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Effect of pressure on the magnetic phase transition in cupric oxide

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The thermal expansion has been measured on the single crystalline CuO under pressure up to 1.3 GPa. Two anomalies in the temperature dependence of thermal expansion were observed at antiferromagnetic transition temperatures, $T_{N1}=230$ K and $T_{N2}=212$ K, at ambient pressure, suggesting a strong magnetoelastic coupling in CuO. T_{N2} is found to decrease with increasing pressure at a rate of $dT_{N2}/dP \sim -2.9$ K/GPa. Detailed comparison was made with a previous study on the rapid suppression of the antiferromagnetic coupling in $Cu_{1-x}Li_xO$. The Seebeck coefficient has been measured on $Cu_{1-x}Li_xO$ as a function of temperature. The results indicate that hole hopping is remarkably enhanced by substituting Cu with Li. The present study suggests that the suppression of the magnetic coupling both in the CuO under pressure and in $Cu_{1-x}Li_xO$ is mainly due to the enhancement of hole hopping.

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I. INTRODUCTION

Cupric oxide, CuO, consists of only Cu-O bonding that has been thought as playing an important role for high-T_C superconductivity because only compounds containing it have shown the high-T_C superconductivity. Recent observation of charge ordering and the existence of strong spin-charge-lattice coupling renewed an interest in this simple copper oxide.[1,2] CuO is composed only of copper and oxygen but still retains the antiferromagnetic (AF) nature. It has a monoclinic structure with four nearest O atoms and two distant apical O atoms (the apical O atoms are also the nearest atoms for neighboring Cu atoms) forming a very distorted octahedron around the Cu atom.[2]

The magnetic structure of CuO consisting of chains along the $[10\bar{1}]$ direction, with a Cu-O-Cu angle of 146°, gives rise to a quasi-one-dimensional superexchange coupling. The antiferromagnetic long-range order develops with two successive phase transitions; one undergoing incommensurate ordering around $T_{N1}=230$ K with a helix period [propagation vector $\mathbf{k}=(0.506,0,-0.483)$], followed by a first-order commensurate transition around $T_{N2}=213$ K with $\mathbf{k}=(0.5,0,-0.5)$.[3–5] It shows a strong low-dimensional nature as demonstrated by the results of specific heat, susceptibility, and neutron scattering measurements.[2,6–9]

The antiferromagnetism in the cuprates is extraordinarily sensitive to hole doping. La_2CuO_4, for example, is considered to be an antiferromagnetic insulator ($T_N=325$ K) with a gap of the charge-transfer-type. Holes are doped into the CuO_2 plane when Li is substitudes for Cu. A rapid suppression of T_N has been observed in the low doping range only with 3% Li substitution without strongly affecting either the on-site Cu moments or the shape of the spin-wave excitation spectrum.[10] Similarly, a rapid decrease of T_N has been reported in $Cu_{1-x}Li_xO$ that was prepared by a usual solid state reaction at ambient pressure, where Li can partially substitute for Cu and introduce holes into CuO without affecting the oxygen stoichiometry. It has been revealed that by 1.7% Li substitution, the antiferromagnetic transition temperatures decrease drastically from $T_{N1}=229$ K and $T_{N2}=213$ K to $T_{N1}=206$ K and $T_{N2}=199$ K, respectively. Furthermore, the resistivity and activation energy decreases by several orders of magnitude. Meanwhile the expansion of the Cu-O-Cu distance along the superexchange direction $[10\bar{1}]$ was also reported.[11]

Similar results have been also obtained with further substitution in $Cu_{1-x}Li_xO$ by using a high-pressure synthesis method[12] and the T_N was reduced largely to 91 K in $Cu_{0.84}Li_{0.16}O$.[13]

It seems to be of great interest to know whether the suppression of the antiferromagnetic interaction comes from the hole doping into CuO or from the lattice change due to the substitution of Cu by Li. Pressure is a useful tool to increase the carrier concentration by decreasing the unit cell volume without doping impurity. This merit enables us to do an investigation of the hole doping effect on single crystalline CuO. In the present work, the thermal expansion of CuO has been measured at high pressure to clarify the effect of pressure on T_N, whether spin-lattice coupling can be directly evidenced or not. A comparison with that of hole doping in $Cu_{1-x}Li_xO$ is also made with supplementary measurement of thermoelectric power on the latter to clarify the origin of the rapid suppression of the AF coupling in hole-doped $Cu_{1-x}Li_xO$.

