

Relation between oxygen hopping activation energy and unit-cell volume for strongly underdoped $RBa_2Cu_3O_x$ ($R = Y, Nd, La$)

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Pressure-controlled oxygen reordering responsible for the appearance of time-dependent superconductivity in originally nonsuperconducting underdoped $RBa_2Cu_3O_x$ ($R = Y, Nd, La$) was studied by magnetization and x-ray diffraction measurements. The rate of the reordering process, determined by the activation energy E_a of oxygen hopping in the basal plane, depends strongly on both pressure and R -ion size. The activation energy was found to decrease linearly with the increase of the unit-cell volume, at a rate of $-0.018 \text{ eV}/\text{\AA}^3$. This E_a dependence on volume for strongly underdoped compounds is shown for both pressure and R -ion substitution. This relation allows understanding the significant differences in time-dependent properties observed among compounds of $RBa_2Cu_3O_x$ series.

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I. INTRODUCTION

Magnetization measurements have demonstrated an appearance of pressure-induced superconductivity in the initially nonsuperconducting $RBa_2Cu_3O_x$ with $R = Nd, La$.^{1,2} The development of a superconducting state in the underdoped samples is caused by prolonged room-temperature storage under pressure, and a slow increase of T_c towards an equilibrium value is observed. A similar evolution of T_c under ambient pressure in $YBa_2Cu_3O_{6.41}$ has been already observed in a quenching experiment by Jorgensen *et al.*³ In that experiment the sample was quenched from high temperature and the subsequent appearance of superconductivity was caused by reordering of oxygen atoms at room temperature. The charge-transfer mechanism responsible for this phenomenon is attributed to oxygen ordering in the CuO_x planes causing hole doping of the CuO_2 planes.

It is commonly believed that the hopping of oxygen atoms between two different sites in the basal plane, O(1) and O(5), plays a key role in oxygen reordering in underdoped $RBa_2Cu_3O_x$ and is responsible for orthorhombic-tetragonal (O/T) phase transition.⁴⁻⁶ Additional (or alternative) possible mechanism O(1)-O(5)-O(1) hopping that includes O diffusion from O(1) site to O(1) site via O(5) intermediate position was suggested by Jorgensen *et al.* (Ref. 3) in order to explain small changes in oxygen site occupancies observed during oxygen ordering in $YBa_2Cu_3O_{6.41}$. For both O(1)-O(5) and O(1)-O(5)-O(1) mechanisms the activation energy is approximately the same [since the activation energy is nearly zero for motion of oxygen atom along O(5) sites] as pointed by Rothman *et al.* in Ref. 6. The value of the activation energy is about 1 eV, therefore, the thermally-activated oxygen reordering occurs at room temperatures. The growth in length of the Cu-O chains is accompanied with a charge transfer between CuO_x planes and CuO_2 planes.

A direct evidence for an importance of oxygen hopping between the O(1) and O(5) sites was shown in a recent time-resolved x-ray study for $NdBa_2Cu_3O_{6.67}$.⁷ For that sample, the charge transfer during disordering was found to be pro-

portional to the changes in the unit-cell volume. There is an evidence for a strong dependence of the oxygen order on the R -ion size, obtained in nuclear quadrupole resonance (NQR) experiments by Lütgemeier *et al.*⁸ The cited work shows clearly that average Cu-O chain length decreases with rising ionic radii due to the change of intra-chain interaction between oxygen atoms. This decrease results, for larger R ions, in a shift of metal-insulator transition in $RBa_2Cu_3O_x$ towards higher oxygen contents. This finding is in qualitative agreement with a large enhancement in oxygen mobility along with increasing lattice parameters of $RBa_2Cu_3O_x$ when R -ion changes from Y to La (Ref. 9) (ionic radii for coordination number 8 for Y, Nd, and La are equal to 1.019, 1.109, and 1.16 Å, respectively¹⁰). The similarity of pressure and R -ion-size effects on oxygen mobility (well pronounced in the pressure-induced time evolution of superconductivity in underdoped $RBa_2Cu_3O_x$) was reported previously.² A strong decrease in oxygen mobility under pressure manifested by a linear pressure dependence of activation energy was found for $YBa_2Cu_3O_x$ by Sadewasser and co-workers.^{11,12} All these facts clearly suggest a direct correlation between the lattice parameters and energy barrier for oxygen hopping in underdoped $RBa_2Cu_3O_x$.

