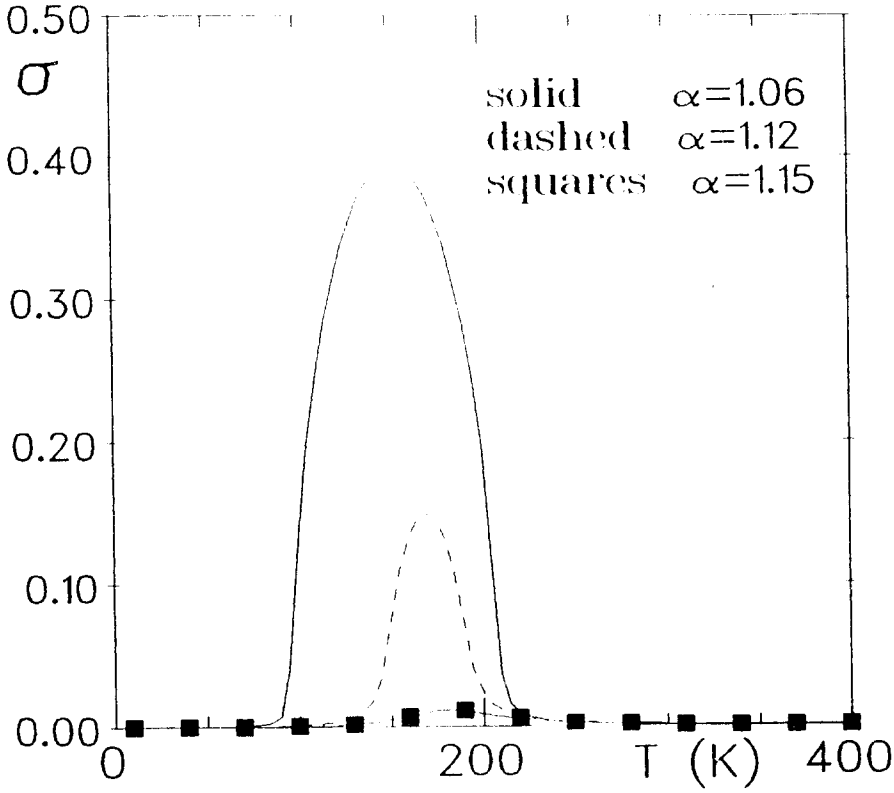

Figure 3: The temperature dependence of the net polarization for various interaction constants J, K.

of its potential whereas O4(2) is localized in the higher(or deeper) well of its potential. This is visualized in Fig. 1 by the U1 (U2) configurations.

In fact YBaCuO was found to be both pyroelectric and piezoelectric, implying the existence of a macroscopic polarization directed along the c-axis [19]. Moreover sign reversal and an increase of the magnitude of the spontaneous polarization with doping has been reported [20]. However it should be noted that this finding has sofar not been confirmed by other groups although similar effects are seen but they disappear after thermal cycling of the samples.

This could be an indication on possible composition dependence of the ferroelectric behaviour. In the present model the composition changes can be simulated by the interaction parameters J, K. The dependence of the net polarization on the variation of these parameters is shown in Fig. 3. One sees that a small change in the parameter $\alpha = (J + K)/\Delta$ strongly influences the magnitude of the polarization. Its increase by only 10% is almost sufficient to completely suppress the macroscopic polarization. Thus the absence of macroscopic polarization does not necessarily deny the asymmetric double-well structure of the potential. Contrarily it could explain in a natural way why the ferroelectric effect has not been observed in all samples.

A question at hand concerns the relationship of this ferroelectric ordering of apical oxygens to superconductivity since empirically these two phenomena are believed to be mutually excluding ones. In Ref. [21] basing on high-resolution thermal-expansion experiments it was proposed that lattice instability may be a limiting mechanism for T_c i.e. the highest T_c attained for optimum doping was found to coincide with a temperature at which the cuprates reveal distinct lattice instability. Temperature-dependent ion channeling experiments of the oxygen sublattice in YBaCuO compound indicate also on some anomaly in the c-axis displacements of the apical oxygen atoms [22] upon cooling through the superconducting transition temperature.

