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**NEUTRON-DIFFRACTION PATTERN
OBSERVED IN $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$:
NO BETTER EXPLANATION THAN OXYGEN ORDERING***

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ABSTRACT

We have looked for the best possible fit of the neutron-diffraction data of $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$ measured by Sonntag *et al.* [Phys. Rev. Lett. 66 (1990) 1497] using the deformation modulated structure for CuO_2 planes proposed by T. Krekels, S. Kaesche and G. Van Tendeloo [Physica C 248 (1995) 317]. The resulting fit is bad. We discuss the reasons of this failure. The best explanation of the neutron data is given by the structure obtained by Aligia [Europhys. Lett. 18 (1992) 181] from the thermodynamics of oxygen ordering. Using a simple highly-correlated electronic model, we also show that there are no theoretical grounds to discard $2\sqrt{2} \times 2\sqrt{2}$ oxygen ordered superstructures. Recent nuclear-quadrupole-resonance spectra support this conclusion.

Keywords: Structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$; Neutron diffraction in $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$; Cu-O chains; Coulomb interactions; Oxygen ordering

Running title: Oxygen ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$

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I. INTRODUCTION.

The subject of the oxygen (O) ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ has been of interest because it is undoubtedly related with the hole count in the superconducting CuO_2 planes [1,2] and therefore to the superconducting critical temperature [3–5]. There is a long standing controversy about the origin of diffraction patterns compatible with superstructures (SS) with unit cell multiple of $2\sqrt{2} \times \sqrt{2}$ [6–18]. These SS have been first observed by transmission electron microscopy (TEM) for low ($x \leq 3/8$) and high ($x \geq 3/4$) O content [6–8], while in the intermediate region, SS composed of infinite CuO chains in the basal plane were observed [6–8,19]. All these diffraction patterns could be explained with the structural lattice-gas model of Aligia, Garcés and Bonadeo (AGB) [1] with one free parameter ΔE which takes into account the effects of charge transfer [2,5,9–11], while within the asymmetric next-nearest-neighbor Ising (ASYNINI) model [12], the so called OII phase of unit cell 1×2 is the only stable SS [20]. However, the TEM experiments which favored $2\sqrt{2} \times 2\sqrt{2}$ SS were objected because they might lead to metastable SS as a consequence of the local heating of the sample [7].

Later, detailed neutron [15] and x-ray diffraction [16] experiments for $x \sim 3/8$ have confirmed the existence of $2\sqrt{2} \times 2\sqrt{2}$ type of SS's, and they were interpreted as due to O ordering. One of us has explained the neutron data using the AGB model [11]. The SS of minimum free energy near room temperatures coincides with the one which best fits the 26 measured neutron intensities [21], and is represented in Fig. 1(a). However, these experimental and theoretical results have been strongly criticised on theoretical grounds [12] and the criticism has been refuted [10,13]. The theoretical discussion is briefly reviewed at the beginning of the next section.

Recently, detailed careful experiments have obtained strong evidence in favor of SS's of unit cell multiple of $2\sqrt{2} \times \sqrt{2}$ which are not due to O ordering. Krekels *et al.* observed a similar diffraction pattern in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with $x \sim 0.15$, and in two other perovskites which do not contain CuO_x planes. They conclude that the observed SS should be due to

atomic displacements within the CuO_2 planes and not to O ordering in the CuO_x planes. They propose the SS shown in Fig. 1(b). It is interesting to note that the symmetry of the displacement mode is similar to that observed on $\text{Ni}(100)$ surfaces after adsorption of N [22], predicted in terms of electronic and steric effects [23], which however, are not applicable to the present case. In fact, the in-plane proposed distortions are hard to justify in these perovskites, which are highly contracted structures, with a large contribution to the total energy from repulsive overlap interactions [24]. On the other hand, Yakhou *et al.* [18] have carried out a very detailed and complete synchrotron radiation study for $x \sim 0.2$ and obtained excellent agreement for the 73 measured reflections, with an explanation based on the presence of about 0.2% of a parasitic phase of BaCu_3O_4 . Since the Ba atoms occupy the same positions as the O atoms in the SS proposed by Zeiske *et al.* [16], and the scattering amplitude for x rays of Ba^{+2} should be 5.4 times larger than that of O^{-2} according to the ratio of the number of electrons (implying a 29 times larger intensity for SS peaks), it is very likely that the x-ray diffraction results reported previously [16] are (at least in part) due to this parasitic phase and not to O ordering. However, as the authors state [18], this cannot be the explanation of the observed neutron experiments [15], and it is pointed out that the latter might be explained in terms of displacively modulated CuO_2 sheets, as proposed in Ref. [17].