In this paper, we present evidence for a common origin of both R -ion size and pressure effects on the activation energy of oxygen hopping between the O(1) and O(5) sites. The rate of reordering process, related to the activation energy E_a by Arrhenius law, depends strongly on unit-cell volume. It is shown that, E_a decreases linearly with the increase of the unit-cell volume independently on the path leading to the volume changes.

II. EXPERIMENTAL

Strongly underdoped $YBa_2Cu_3O_{6.38}$, $LaBa_2Cu_3O_{6.74}$, and $NdBa_2Cu_3O_{6.67}$ ceramic samples located very close to orthorhombic-tetragonal transition, were prepared by suitable heat treatments of optimally doped samples in flowing N_2 . For these samples, the superconducting state was found to be controlled precisely by pressure: it appears after a certain time of room temperature (RT) storage under pressure and disappears (or T_c decreases gradually) after pressure re-

lease. The relaxation process of both superconductivity and lattice parameters was studied by magnetization measurements and time resolved x-ray diffraction, respectively.

The low-temperature magnetization measurements were performed under a hydrostatic pressure of about 0.5 GPa for $\text{NdBa}_2\text{Cu}_3\text{O}_{6.67}$ and 1.0 GPa for $\text{LaBa}_2\text{Cu}_3\text{O}_{6.74}$ using a vibrating sample magnetometer and a miniature Be-Cu pressure container. The value of T_c was determined by the onset of diamagnetism in $M(T)$ dependence measured at 10 Oe. After measurement at each temperature point, the sample was heated to RT and kept under pressure for a certain time in order to change the degree of oxygen order in the lattice. The procedure was repeated for different RT elapsed times until equilibrium caused by oxygen rearrangement was reached. The time-resolved x-ray diffraction investigations for oxygen disordering process in $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$ were performed using a Bragg-Brentano diffractometer employing monochromatized CuK_α radiation. Before the measurements, the sample was kept for six days under 1.3 GPa pressure at room temperature in order to reach the equilibrium in the oxygen sublattice. Immediately following the pressure release, short time scans of 2θ range including 006, 020, and 200 Bragg peaks was monitored continuously for 60 h at RT. The lattice parameters a , b , and c , were calculated from the fitted peak positions for each scan.

III. RESULTS AND DISCUSSION

The evolution of the lattice parameter c , unit-cell volume V , and T_c during the disordering process after pressure release for underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$ are presented in Figs. 1(a), 1(b), and 1(c), respectively (some data of Refs. 3 and 13 are included in Fig. 1). Due to oxygen disordering at RT, T_c decreases from the value of 17 K obtained immediately after 1.3 GPa pressure release, approaching the equilibrium value of 8 K.

Temporal changes in T_c during pressure-controlled oxygen reordering are well described by the Kohlrausch stretched-exponential function of time

$$T_c(t) = T_c^{\text{eq}} + [T_c(0) - T_c^{\text{eq}}] \exp[-(t/\tau)^{0.5}], \quad (1)$$

where T_c^{eq} is an equilibrium value, and τ is the relaxation time constant related to the activation energy of oxygen hopping $E_a \approx 1$ eV by the Arrhenius law $\tau = \tau_0 \exp(E_a/kT)$ with the attempt period τ_0 equal 1.4×10^{-12} s.¹⁴

The time dependences of lattice parameters are well approximated by Eq. (1). Almost identical τ values were obtained for $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$ at oxygen disordering from the analysis of the structural changes and T_c relaxation data shown in Fig. 1. This demonstrates a correlation between oxygen order and superconductivity.