From the commonly accepted point of view that superconductivity is realized in Cu2-O2,O3 plane it seems that there is no direct relation between the ferroelectric behaviour of the apical oxygen and superconductivity in the plane because of the various dimensionality of the phenomena and also of the spatial separation of these two structural units although the former effect could indirectly affect the latter one via the charge transfer mechanism. However, for the ((bi)polaronic [23, 24] or two-component [25]) pairing theories employing the anharmonic feature of O4 this model should bring about certain implications.

In conclusion, we discuss briefly some implications of the assumption of this model for the vibrational properties. For this purpose we introduce phonon modes corresponding to the IR and Raman modes defined as follows

$$Q_{iu} = \frac{1}{2}(S^z_{i1} + S^z_{i2}). \qquad Q_{ig} = \frac{1}{2}(S^z_{i1} - S^z_{i2}). \tag{10}$$

For the infrared active (IR) mode Q_{iu}, involving in-phase displacements of O4(1) and O4(2) (see Fig. 1) the two U1 and U2 configurations are degenerate and therefore the only possible form of the potential for the IR mode is a symmetric double-well potential. We recall that similar conclusion has been drawn in [11].

For the Raman active normal mode Q_{ig} associated with the two O4 atoms involving anti-phase displacements of these atoms i.e. O4(1) is displaced to the right (or left) well while O4(2) is displaced to the left (or right) one as represented in Fig. 1 by G1 and G2 configurations. These two configurations differ by an energy $2\Delta \approx 66$ meV (11) which gives an estimate for the energy of the A_g Raman active mode in an effective asymmetric potential.

In terms of these new pseudospin phonon variables the Hamiltonian (1) can be rewritten as follows

$$H = -\sum_{ij} J_{ij}[Q_{iu}Q_{ju} + Q_{ig}Q_{jg})] -$$

$$\sum_{ij} K_{ij}(Q_{iu}Q_{ju} - Q_{ig}Q_{jg}) + 2\Delta \sum_{i} Q_{ig} - \Omega \sum_{i} (S^x_{i1} + S^x_{i2}). \qquad (11)$$

It is readily seen that this Hamiltonian is symmetric with respect to the Q_{iu} variables while it is asymmetric in terms of Q_{ig}. Therefore one can conclude that within the present model the potential for the IR active mode is of a symmetric double-well type whereas for the Raman active mode one has an asymmetric double-well one. These conclusions have important consequences for the IR and Raman spectroscopies. They concern the (non)-existence of low frequency tunneling modes, temperature dependence of phonon energy and anamalous isotope shifts, the symmetry breaking of optical selection rules for these higly anharmonic phonon modes described by the pseudospin variables in the model (11). Some of these problem are discussed in [15] and [26].

In Fig. 4 we compare the wavefunctions corresponding to the two lowest eigenstates Ψ_0, Ψ_1 and a higher excited state (fourth) Ψ_4 in the asymmetric and symmetric double-well potentials with similar barrier heights. In the case of a symmetric double-well the wavefunctions are spread symmetrically or (antisymmetrically) over the two wells implying that the minimal root mean square amplitude (RMSA) of the displacement is given by the distance between the minima. As for the asymmetric potential the lower eigenstates are localized in the one (deeper) well whereas the higher eigenstates are delocalized. It is demonstrated in Fig. 4 by the wavefunction corresponding to the fourth eigenstate, which has a finite weight in the higher well. Therefore at low temperature when only the lowest eigenstates are occupied the RMSA given by

$$< u^2 >= \frac{\sum_n < \Psi_n \mid u^2 \mid \Psi_n > \exp(-\beta E_n)}{\sum_n exp(-\beta E_n)} \qquad (12)$$