The aim of the present work is to investigate to what extent the above mentioned displacively modulated SS (Fig. 1(b)) can explain the reported 26 neutron intensities [21]. In the next section, after a short review of the theoretical discussion, we present new simple calculations to show that there is no theoretical ground to discard " $2\sqrt{2} \times 2\sqrt{2}$ " ordered SS's. In section 3 we look for the best three-parameter fit of the neutron data using the displacively modulated SS, and compare it with the best two-parameter fit of the O ordered SS obtained before (Fig. 1(a) and Ref. [11]). Section 4 contains a discussion.

II. THEORETICAL BASIS AND SIGN OF THE EFFECTIVE O-CU-O INTERACTION.

Among the different approaches to O ordering, there are two which start from extremely different points of view. The starting point of one of them are interactions appropriate for an insulating oxide [1,2,5,25]. In this case, the effective-cluster interactions are only pair ones, long-range of Coulombic origin [10,26] (it is interesting to note that a rapidly convergent cluster expansion can be constructed for the low-energy configurations [26]). These interactions are corrected taking into account screening and charge-transfer effects on the basis of available methods to treat strongly-correlated electronic systems. This allows a harmonious qualitative explanation of the main electronic and structural properties of the system [2,5], including superconducting critical temperature as a function of doping [5], effects of pressure and alloying [2], optical conductivity of the chains, effect of Pr substitution, charge corrugation on the chains [27], photoinduced changes in transport properties [2,28], O ordering [2,9,10] and its thermodynamics [29]. This approach is justified by the fact that the average distance between the carriers in the cuprates is larger than $7 \text{ \AA}$ and thus, the Coulomb interactions are expected to be poorly screened [2,10]. In fact, as shown in Ref. [30], sizable O-O repulsion at these distances should exist to explain the split diffuse diffraction peaks [19] and other observed SS's [8,19]. However, the lattice-gas AGB model for O ordering is oversimplified, and neither it nor the ASYNNNI model can explain the shape of the observed derivative of the composition with respect to the O chemical potential, which requires to take into account additional electron charge and spin degrees of freedom [31]. These might be due to doped isolated CuO_2 clusters present in the compound [1,2].

The other extreme approach, valid in principle only for good metals, neglects completely the correlations and only three short-range effective pair interactions (EPI's) are included in the resulting ASYNNNI lattice-gas model [12,14]. The three EPI's are obtained from first-principles linear-muffin-tin orbital (LMTO) calculations and the resulting phase diagram agrees semiquantitatively with experiment [32]. However, the LMTO method is unreliable

and predicts *metallic* behavior for all O contents, while for $x < 0.4$ (the region where all the diffraction studies under discussion here were measured), the system is *insulating*. Furthermore, the correlation energy (the difference between Hartree-Fock and exact energies) has been estimated in the order of 0.6 eV per unit cell (an order of magnitude larger than the EPI's) and depend on the doping of the CuO_2 planes and hence on O ordering [2,10].