The change in T_c observed for $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$ during the thermally activated disordering process after pressure release is the reverse of the change in T_c observed during oxygen ordering process under pressure. However, the process of oxygen ordering under pressure is considerably slower as compared with disordering one after pressure release as shown in Fig. 1(c). The behavior correlates with a strong

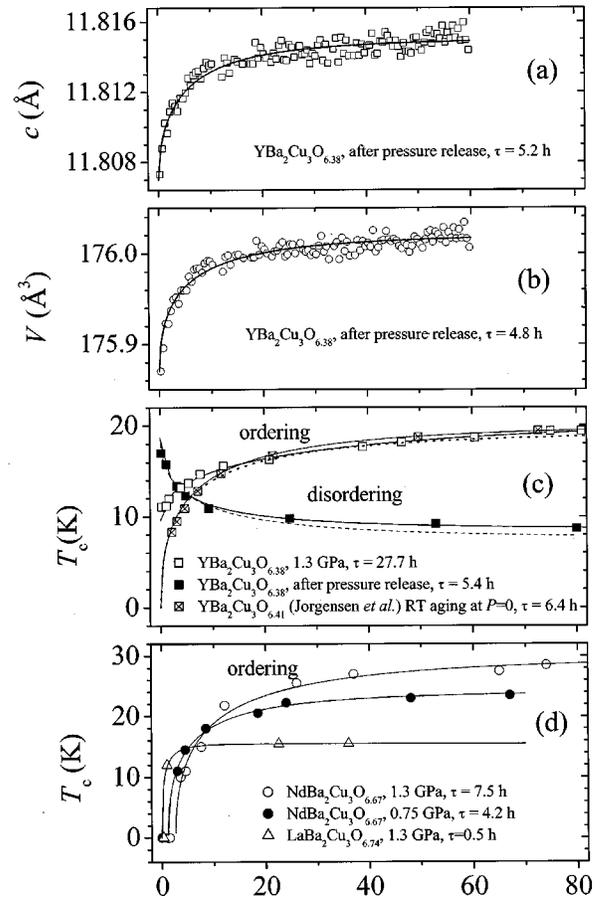


FIG. 1. Time evolution of $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$ lattice parameter c (a) and unit-cell volume (b) in disordering process at 298 K after 1.3 GPa pressure release. Changes in T_c for $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$ during oxygen ordering under 1.3 GPa pressure and disordering after pressure release and for $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ during oxygen ordering after quenching (c). Time evolution of T_c caused by pressure-induced oxygen ordering at RT in strongly underdoped $\text{NdBa}_2\text{Cu}_3\text{O}_{6.67}$ subjected to different pressure cycling and in $\text{LaBa}_2\text{Cu}_3\text{O}_{6.74}$ (d). Solid lines represent the best fits of Eq. (1). The dashed lines represent the $T_c(t)$ dependence for $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$ (data from Ref. 13) and $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ (Ref. 3), calculated using volume relaxation data.

reduction of oxygen mobility under increasing pressure observed in $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$.¹¹ It is important to stress that the superconductivity created by prolonged room-temperature pressure treatment would be maintained over a long time at low temperatures with frozen oxygen order in the sample.