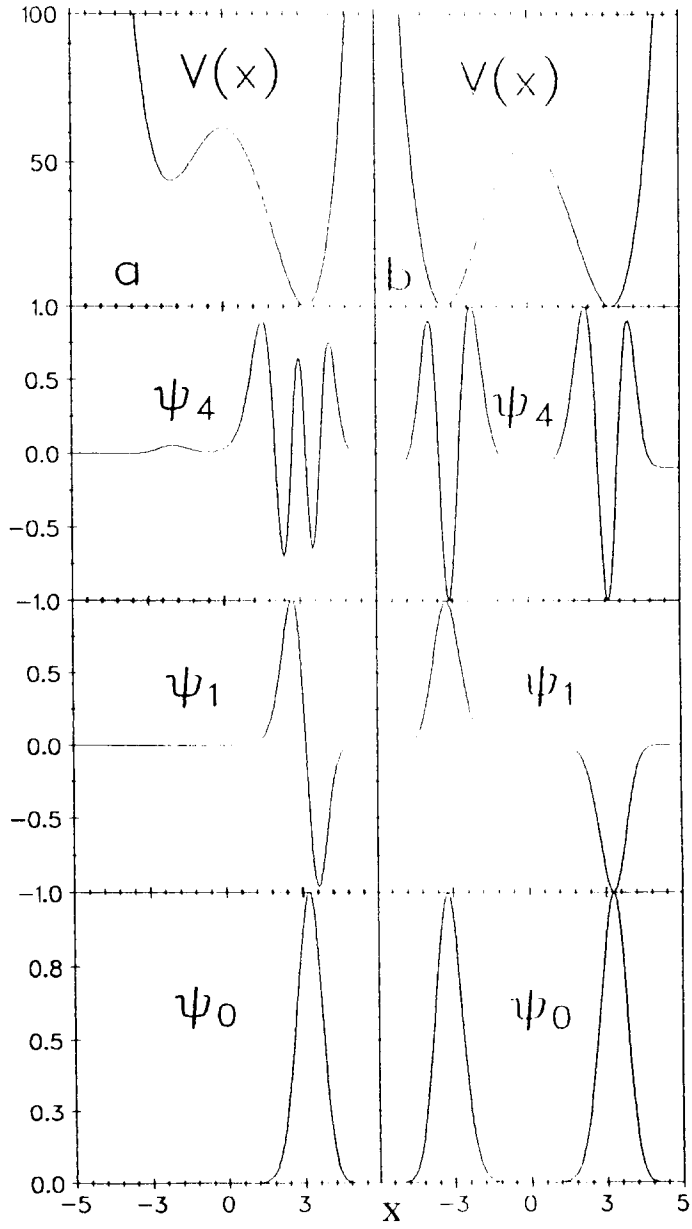

Figure 4: Two anharmonic potentials (a-asymmetric double well and b-symmetric double well) and the wavefunctions corresponding to the two lowest eigenstates Ψ_0, Ψ_1 and a higher (fourth) excited state Ψ_4.

would have a behaviour essentialy like in a single well potential. The double-well character of the potential will come into light when the higher levels become occupied e.g. if the temperature is raised or the particle is excited by other excitations.

The Debye-Waller factor or the RMSA is an exceptionally important and useful quantity providing information of the vibrational potential which can be obtained directly from inelastic neutron scattering (INS) experiments. As stressed in [10] the INS data do not lend support for a double-well potential