II. EXPERIMENT

A single crystal CuO was prepared from the chemical vapor transport method as reported previously.[2,14] The struc-

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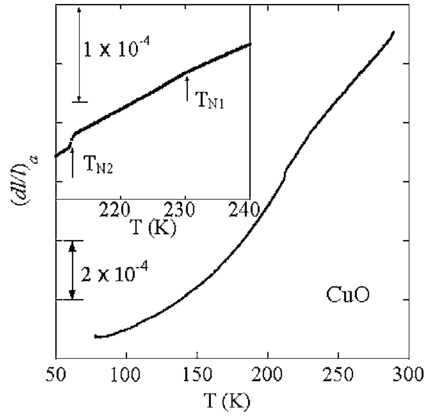

FIG. 1. Linear thermal expansion along the a axis at ambient pressure. T_{N1}(=230 K) and T_{N2}(=212 K) are shown by arrows.

ture is monoclinic with unit cell dimensions of a=4.69 Å, b=3.42 Å, c=5.13 Å, and β=99.5°.

Thermal expansion $\Delta l/l$ was measured in the temperature range between 77 K and 300 K by means of the strain gauge method,[15,16] in which two gauges were used as an active (sample) and a dummy (reference) gauge. The strain gauge was glued on a clean surface of the specimen and cured in accordance with the prescription. Molybdenum (5N) was used as a reference material. Hydrostatic pressure up to 1.3 GPa was generated by using a piston-cylinder device which is made of Ni-Co-Cr-Mo (MP35N) alloy. A 1:1 mixture of Fruorinert FC 70 and FC 77 was used as a pressure transmitting medium. The details of high pressure apparatus have been reported previously.[17]

Thermoelectric power (Seebeck coefficient) of hole doping in $Cu_{1-x}Li_xO$ was measured in a temperature range of 298–1000 K. The polycrystalline samples were prepared with different amounts of Li by the usual solid-state reaction method such as reported previously.[11] Sintered samples cut into dimensions of $\sim 3\times 3\times 20$ mm^3 were used with a temperature difference of 5 K between the two ends of the specimen.

III. RESULTS

A. Thermal expansion of CuO under high pressure

Figure 1 shows a fractional change of relative length $(\Delta l/l)_a$ of the a axis at ambient pressure. $(\Delta l/l)_a$ decreases with decreasing temperature, shows a discontinuity and a kink near two magnetic ordering temperatures, and the two magnetic ordering temperatures T_{N1} and T_{N2} are defined, as the temperature where the temperature-derivative of $(\Delta l/l)_a$ shows a peak, to be T_{N1}=230 K and T_{N2}=212 K, which will be mentioned in the following paragraph. The present result is consistent with the previous magnetic susceptibility and heat capacity measurements.[2] On the other hand, Krynetskii *et al.* measured the thermal expansion along the c axis, and detected no anomaly near the magnetic transition temperatures.[18] It implies that the change in the thermal expansion should be anisotropic at T_{N1} and T_{N2}.

Figure 2 shows the temperature dependence of the thermal expansion coefficient α_a at ambient pressure. α_a was obtained by differentiating $(\Delta l/l)_a$ with respect to T. α_a increases with increasing temperature and two peaks are clearly seen at T_{N1}(=230 K) and T_{N2}(=212 K). The present result is comparable to that of the heat capacity $C_p(T)^2$, in which two peaks are observed at 211 K and 227 K and the peak at T_{N2} is especially sharp, indicating that this transition is first order. There is a discontinuous change in the propagation vector at T_{N2}.[3–5] At room temperature, the value of thermal expansion coefficient, $\alpha_a=6.0\times 10^{-6}$ K^{-1}, is comparable to $\alpha_a=7.5\times 10^{-6}$ K^{-1}, which is calculated from the result of the temperature dependence of lattice parameters in the previous study.[2]