The T_c evolution for compounds with different R ions is presented in Figs. 1(c) and 1(d). For nonsuperconducting $\text{NdBa}_2\text{Cu}_3\text{O}_{6.67}$ and $\text{LaBa}_2\text{Cu}_3\text{O}_{6.74}$, superconductivity does not immediately appear after applying the pressure, but after some storage time at RT. In the Nd-based compound it was detected in about 2.6 h under 1.3 GPa and in 1.2 h under 0.75 GPa, indicating a faster transfer of holes at lower pressure. The pressure values given in Fig. 1 correspond to pressure at room temperature whereas the corresponding low-temperature values are smaller by about 0.3 GPa for the highest applied pressures, due to thermal effects. Smaller changes in T_c were observed during relaxation process at 1.3

GPa for superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$ with T_c at ambient pressure equal to 8 K. One can see in Figs. 1(c) and 1(d) that the rate of pressure-induced oxygen ordering (responsible for the time changes of T_c) strongly increases with raising R -ion size in $R\text{Ba}_2\text{Cu}_3\text{O}_x$. In conclusion, these results show a clear analogy between the influence of pressure and of R -ion size on the rate of oxygen rearrangement in $R\text{Ba}_2\text{Cu}_3\text{O}_x$ series.

In Ref. 7 we established a simple relation between the charge transfer and the unit-cell volume variations that occur during oxygen reordering for $\text{NdBa}_2\text{Cu}_3\text{O}_{6.67}$, $\Delta V/\Delta n \approx -12 \text{ \AA}^3/(\text{hole}/\text{CuO}_2)$. The same $\Delta V/\Delta n$ value was derived for $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$ from present relaxation data, hence it is common for both Nd- and Y-based compounds. The $T_c(t)$ dependence for $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$ at oxygen disordering, shown by dashed line in Fig. 1(c), was calculated based on (i) the experimentally determined time-dependent unit-cell volume data, (ii) the above relation between ΔV and Δn , and (iii) the universal (for high- T_c superconductors) inverted parabolic $T_c(n)$ dependence¹⁵

$$T_c(n)/T_{c,\text{max}} = 1 - [(n_{\text{opt}} - n)/(n_{\text{opt}} - n_c)]^2, \quad (2)$$

with optimal hole concentration in CuO_2 planes $n_{\text{opt}} = 0.25$ hole/ CuO_2 and minimal concentration required for occurrence of superconductivity $n_c = 0.06$ hole/ CuO_2 . Moreover, we find that the changes in T_c and unit-cell volume obtained by Jorgensen *et al.*³ for quenched $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ during oxygen ordering correlate well with our predictions. The dashed line in Fig. 1(c) represents $T_c(t)$ dependence for $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ calculated using the above approach. The ability to fit both sets of data gives support for a common origin of charge transfer occurring during oxygen reordering in underdoped $R\text{Ba}_2\text{Cu}_3\text{O}_x$ controlled by pressure or temperature. These results indicate that the variation in unit-cell volume is directly related to charge redistribution within unit cell at oxygen reordering in $R\text{Ba}_2\text{Cu}_3\text{O}_x$. The behavior correlates well with salient features of 1-2-3 structure to decrease the orthorhombic cell volume with oxygen doping.

Figure 2 presents a logarithmic dependence of normalized quantity $[A(t) - A^{\text{eq}}]/[A(0) - A^{\text{eq}}]$ on $t^{0.5}$, with A representing T_c , V , or resistance R for the data presented in Fig. 1 and for $\text{LaBa}_2\text{Cu}_3\text{O}_{6.76}$.² The relaxation data satisfying Eq. (1) would exhibit a linear dependence with a slope equal to $-(1/\tau)^{0.5}$. Thus, Fig. 2 demonstrates the rate of oxygen reordering $1/\tau$ for different $R\text{Ba}_2\text{Cu}_3\text{O}_x$ compounds, derived from measurements of various physical quantities. The same value of $\tau \approx 5$ h was derived from two sets of data, T_c and structural relaxation, for disordering process at ambient pressure in $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$. Also for $\text{LaBa}_2\text{Cu}_3\text{O}_{6.76}$ the τ values derived from both, T_c and resistance, data at oxygen ordering under 1.2 GPa are in perfect agreement ($\tau \approx 0.5$ h).