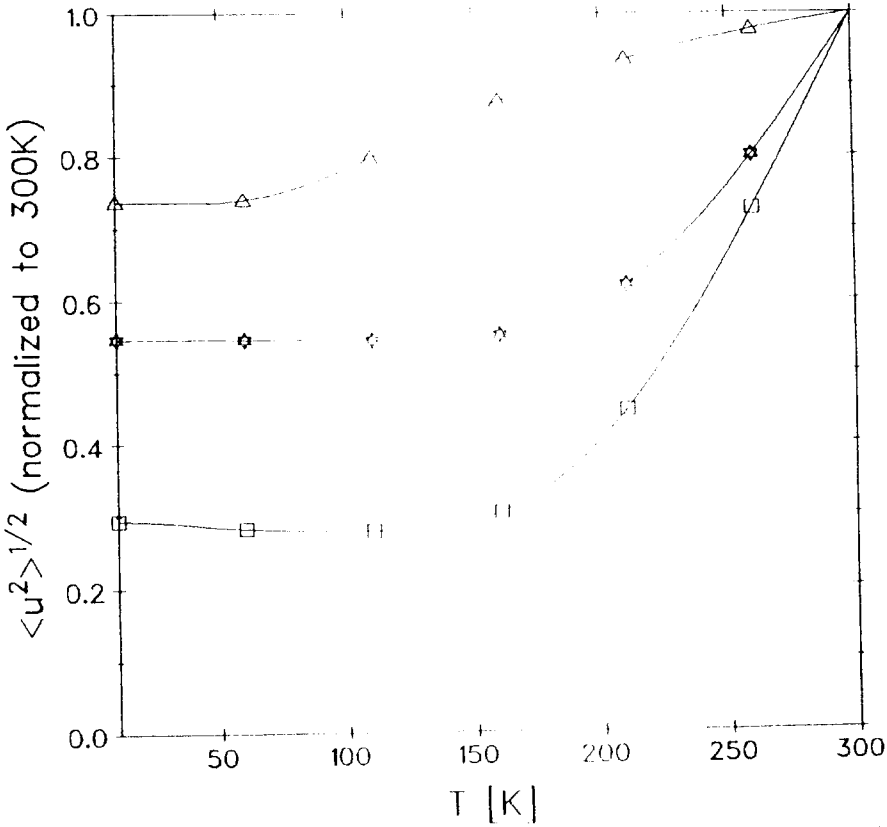

Figure 5: The temperature dependence of the RMSA for harmonic (squares), asymmetric double-well (stars) and symmetric double-well (triangles) potentials.

for the O4 atom since the temperature dependence of the RMSA $< u^2 >$ does not show any noticeable anomaly in the temperature dependence. As mentioned above, however in a sufficiently asymmetric double-well potential at low temperatures the atom could behave itself as though in a single-well potential. We have calculated the RMSA for harmonic, asymmetric double-well and symmetric double-well potentials as function of temperature. They are compared in Fig. 5. At low temperatures the RMSA in the symmetric double-well potential is bounded by the distance between the two minima of the potential while that one of the harmonic oscillator by the zero-point amplitude. The RMSA in the asymmetric double-well potential tends to a value inbetween because of the different population in the two wells. Therefore under certain circumstances it might be difficult by comparing the Debye-Waller factors to distinguish a harmonic potential from an asymmetric double-well one.

4 Summary

To summarize, we have studied a model assuming an asymmetric double-well form for the vibrational potential for the apical oxygen in the 1-2-3 superconductor and shown that it could give rise for a ferroelectric behaviour. We found that the magnitude of the macroscopic polarization is strongly dependent on the interaction constants between the apical oxygen sites. This prompts us to conclude that the absence of macroscopic polarization does not rule out the possibility of realization of this model. As a by-product of the study the effective potential for the IR active mode involving the vibration of O4 atoms is shown to be of a double-well form. We note that a similar conclusion has been drawn in charge transfer models and we arrived at it by an alternative way. As for the Raman active mode, it is tempting to conclude a double-well potential with a considerable asymmetry which can be regarded at lower temperatures

essentially a single-well one. The temperature dependence of RMSA in the asymmetric double-well potential interpolates between those ones of the symmetric double-well and the harmonic potentials depending on the magnitude of the asymmetry energy Δ.

The study of the dynamics of the model is reserved for a subsequent publication.

Acknowledgements. We would like to thank Dr. D. Mihailovic for a useful discussion and the Landau-Heisenberg Programme for partial support.

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Received by Publishing Department
on July 29, 1994.

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E17-94-299

Ангармонизм апексного кислорода
и сегнетоэлектричество в $YBa_2Cu_3O_7$

Предложена псевдоспиновая двухподрешеточная модель асимметричного двухямного потенциала для описания ангармонических колебаний атомов апексного кислорода в соединении $YBa_2Cu_3O_7$. Рассмотрена фазовая диаграмма модели. Показано, что существует такой набор параметров модели, при котором возможно появление спонтанной поляризации и сегнетоэлектрического состояния в области температур 90—250 К.

Работа выполнена в Лаборатории теоретической физики им. Н.Н.Боголюбова ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна, 1994

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E17-94-299

Apical Oxygen Anharmonicity and Ferroelectricity in $YBa_2Cu_3O_7$

A model suggesting an asymmetric double-well form for the effective vibrational potential for the apical oxygen atoms in the $YBa_2Cu_3O_7$ superconductor is formulated in the pseudo-spin representation and its phase diagram is studied. It is found that there exists a set of parameters for which a spontaneous polarization may occur at a temperature close to the supperconducting T_c, implying the possibility of formation of a ferroelectric state in the temperature region 90K—250K.

The investigation has been performed at the Bogoliubov Laboratory of Theoretical Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna, 1994

Макет Н.А.Киселевой

Подписано в печать 29.09.94
Формат 60×90/16. Офсетная печать. Уч.-изд.листов 1,67
Тираж 310. Заказ 47611. Цена 301 р.

Издательский отдел Объединенного института ядерных исследований
Дубна Московской области