Another strong-coupling approach, but which neglects apical O ions and O-O repulsions is that of Uimin and coworkers [33]. The crystal electric field at the end of a chain is taken as a free parameter. However, if the origin of the crystal electric field is electrostatic, it should be expressed in terms of the nearest-neighbor Cu-O Coulomb repulsion U_{pd} as correctly done in the AGB model [2,13]. While in the ASYNNNI model only infinite CuO chains are stable and in the AGB model an abrupt transition from extremely short to very long chains takes place at the metal-insulator transition as x is increased, Uimin and coworkers obtained a continuous smooth increase of the chain length and the number of carriers as x increases. The form of the measured optical conductivity of the chains as a function of x in the metallic phase [34], seems to agree with a large chain length (~ 20) independent of x in this phase [27]. The neutron-diffraction data for $x \sim 3/8$ [15] rules out clearly second-neighbor O atoms and with, any O-Cu-O segment in this semiconducting sample [2,10].

The key parameter in determining the type of stable SS's in lattice gas models: ordered in CuO chains (CS) or with the O atoms or O vacancies forming "deformed" hexagonal structures (DHS) [9] (which include the previously mentioned SS with unit cell multiple of $2\sqrt{2} \times \sqrt{2}$), is the interaction between second-neighbor O atoms with a Cu in between V_{2Cu} (called $4V_2$ in the ASYNNNI model [12]). In the short-range ASYNNNI model it should be attractive ($V_{2Cu} < 0$) to stabilize the observed OII (1×2) phase at $x = 0.5$ [20], while when repulsions beyond second nearest-neighbor O atoms are present in the model, moderate positive V_{2Cu} stabilizes CS near $x = 0.5$ and DHS near $x = 0$ or $x = 1$ [1,2,9,10]. Unfortunately, the precise value of V_{2Cu} is not known yet. In the highly-correlated calculations, V_{2Cu} is very sensitive to the parameters of the multiband Hubbard model used [2,5], while as explained above, the attractive value found with the LMTO method (or any

calculation like tight-binding ones which neglects correlations) is unreliable.

In this situation, general arguments or calculations which help to determine just the sign of V_{2Cu} are very useful. One of us has shown that in the semiconducting phase (the one of interest here) if it is assumed that no holes enter apical O ions, then $V_{2Cu} > 0$ (repulsive) [13]. The calculations have been done in two different limits (infinite on-site Coulomb repulsions or small Cu-O hopping) in which the ground state of the appropriate highly correlated model could be solved exactly. The model is an extension of the three-band Hubbard model to take into account the crystal-field effect of O vacancies on their nearest-neighbor Cu atoms [2,13]. However, it has been argued that $V_{2Cu} < 0$ “unambiguously” because “strong O-Cu attraction, brought about by Cu d -orbital and O p -orbital coupling, clearly favors O-Cu-O configurations” [12]. It seems that this phrase means that covalency should favor an attractive V_{2Cu} [14]. We show below a very simple calculation which shows that this is not necessarily the case, and at the same time displays the importance of the strong correlations in the problem, and describes qualitatively the main physics involved.

To see the effect of covalency, it is sufficient to take into account only the first nearest neighbors of the Cu ions of the CuO_x planes. They are two apical O ions and 0, 1 or 2 O ions in the plane depending on the type of ordering. Thus, let us consider two systems: A containing a CuO_4 cluster and a CuO_2 cluster, and B consisting of two CuO_3 clusters. Both systems contain the same number of electrons, compatible with ionization states Cu^{+2} and O^{-2} . The energy difference represents V_{2Cu} [12,10] ($V_{2Cu} = E_A - E_B$). Let us describe both systems by the simplest highly correlated model of the type of the three-band Hubbard one [35,36]:

$$H = U_d \sum_i d_{i1}^\dagger d_{i1} d_{i1}^\dagger d_{i1} + \Delta \sum_{j\sigma} p_{j\sigma}^\dagger p_{j\sigma} + t_{pd} \sum_{i\delta\sigma} (p_{i+\delta,\sigma}^\dagger d_{i\sigma} + H.c.). \quad (1)$$

$d_{i\sigma}^\dagger$ creates a hole with spin σ on the Cu $3d_{x^2-y^2}$ orbital at site i , $p_{j\sigma}^\dagger$ creates a hole with spin σ on the p orbital of O directed towards the Cu atom at site j , and $i + \delta$ runs over the nearest-neighbor O atoms of the Cu atom at site i . The first term represents the on-site

Coulomb repulsion at Cu sites. Other repulsions are neglected for simplicity. The second term is the (positive) difference between O and Cu on-site hole energies, and the last term is the hopping term, responsible of covalency.