Clearly, the rate of thermally activated process varies with both R -ion size and pressure value, suggesting a strong dependence of oxygen hopping activation energy on lattice parameters. Assuming the validity of the Arrhenius law, we calculated the values of the activation energy for $R\text{Ba}_2\text{Cu}_3\text{O}_x$ at different pressures using the τ values derived from relaxation data (presented in Fig. 2). Figure 3 shows the activation energy for oxygen atom hopping E_a as a function of unit-cell

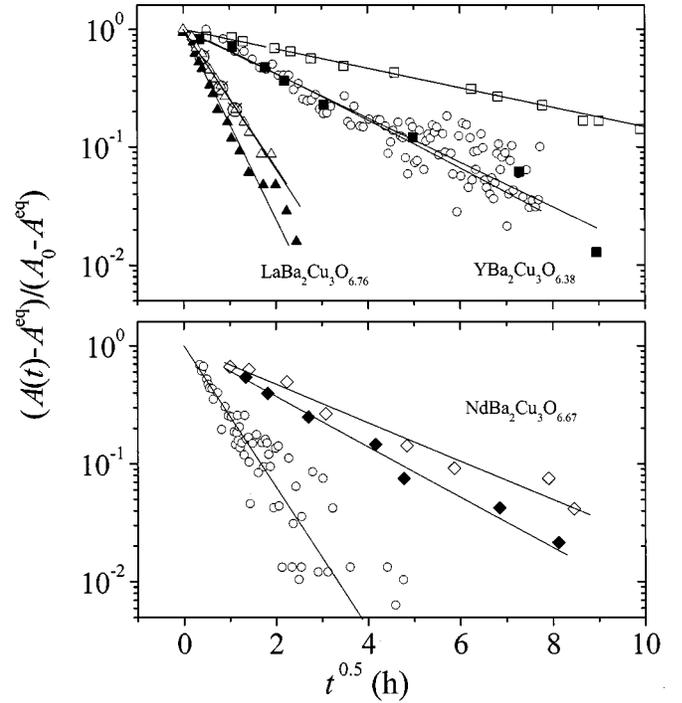


FIG. 2. Relative changes in T_c , unit-cell volume V , and resistance R (all denoted by A) vs $t^{0.5}$ for pressure-controlled oxygen reordering at 297 ± 2 K for $R\text{Ba}_2\text{Cu}_3\text{O}_x$. Upper panel presents relaxation data for $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$: $T_c(t)$ at 1.3 GPa (open squares), $T_c(t)$ (solid squares), and $V(t)$ (circles) after pressure release, and for $\text{LaBa}_2\text{Cu}_3\text{O}_{6.76}$: $T_c(t)$ at 1.2 GPa (crossed circles), $R(t)$ at 1.2 GPa (open triangles), and after pressure release (solid triangles). Lower panel presents data for $\text{NdBa}_2\text{Cu}_3\text{O}_{6.67}$: $T_c(t)$ at 1.3 GPa (open diamonds) and at 0.75 GPa (solid diamonds), $V(t)$ after pressure release (circles). Straight lines are a fit of Eq. (1).

volume including both pressure and R -ion size effects. The unit-cell volume V for $R\text{Ba}_2\text{Cu}_3\text{O}_x$ samples was determined at ambient pressure basing on x-ray diffraction data. The changes in volume under pressure were estimated using the volume compressibility $k_V = -(1/V_0)(dV/dP)$, data obtained by Suenaga and Oomi¹⁶ for underdoped $\text{YBa}_2\text{Cu}_3\text{O}_x$. According to these data, the volume compressibility depends strongly on oxygen content and peaks around the metal-insulator (orthorhombic-tetragonal) transition, reaching the value of $k_{V,\text{max}} = 1.42 \times 10^{-2} \text{ GPa}^{-1}$ at $x = 6.3$ (most likely, the lattice softening at approaching the phase transition point originates from oxygen reordering in the sample subjected to pressure). We used the above maximal value $k_{V,\text{max}}$, for the estimation of volume changes under pressure for $\text{NdBa}_2\text{Cu}_3\text{O}_{6.67}$ and $\text{LaBa}_2\text{Cu}_3\text{O}_{6.76}$ compounds, since both samples are located in the region of metal-insulator transition. The influence of R -ion size on compressibility is expected to be small:¹⁷ the results of model calculation for optimally doped $R\text{Ba}_2\text{Cu}_3\text{O}_x$ predict an increase in volume compressibility by only about 1.6% when the R ion is changed from Yb to Nd. In Fig. 3, we also present the activation energy as a function of unit-cell volume for $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ single crystal determined using the linear pressure dependence $E_a(P)$ found up to 2.3 GPa by Sade-