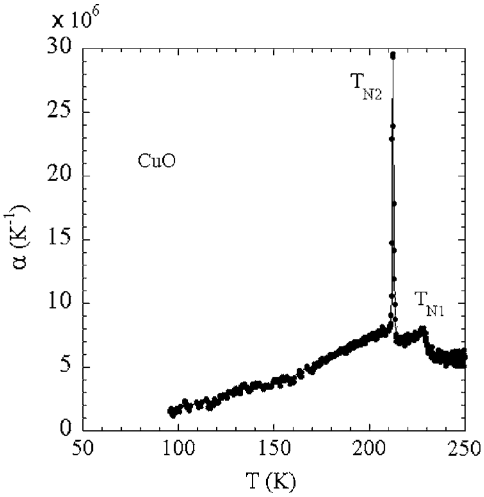

FIG. 2. Thermal expansion coefficient $\alpha_a=(\Delta l/l)/\Delta T$ at ambient pressure. Sharp peaks are seen at T_{N1} and T_{N2}.

Next we attempt to estimate the Grüneisen parameter γ which is defined by the following thermodynamical equation:

$$\gamma=\frac{V\beta B_T}{C_v}, \qquad (1)$$

where β is the volume thermal expansion coefficient, B_T is the isothermal bulk modulus, C_v is the heat capacity at constant volume, and V is the volume of the specimen. Since the temperature dependence of lattice parameters is not so anisotropic near room temperature,[2] β may be approximated to be $\beta_{300\ \mathrm{K}}\simeq 3\alpha_{300\ \mathrm{K}}=18\times 10^{-6}$ K^{-1}. Substituting β, B_T=72 GPa,[19] and $C_v\simeq C_p$=42 J/mol K (Ref. 13) into Eq. (1), we obtain γ=0.37, which is smaller than the usual value $\gamma\sim 2.0$ in the Debye model.[20] Since charge-ordering transition is observed at high temperature around 880 K,[2]it suggests that the main part of the heat capacity and thermal expansion consists of not only the phonon but also other effects such as charge-spin-orbital coupling.

The thermal expansion coefficient $\alpha(T)$ at high pressure are shown in Fig. 3. T_{N2} is defined as the temperature where $\alpha(T)$ shows a peak, while it is difficult to detect an anomaly near T_{N1} at high pressure since the pressure transmitting medium freezes near 250 K, which affects strongly the resistance of strain gauge. It is found that T_{N2} decreases with increasing pressure, that is, the superexchange interaction is

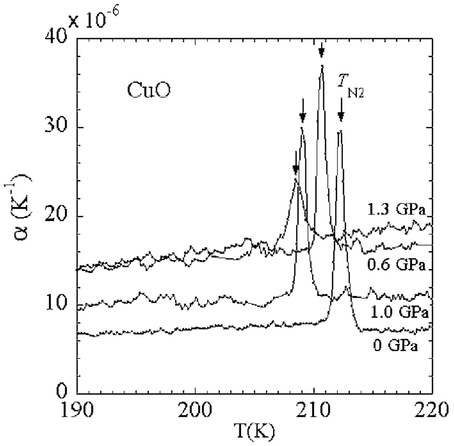

FIG. 3. Thermal expansion efficient $\alpha(T)$ along the a axis at high pressures.

suppressed in spite of a decrease in the unit cell volume. This tendency resembles the result which is observed in the $Cu_{1-x}Li_xO$ substituting system. We will discuss this point in the following section.

B. Seebeck coefficients for hole-doped $Cu_{1-x}Li_xO$

For the purpose of comparison between the pressure effect on the magnetic transition and that of hole doping in $Cu_{1-x}Li_xO$, a supplementary measurement of thermoelectric power (Seebeck coefficient) on ambient pressure synthesized $Cu_{1-x}Li_xO$ was carried out. Figure 4 shows the Seebeck coefficient S of $Cu_{1-x}Li_xO$ as a function of reciprocal temperature. Since $S > 0$ for all samples in the wide temperature range and $Cu_{1-x}Li_xO$ is apparently still a semiconductor at $x < 0.02$,[11] it is clear that the conduction mechanism is largely influenced by hole hopping.