Each system has two holes. The ground state energy of system B corresponds to one hole in each cluster and is:

$$E_B = \Delta - 2[(\Delta/2)^2 + 3t_{pd}^2]^{1/2}. \quad (2)$$

Instead, the energy of system A depends on U_d . For small U_d both holes enter the CuO_4 cluster and the ground state is similar to the so-called Zhang-Rice singlet [36]. The energy is given by the smallest eigenvalue of a 3×3 matrix [37]. For $U_d > U_2$ where U_2 is a function of Δ and t_{pd} , the ground state of system A has one hole in each cluster. In particular, for the two limiting values of U_d , the energy is:

$$E_A(0) = \Delta - 2[(\Delta/2)^2 + 4t_{pd}^2]^{1/2}, \quad (3)$$

$$E_A(+\infty) = \Delta - [(\Delta/2)^2 + 4t_{pd}^2]^{1/2} - [(\Delta/2)^2 + 4t_{pd}^2]^{1/2}. \quad (4)$$

It is easy to see that while in the uncorrelated case $V_{2Cu}(0) = E_A(0) - E_b < 0$ (attractive), for $U_d > U_2$ is $V_{2Cu}(+\infty) = E_A(+\infty) - E_b > 0$ (repulsive) independently of U_d . Thus, the sign of V_{2Cu} is the same as that of $U_d - U_1$ where the critical value $U_1(\Delta, t_{pd}) < U_2(\Delta, t_{pd})$.

In Fig. 2 we represent the energy of the CuO_4 cluster with two holes as a function of U_d for $t_{pd} = 1.5\text{eV}$ and $\Delta = 3\text{eV}$, typical values for the cuprates [38]. The value of U_1 is determined by the equality of this energy with E_B and is exactly $U_1 = 1.5\text{eV}$ for the chosen parameters. Realistic values of U_d are seven times larger [38] and therefore $V_{2Cu} = E_A(+\infty) - E_b \sim 0.048\text{eV} > 0$ is expected. A tight-binding calculation ($U_d = 0$) gives a wrong result and a wrong Cu valence (near +3).

Direct O-O repulsion increases V_{2Cu} . As explained in simple terms [2] and calculated with more realistic approximations [5] elsewhere, V_{2Cu} is reduced (and becomes dependent on composition) when transfer of holes from the systems A and B to the superconducting planes (in the metallic phase) is allowed, or the energy of the apical O ions is reduced. However, clearly there is no physical basis to assure that V_{2Cu} should be attractive.

III. FITS OF THE NEUTRON DATA.

We have looked for the best possible fit of the observed neutron intensities in $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$ [15], using the SS based on displacements within CuO_2 planes proposed in Ref. [17] (Fig. 1(b)). Taking into account that the sample studied by these authors had a lower O content than that of the neutron experiments, we have looked for the optimum magnitude of the displacements of Cu and O atoms, following the proposed pattern, instead of using the value given in Ref. [17]. We used three fitting parameters: the magnitude of one Cu displacement d , a temperature (Debye-Waller) factor [15,9] and a constant amplitude. For the Cu and O scattering amplitudes we used the isotope average: $f_{\text{Cu}} = 7.718 \times 10^{-13}\text{cm}$ and $f_{\text{O}} = 5.805 \times 10^{-13}\text{cm}$ [40]. We have also looked for the optimum fitting of the neutron data using the O ordered SS shown in Fig. 1(a), with the Debye-Waller factor and the scaling constant as parameters. The results are shown in Table I.