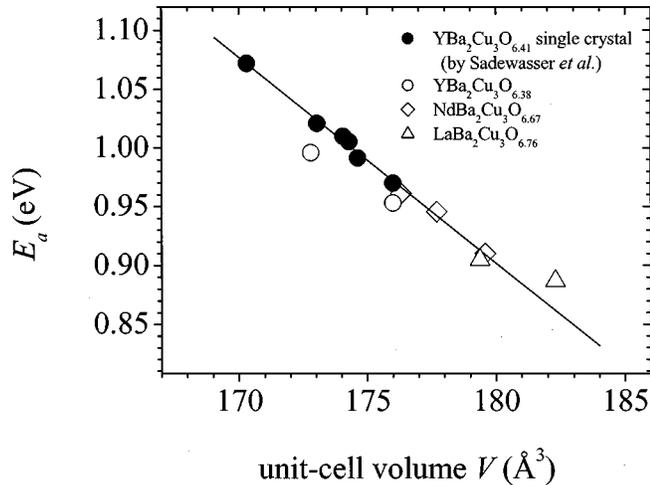


FIG. 3. Dependence of oxygen hopping activation energy E_a on unit-cell volume of $RBa_2Cu_3O_x$ compositions located near the metal-insulator transition: $R=Y$ (open circles), $R=Nd$ (diamonds), $R=La$ (triangles). The solid line and circles represent the $E_a(V)$ dependence for $YBa_2Cu_3O_{6.41}$ calculated according to the pressure dependence $E_a(P)$ reported by Sadewasser *et al.* (Ref. 11) and compressibility data (Ref. 16).

wasser *et al.*¹¹ For $YBa_2Cu_3O_{6.41}$, the solid line with the slope $dE_a/dV = -0.018 \text{ eV}/\text{\AA}^3$, obtained by linear approximation of the $E_a(V)$ data, agrees precisely with the $E_a(V)$ data for $NdBa_2Cu_3O_{6.67}$. The known $E_a(V)$ slope is expected to allow for estimation of oxygen-hopping activation energy for other 1-2-3 compounds.

It is essential for understanding of $E_a(V)$ dependence shown in Fig. 3 that the energy E_a is attributed mainly to the oxygen hopping between O(1) and O(5) sites. Since the samples studied in the present paper, namely, $YBa_2Cu_3O_{6.38}$ ($T_c = 8 \text{ K}$ at equilibrium), $NdBa_2Cu_3O_{6.67}$ ($T_c = 0$ at equilibrium), $LaBa_2Cu_3O_{6.74}$ ($T_c = 0$ at equilibrium) are closer to O/T transition than the $YBa_2Cu_3O_{6.41}$ sample ($T_c = 20 \text{ K}$ at equilibrium³), we believe that, in the studied samples the O(1)-O(5) oxygen jumps are likely to be a leading mechanism in oxygen reordering process. One should remember that the E_a value determined from the Arrhenius law is averaged over a variety of slightly different activation energies depending on local oxygen order. The O(5)→O(1) hopping is of crucial importance for tetragonal to orthorhombic phase transition as well as for oxygen reordering in the vicinity of the metal-insulator transition where short Cu-O chains dominate. For this region of phase diagram, our results suggest an equivalent effect of both external and chemical pressure: the E_a values coincide for different compounds when their unit-cell volumes become equal. In contrast, in optimally doped $RBa_2Cu_3O_{7-\delta}$ compounds a slight reduction of oxygen activation energy with unit-cell volume $dE_a/dV = -0.0054 \text{ eV}/\text{\AA}^3$, has been observed by variation of unit-cell volume with R -ion substitution.¹⁸ Recently single crystal thermal-expansion measurements under pressure for $YBa_2Cu_3O_{6.94}$ have shown $dE_a/dV = -0.048 \text{ eV}/\text{\AA}^3$.¹⁹ These large differences between the external and chemical pressure effects have been attributed¹⁹ to nonuniform reduction of interatomic distances within unit cell. We suppose