It is found that $S(T)$ is described as

$$S(T) = S_0 + \frac{A}{T}, \tag{2}$$

where S_0 and A are the constants. The values of S_0 and A are plotted in Fig. 5 as a function of Li concentration. A decreases with the substitution of Li. Since the magnitude of A is proportional to the activation energy in the semiconductor, the result suggests that the activation energy decreases as increases the Li concentration, and is qualitatively consistent with that of the electrical resistivity, in which the activation energy is obtained in the slope of log ρ versus the reciprocal temperature for $Cu_{1-x}Li_xO$.[11]

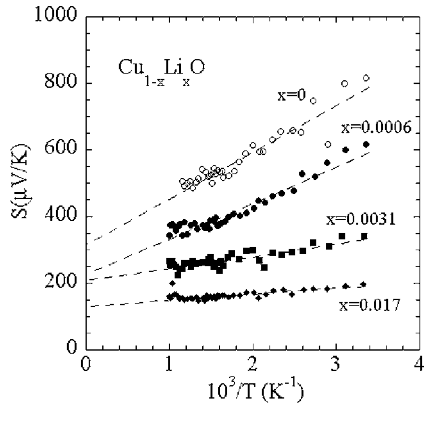

FIG. 4. Seebeck coefficient S of $Cu_{1-x}Li_xO$ as a function of reciprocal temperature for CuO doped with different amounts of Li. Broken lines are extrapolations by Eq. (2).

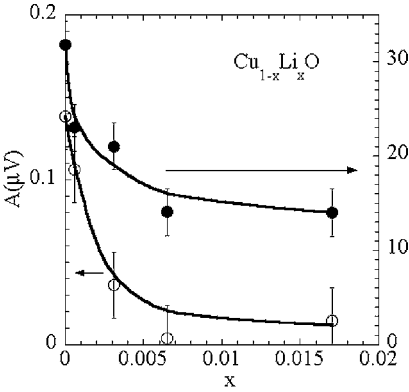

FIG. 5. The values of S_0 and A as a function of Li concentration. The solid lines are guides to the eye.

On the other hand, S_0 means the high temperature limit of the Seebeck coefficient. Since the doped holes in a semiconductor are all activated at sufficiently high temperature, the values of S_0 at the high temperature limit reflect the hole concentration in $Cu_{1-x}Li_xO$. Since the value of S_0 decreases with the substitution of Li, it demonstrates that the concentration of the localized holes increases with the substitution.

IV. DISCUSSION

Here we discuss the thermodynamical properties of the phase transition at T_{N2}. T_{N1} and T_{N2} are shown in Fig. 6 as a function of pressure. T_{N2} is found to decrease almost linearly with pressure up to 1.3 GPa at a rate of $dT_{N2}/dP=$

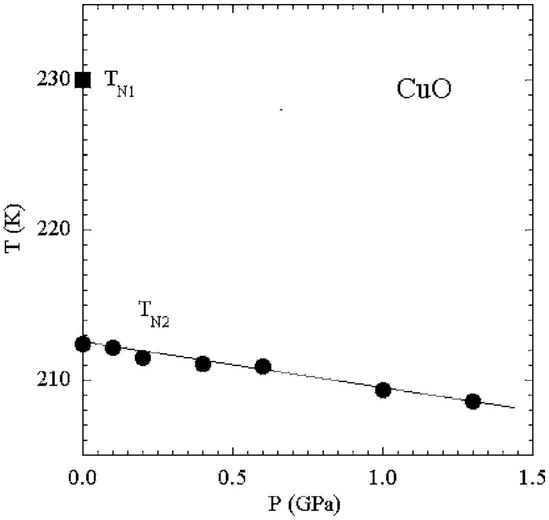

FIG. 6. Pressure dependence of antiferromagnetic ordering temperature T_{N1} and T_{N2}.