The difference between the quality of both fits is apparent. For the O ordered SS, the only discrepancy with the observed results significantly larger than the statistical error corresponds to the peaks at wave vectors $\mathbf{q} = (2\pi/a)(1/2, 0)$ (and $(2\pi/a)(0, 1/2)$), but this can be due to the presence of less than 1% of the OII phase (in both possible orientations), which is always present for O content near 0.5 [7,19].

Instead, the fitting using the modulated SS is rather bad, particularly taking into account the unphysical resulting optimum displacement (54% of the lattice parameter a of the undistorted structure), and a Debye-Waller factor 1.07, 20 times larger than reasonable ones corresponding to O ordered SS [15,9]. The main grounds for this failure are easy to understand: the wave length of the modulation is $4a$, and thus one expects intense diffraction peaks at wave vectors of the form $\mathbf{q}' = (a/2\pi)\mathbf{q} = (\pm 1/4, \pm 1/4) + (m, n)$ with m, n integers. Also for small (realistic) displacements and realistic Debye-Waller factors, one expects larger intensity for larger wave vectors, since the change of phase factor ($e^{i\mathbf{q}\cdot\mathbf{d}}$ or $e^{i\mathbf{q}\cdot\mathbf{d}/2}$) for each term in the structure factor increases (this fact has also been used by Yakhou *et al.* to discard displacements as the origin of the SS they observe [18]). Except for some cancellation

of phases for certain wave vectors, the results coincide with this analysis: displacing only the Cu atoms a small amount, there is a significant intensity for $\mathbf{q}' = (3/4, 1/4)$, $(5/4, 1/4)$, $(5/4, 3/4)$, $(7/4, 1/4)$, $(7/4, 3/4)$ and $(7/4, 5/4)$. The latter is the most intense and the second intensity corresponds to $\mathbf{q}' = (7/4, 1/4)$ at zero temperature (or with small Debye-Waller factor). If instead, only the O atoms are displaced slightly, the only significant intensity is obtained for $\mathbf{q}' = (5/4, 3/4)$ and $(7/4, 1/4)$. None of these peaks correspond to the two intense observed neutron reflections. An unphysically large displacement ($d = 0.5a$) of only Cu atoms gives rise in fact to intense peaks at $\mathbf{q}' = (1/2, 1/2)$ and $(3/2, 3/2)$, but also at $(3/2, 1/2)$ with the same intensity, at four other wave vectors with half of the intensity, and there are still some peaks with less intensity. Large displacements of O atoms only, leads mainly to an intense peak at $\mathbf{q}' = (5/4, 3/4)$.

Thus, even considering arbitrary independent Cu and O displacements, it is not possible to explain the neutron data in terms of the SS of Fig. 1(b).

IV. DISCUSSION.

The lattice-gas model of Aligia, Garcés and Bonadeo (AGB) predicted “deformed hexagonal structures” (DHS) in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, for certain values of the charge-transfer parameter ΔE and x near 0 or 1 [1,2,9,10]. Diffraction patterns with unit cells multiple of $2\sqrt{2} \times \sqrt{2}$ compatible with these DHS have been observed [6,7,15,16], but strong experimental evidence against O ordering as the origin of some of these diffraction patterns has been obtained [17,18].

We have shown that in spite of recent claims [14,17], there is not enough theoretical or experimental evidence to rule out completely O ordering as the origin of all diffraction patterns compatible with unit cells multiple of $2\sqrt{2} \times \sqrt{2}$. In particular, the superstructure (SS) which by far best fits the neutron diffraction experiments of Sonntag *et al.* [15] for $x \sim 3/8$ is an O ordered one (Fig. 1(a)), obtained minimizing the free energy of the AGB model [11]. Instead, these experiments cannot be explained in terms of the displacively

modulated SS (Fig. 1(b)) proposed by Krekels, Kaesche and Van Tendeloo [17] on the basis of electron-diffraction experiments for $x \sim 0.15$ and in other perovskites.