that different $E_a(V)$ dependences in optimally doped and strongly underdoped samples are due to different oxygen hopping involved in the oxygen rearrangement. Whereas the hopping between the O(5) and O(1) sites dominate at oxygen ordering in the vicinity of metal-insulator transition, more complex oxygen diffusion involving an additional hopping is expected for nearly optimally doped compounds with well ordered chain structure.

Further insight into the of origin $E_a(V)$ dependence maybe gained based on the NQR data⁸ which showed that the average Cu-O chain length decreased with increasing lattice parameters when Nd or La substitutes Y. The reduction of attractive interaction between oxygen atoms placed along the Cu-O chains (the next-nearest-neighbor coupling with a Cu atom in between, V_2) was found to be responsible for this behavior. The essential role of the intrachain interaction was confirmed by Monte Carlo simulation in the extended ASYNNNI model of Haugerud *et al.*²⁰ who reproduced the reduction of Cu-O chain fragments for $RBa_2Cu_3O_x$ with expansion of the unit cell. In contrast, the applied pressure is expected to increase the attraction V_2 , favoring the lengthening of chains with contraction of unit-cell volume. Therefore, the pressure-induced insulator-superconductor transition is realized in underdoped $RBa_2Cu_3O_x$. Based on the results of Refs. 8 and 20, we suggest that the relation between oxygen hopping activation energy and unit-cell volume $E_a(V)$ is governed by the intrachain oxygen interaction parameter V_2 .

IV. CONCLUSIONS

We studied pressure-controlled oxygen reordering processes causing the time-dependent superconductivity in strongly underdoped $RBa_2Cu_3O_x$ ($R=Y, Nd, La$) by magnetization and x-ray diffraction measurements. Structural data for $YBa_2Cu_3O_x$ show that its unit-cell evolves during oxygen *disordering* after pressure release in the same way as during oxygen *ordering* process in a quenched sample. The relation between the charge transfer and unit-cell volume variations during oxygen reordering established for $NdBa_2Cu_3O_{6.67}$, $\Delta V/\Delta n \approx -12 \text{ \AA}^3/(\text{hole}/\text{CuO}_2)$, is well applicable for both, the data obtained for $YBa_2Cu_3O_{6.38}$ during oxygen disordering and for $YBa_2Cu_3O_{6.41}$ during oxygen ordering in a quenched sample. The results demonstrate that for strongly underdoped $RBa_2Cu_3O_x$ the relation describes well not only the pressure-controlled oxygen reordering but the oxygen reordering process in general. We found a common linear dependence of oxygen atom activation energy E_a on unit-cell volume. The activation energy decreases linearly with unit-cell volume at the rate of $-0.018 \text{ eV}/\text{\AA}^3$. The derived $E_a(V)$ slope is expected to allow for estimation of oxygen-hopping activation energy for other 1-2-3 compounds. The results show that the unit-cell volume relaxation data are helpful for the analysis of time scale and magnitude of charge transfer occurring at oxygen reordering in underdoped $RBa_2Cu_3O_x$.

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