-2.9 K/GPa, while T_{N1} is not observed at high pressure since the freezing of the pressure transmitting medium around T_{N1} smeared out the transition.

By using the Clausius-Clapeyron relation,

$$\frac{\partial T_{N2}}{\partial P} = \frac{\Delta V}{\Delta S}, \tag{3}$$

ΔV is obtained to be -8.7×10^{-11} m^3/mol, where the discontinuity of the entropy ΔS is estimated to be 0.029 J/mol K from the result of heat capacity.[2] From the result at ambient pressure, the small volume change, $\Delta V/V = -2.0 \times 10^{-6}$, is obtained. On the other hand, the large value, $\Delta a/a \sim 2.5 \times 10^{-5}$, is obtained from the present thermal expansion measurement. Considering the relation, $V = abc \sin \beta$, the result indicates that the other axes (b and c) may expand at T_{N2}, i.e., the thermal expansion is highly anisotropic as was emphasized before. However, to make it clear, the thermal expansion data along other axes are needed.

Next, we estimate the Grüneisen parameter Γ for T_{N2} in order to evaluate the stability of magnetic coupling in the CuO system. Γ is defined as

$$\Gamma(T_{N2}) = -\frac{\partial \ln T_{N2}}{\partial \ln V} = -V\frac{\partial \ln T_{N2}}{\partial V}. \tag{4}$$

Using the isothermal bulk modulous B_T, Eq. (4) is written as

$$\Gamma(T_{N2}) = B_T \frac{\partial \ln T_{N2}}{\partial P}. \tag{5}$$

By using the value of $\partial \ln T_{N2}/\partial P$ and $B_T = 72$ GPa,[19] $\Gamma(T_{N2}) = -1.1$ is obtained for CuO.

On the other hand, T_{N2} also decreases drastically from 213 K to 199 K when Cu is substituted by 1.7% Li with Refs. 11 and 13. By substituting the value of volume change into Eq. (4), $\Delta V/V = 0.003$, which is the volume shrink in by adding 1.7% Li to CuO, $Cu_{0.983}Li_{0.017}O$, the Grüneisen parameter of T_{N2} is obtained to be $\Gamma(T_{N2}) = -22$, which is 20 times larger than that of pure CuO under pressure. It suggests that the change of T_{N2} does not arise simply from a change in lattice constant, but also the rapid suppression of the AF coupling in $Cu_{1-x}Li_xO$ comes from the hole doping by substituting Cu by Li.

In order to clarify the origin of the spin-lattice coupling in CuO, we have to consider the effect of pressure both on the magnetic properties and on the change of the lattice parameters. In the low-dimensional cuprates, the superexchange interaction J is strongly correlated to the structural properties. Mizuno *et al.*[21] calculated J for several cuprates containing edge-sharing Cu-O chains, which has nearly 90° Cu-O-Cu bonds, and discussed the dependence of the exchange interactions on the bond angle θ and the bond length $d_{\text{Cu-O}}$. The typical examples of J obtained experimentally have been reported by Shimizu *et al.*[22] for the series of cuprates with θ ranging from 98° to 180°. They revealed that J increases monotonically with increasing θ while $d_{\text{Cu-O}}$ is almost independent of$J$.

In CuO at ambient pressure, each Cu site is connected by four kind of Cu-O-Cu superexchange paths.[23] One is the Cu-O-Cu bond near the direction $[10\bar{1}]$, which has the largest angle $\theta[10\bar{1}] \sim 146°$, and antiferromagnetic order occurs. The others are regarded as weak because the associated angles of Cu-O-Cu bond are much closer to 90° than 180°. Since the lattice compression is highly anisotropic and the angles of the Cu-O-Cu bond may change drastically by applying pressure, we calculated the angles of the Cu-O-Cu bond from the recent result of neutron diffraction study under high pressure.[19] In Table I, the largest two angles of the Cu-O-Cu bond are illustrated at several pressures near the direction $[10\bar{1}]$,$\theta[10\bar{1}]$, and near $[101]$, $\theta[101]$. Only $\theta[10\bar{1}]$ increases as increasing pressure while the others decrease. It indicates that pressure keeps a quasi-one-dimensional superexchange coupling. According to Goodenough rules for superexchange interaction, the magnetic structure of CuO is viewed as consisting of chains along the $[10\bar{1}]$ direction, which has the largest ∠Cu-O-Cu angle, and the spin exchange parameter $|J|$ increases with increasing $\theta[10\bar{1}]$.[22] Since $\theta[10\bar{1}]$ increases with increasing pressure, the magnitude of $|J|$ increases by applying pressure.