While in x-ray or electron diffraction experiments, the scattering amplitude of the cations is much larger than that of the O anions, this is not the case of the neutron experiments. Thus, the latter are a better tool for studying O ordering. In particular, while near 0.2% of BaCu_3O_4 , can affect considerably or even determine the x-ray SS reflections for $x = 0.35$ [16] as shown by Yakhou *et al.* [18], this amount of parasitic phase practically does not affect the neutron results if as reported [15], 15% of the sample contributes to them. The Ba scattering amplitude for neutrons is actually a factor 0.9 smaller than that of O [40]. Thus, for two identical SS, one composed of Ba^{+2} and the other of O^{-2} ions, the ratio of the intensity of the latter to that of the former is 36 times larger in neutron experiments than in x-ray diffraction ones. The presence of BaCu_3O_4 and O ordering simultaneously, is the most likely explanation of the different results displayed by both diffraction techniques [15,16] on two portions of the same crystal with $x = 0.35$.

Assuming that holes do not enter apical O ions for $x < 0.5$, the results of section 2 and Ref. [13] are strong indications that in the semiconducting phase (without charge transfer to the superconducting CuO_2 planes), the DHS are stable. These results cannot rule out however that *semiconducting* DHS are metastable and the true ground state is *metallic* displaying ordering in full and empty CuO chains in the CuO_x planes, or quasi one-dimensional O ordering [30]. In spite of the fact that stable DHS for $x < 0.4$ are compatible with most experimental evidence (see section IV of Ref. [2]), in particular with the return to equilibrium after illumination ceases in photoconductivity experiments [2,28], further experimental and theoretical work seems necessary to settle the issue of O ordering for $x < 0.4$ and eventually also for $x \geq 7/8$. New neutron-diffraction experiments would be desirable, particularly in samples with Y replaced by rare earths of larger ionic radius, since in this case the semiconducting region extends to O contents greater than $x = 0.4$. In particular, the $2\sqrt{2} \times \sqrt{2}$ "herringbone" SS [18] is expected to be the ground state for semiconducting $R\text{Ba}_2\text{Cu}_3\text{O}_{6.35}$ (with $R = \text{Y}$ or rare earth) for $x = 0.5$ *but not* for $x \sim 3/4$

[9].

Note added: After completion of this work we become aware of recent nuclear quadrupole resonance experiments in several $R\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$ systems as a function of x [41,42]. These experiments are sensitive to the local Cu environment, and can therefore be considered as a direct measure of $V_{2\text{Cu}}$. The results show the absence of long CuO chains in all semiconducting samples and are consistent with $V_{2\text{Cu}} \geq 0$ in the semiconducting phase and an abrupt change to negative $V_{2\text{Cu}}$ in the Y compound as the metallic phase ($x \geq 0.5$) is entered. This is in agreement with Refs. [2,9,10]. The results are compatible with DHS (like that of Fig. 1(a)) in the semiconducting phase.

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TABLES

2θ	h	k	I_{obs}	I_a	I_b
18	1/2	0	40	0	157.2
25	1/2	1/2	420	420.7	162.8
28	3/4	1/4	50	41.8	41.9
38	3/4	3/4	$< \sigma$	0	0
40	1	1/2	$< \sigma$	0	1.3
46	5/4	1/4	$< \sigma$	0	15.2
53	5/4	3/4	$< \sigma$	22.5	51.3
55	3/2	0	$< \sigma$	0	28.2
58	3/2	1/2	30	20.8	5.5
66	5/4	5/4	$< \sigma$	0	0
66	7/4	1/4	$< \sigma$	18.7	2.4
67	3/2	1	$< \sigma$	0	4.4
72	7/4	3/4	$< \sigma$	0	0.4
81	3/2	3/2	150	143.1	0.3
83	7/4	5/4	$< \sigma$	15.7	0.2
			<i>msd</i>	14.2	68.6

Table caption: Table I: Observed (I_{obs}), and calculated (I_a and I_b) neutron intensities for the superstructures shown in Fig. 1 (a) and Fig. 1 (b) (with optimum displacement) respectively, for each of the 26 studied wave vectors $\mathbf{q} = (2\pi/a)(h, k, 0)$ [21]. Since the interchange of h and k gives the same result, only the values for $k \leq h$ are shown. 2θ is the scattering angle in degrees, $\sigma = 10$ the statistical error and *msd* the mean square deviation between observed and calculated intensities.