TABLE I. θ near $[10\bar{1}]$ and near $[101]$ of CuO under several pressures, which is calculated from recent results (Ref. 19). T_{N2} is estimated from the present result.

P (GPa)	$\theta\,[10\bar{1}]$	$\theta\,[101]$	T_{N2}(K)
0.148	146.31	108.62	211.6
1.505	149.28	106.85	207.5
2.297	150.33	106.47	
3.243	151.56	105.24	

These results suggest that T_{N1} and T_{N2} increase with increasing pressure if magnetic interaction comes only from superexchange coupling of the Cu-O-Cu bond. However, in the present result, T_{N2} is suppressed by pressure. It is reasonable to assume that there must be another factor to explain the suppression of the AF in CuO by applying pressure.

Here we discuss the stoichiometry of CuO. As shown by previous studies,[24] CuO is close to stoichiometry and only allows a limit of an excess oxygen of less than 0.7%, which explains p-type conductance in this insulator. Previous electron diffraction study on thin flakes of CuO single crystals shows that the holes due to excess oxygen produce weak superlattice reflections,[1] which are suggested to be bound to Cu and hole hopping between Cu^{2+} and Cu^{3+} is indicated to bring out a semiconductive electric behavior.[2] Moreover, a synchrotron x-ray and neutron diffraction study with a resonant method on bulk single crystals showed traces of the superlattice reflection, which is suspected to be a magnetic superlattice associated with the charge order.[25,26] On the basis of the previous experimental results, we consider a possible scenario by assuming that the pressure enhances the hopping of holes which effectively destroys the superexchange coupling in CuO.

Fritzsche discussed the processes of impurity conduction of p- and n-type germanium from the results of the resistivity and Hall effect,[27] in which the activation energy of the hole

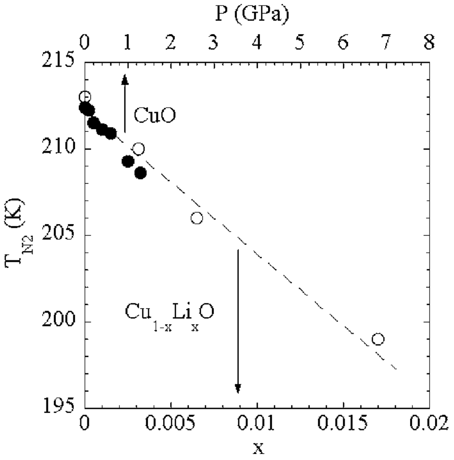

FIG. 7. Open circles are antiferromagnetic temperature T_{N2} of $Cu_{1-x}Li_xO$ as a function of x, which is taken from Ref. 11. The solid circle is T_{N2} of CuO as a function of pressure in the present study. The dashed line is a guide to the eye.

hopping depends on the hole concentration per volume, N_A. In the case of nonstoichiometric CuO, N_A increases as increasing pressure since N_A is proportional to the quantity of Cu^{3+} and is inversely proportional to the volume of CuO. Okayama *et al.* measured the electrical resistivity of CuO under high pressure, in which the activation energy decreased with applying pressure up to 2.4 GPa (Ref. 28) which is consistent with the fact that hole hopping is enhanced by applying pressure.

Similar results have been also obtained with Li substitution in CuO, in which N_A increases when holes are doped by Li substitution. As discussed in Sec. III B, the result of the Seebeck effect shows that the activation energy decreases as the Li concentration increases and is qualitatively consistent with that of the electrical resistivity.[11] In Fig. 7, T_{N2}s are plotted as a function of x in $Cu_{1-x}Li_xO$ and as a function of pressure in CuO. Assuming that the superexchange coupling is affected by the hopping of holes, T_{N2} may be able to form a universal curve when plotted versus the hole concentration N_A. To make it clear, the Hall effect of $Cu_{1-x}Li_xO$ and that of CuO under pressure are needed to estimate N_A quantitatively.