FIGURE CAPTIONS

Fig. 1. (a) Oxygen ordered superstructure (SS) for the CuO_x planes obtained for $x = 3/8$ from the minimum free energy of a model based on O-O Coulomb repulsions [11]. (b) Displacively modulated SS for CuO_2 planes proposed on the basis of experimental information for $x \sim 0.15$ and two perovskites without CuO_x planes [17]. Solid (open) circles denote Cu (O) atoms.

Fig.2. Energy of a CuO_4 cluster with two holes as a function of on-site Cu Coulomb repulsion U_d for $\Delta = 3\text{eV}$ and $t_{pd} = 1.5\text{eV}$.

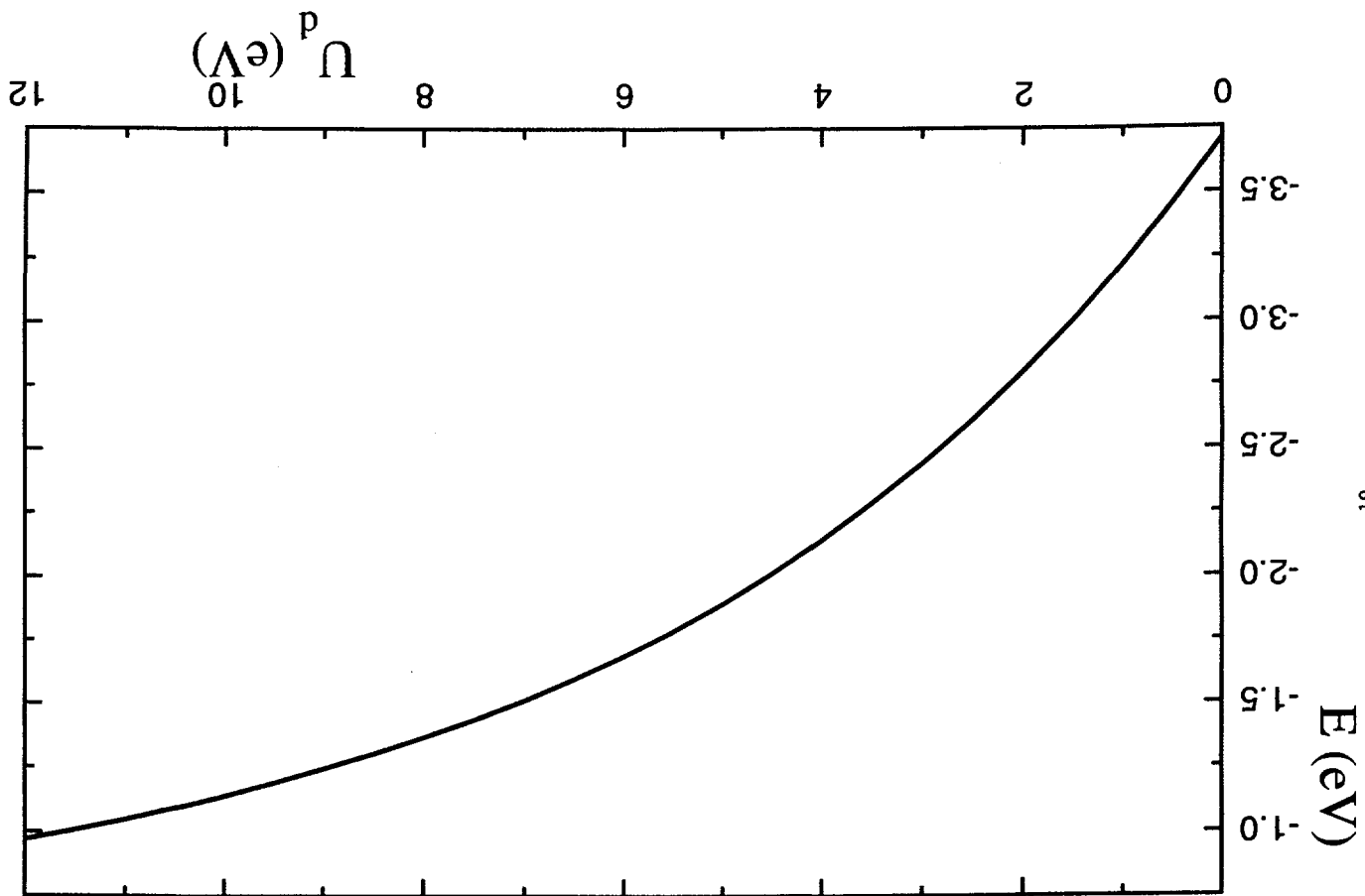


Fig. 2

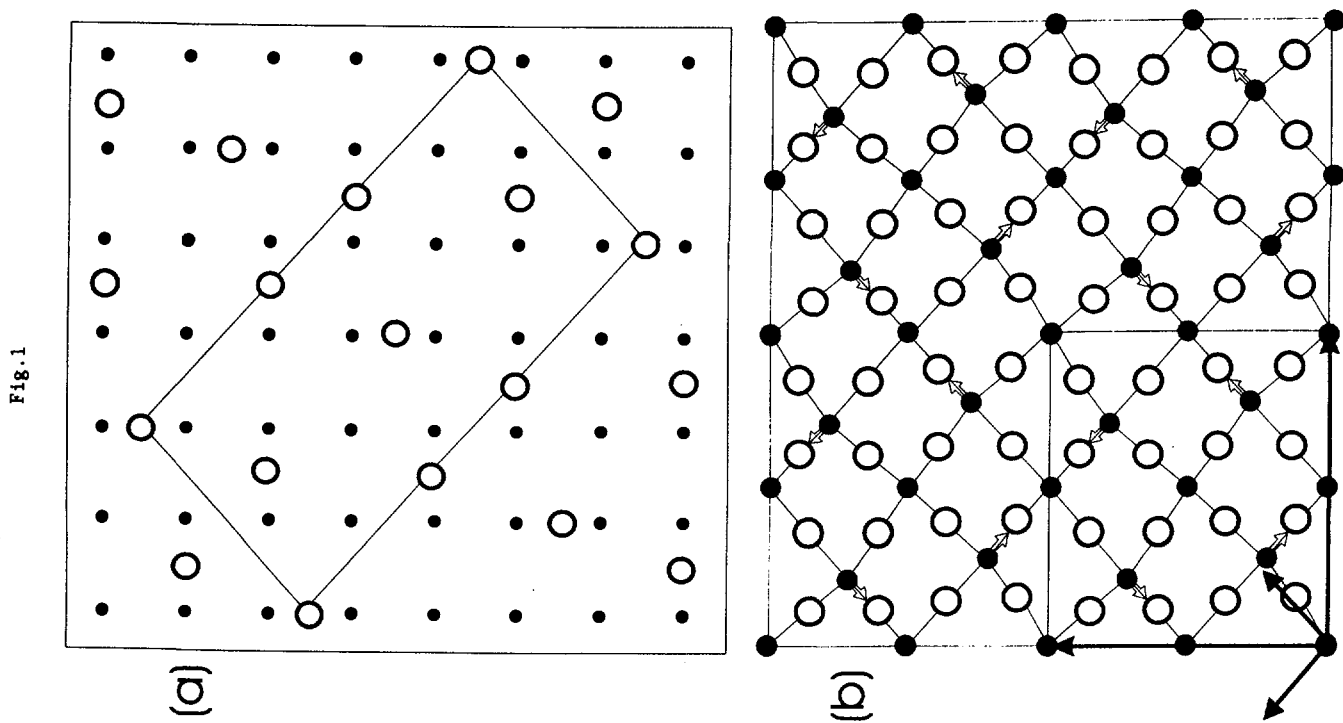


Fig. 1