In order to compare the effect of pressure in CuO with that of substituting Li, the change in $\theta[10\bar{1}]$, $\theta[101]$ and T_{N2} are summarized for $Cu_{1-x}Li_xO$ in Table II. It should be noted that the similar tendency of the decrease in T_{N2}, increase in $\theta[10\bar{1}]$, and decrease in $\theta[101]$, is clearly seen by doping Li in CuO. The suppression of the antiferromagnetic transition temperatures of $Cu_{1-x}Li_xO$ were described as a function of the concentration of impurity,

$$T_N(x) = T_N(0)[1 - Ax], \tag{6}$$

where $A=5.9$ and 3.8 are obtained for T_{N1} and T_{N2}, respectively,[11] which is much larger than $A=1.5$ predicted from a mean field treatment for diluted magnets.[29] A previous study on $Cu_{1-x}Zn_xO$ showed that dilution by $x=1.5\%$ Zn scarcely altered the T_N,[30] which strikingly differs with the result in $Cu_{1-x}Li_xO$. It comes from the result that hole is doped by substituting Li^+ by Cu^{2+} while Zn^{2+} only introduces local diamagnetic impurity in $Cu_{1-x}Zn_xO$.

TABLE II. θ near $[10\bar{1}]$ and near [101] of $Cu_{1-x}Li_xO$ and T_{N2} (Refs. 11 and 31).

x	$\theta[10\bar{1}]$	$\theta[101]$	$T_{N2}(K)$
0	144.85	109.69	213
0.0031	145.05	109.58	210
0.0065	145.18	109.55	206
0.017	145.72	109.17	199

From the analysis in the recent results, it was found that in $Cu_{1-x}Li_xO$ the Cu-O-Cu angle along the superexchange interaction direction increases simultaneously, which would cancel the effect from the increase in the Cu-O distance by Li substitution. It is well known that the increase in the bond angle usually has a bigger contribution than that in the Cu-O distance as reported previously.[22] Therefore, we infer that the rapid suppression of the AF in $Cu_{1-x}Li_xO$ mainly originated from the doped holes. The effect of hole doping and hole hopping is extraordinarily large in copper oxides. As a matter of fact, the rapid suppression of T_N for initial doping was reported for $La_2Cu_{1-x}Li_xO_4$, in which T_N is described as in Eq. (6), where $A=10$.[10]

The suppression of the AF transition is reported for other monooxide antiferromagnetic systems. In the case of the diluted NiO system, for example, T_N is described as a function of impurity concentration in $Ni_{1-x}Li_xO$ and in $Ni_{1-x}Mg_xO$,[32] in which the hole is doped by substituting Li^+ by Ni^{2+} while the Mg^{2+} ion only introduces local diamagnetic impurity. The authors suggested that the supression in $Ni_{1-x}Li_xO$ is brought out by hole hopping. In $Ni_{1-x}Li_xO$ besides the dilution of the magnetic Ni by diamagnetic Li, the hopping holes effectively cancel the Ni spins at other sites. Therefore, it is interpreted in $Ni_{1-x}Li_xO$ that the T_N is decreased as Eq. (6), where $A=2.2$, which is larger than that for $Ni_{1-x}Mg_xO$, $A=1$.

V. CONCLUSION

In this work, strong magnetoelastic coupling in CuO is directly evidenced in the thermal expansion. Significant effect of pressure on the magnetic transition as shown by the decrease in $T_{N2}(P)$, is observed. The results are compared in detail with those of Li substitution in $Cu_{1-x}Li_xO$, and discussed on the basis of the quasi-one-dimensional superexchange coupling of Cu-O-Cu along $[10\bar{1}]$. The present work clarifies that strong hole doping effect on the suppression of the AF coupling exists in the CuO system.

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