Cu-O-Cu Bond-Angle Dependence of Magnetic Interactions in Antiferromagnetic Cuprates

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Abstract

We present an experimental evidence for systematics to show the bond-angle dependence of the supertransferred hyperfine (STH) interaction and of the superexchange (SE) interaction in Cu - O - Cu bonds with the bond-angle ranging from 98 to 180 degrees.

Key words: superexchange interaction, antiferromagnet, cuprate

A family of cuprates is a preferable candidate to examine a correlation between SE and structural features. While the chemical bonding in cuprate family is constructed commonly by the copper-oxygen bond in the 1st approximation, on the other hand, the structural feature has a great variety, such as the bond angle of Cu-O-Cu available from 90 (edge sharing) to 180 degrees (corner sharing), bond length (1.905 - 2.019 Å), and dimensionality (1D, ladder, 2D and 3D).

We have another magnetic interaction possible in cuprates, i.e., the supertransferred hyperfine interaction [1], which works between the electron spin of a copper ion and the nuclear spin of the near neighbor copper ion. STH includes partially the same mechanism as SE, which is the covalent polarization in terms of the atomic orbital model, i.e., the spin polarization of the oxygen p_σ-orbital covalently bonding with the copper d-orbital.

We will make a standard explanation of STH mechanism below [2]. For the convenience, we call the copper ion causing the covalent polarization into an oxygen ion the "1st copper ion" and the other copper ion behind the oxygen the "2nd copper ion", although both coppers may be crystallographically equivalent. The covalent polarization carries the effective spin opposite to the 1st copper electron spin direction, because only a single state in the 1st copper d-orbital is empty to be taken by the covalent transfer from the oxygen p_σ-orbital.

The difference of STH from SE is only made after the covalent polarization is achieved. The covalent polarization gives rise to s-spin polarization at the 2nd copper ion via the sp-hybridization effect in the case of STH, instead of d-spin polarization at the 2nd copper ion via the dp-direct exchange interaction in the case of SE. The s-spin polarization then goes to the Fermi contact hyperfine interaction with the 2nd copper nuclear spin to complete the STH interaction.

We can expect that STH interaction thus achieved would be less sensitive to the bond angle compared to SE. The investigation of the bond angle dependences may provide a microscopic test for the theoretical model describing SE and STH.

We define B as STH coupling strength arising from a unit electron spin in a bond, and J as a Heisenberg exchange written by $\mathcal{H} = JS_iS_j$. Less experimental data have been available for B than J, because B can only be observed by NMR measurement. Fortunately, cuprates have been accumulating the B data as well as J since the discovery of the cuprate high-T_c superconductors has accelerated the extensive researches. Both the B and J data of cuprates are now available to make

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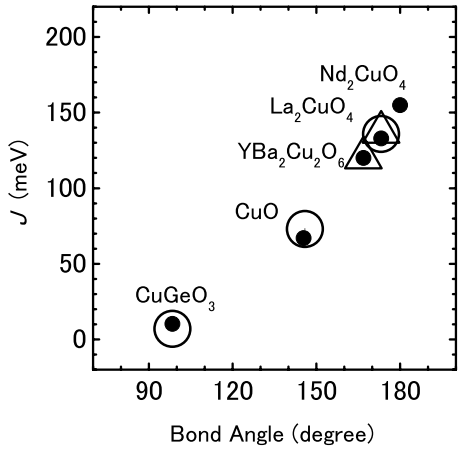

Fig. 1. The superexchange coupling J versus the bond angle. The open circles are J values taken from susceptibility, closed circles from neutron and triangles from Raman measurements.

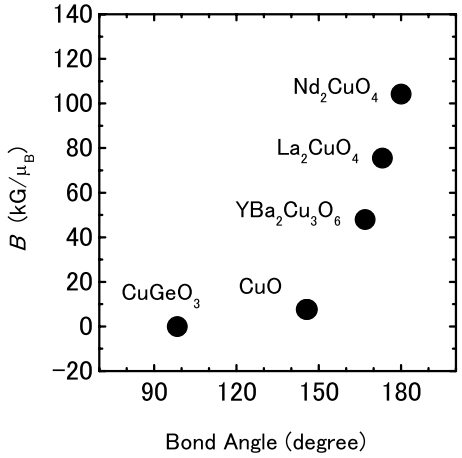

Fig. 2. The supertransferred hyperfine coupling B form a single Cu-O bond is plotted against the bond angle.

the comparison possible.

In the present paper we report a systematics found experimentally for the J (Fig. 1) and B (Fig. 2) as a function of the bond angle in insulating antiferromagnetic cuprates. To make a comparison possible, we are focused to the cuprates for which both the J and B data are available. The J values are taken from the literatures as follows: $CuGeO_3$ [3], CuO [4] and [5], $YBa_2Cu_3O_6$ [6] and [3], La_2CuO_4 [7], [6] and [8], and Nd_2CuO_4 [7]. The B values are evaluated using the data of $CuGeO_3$ [9], CuO [10] and [11] $YBa_2Cu_3O_6$ [12] and [13], La_2CuO_4 [10], and Nd_2CuO_4 [14].

We will describe below how to evaluate the B value. Since both the covalent polarization and Fermi contact hyperfine interaction is isotropic as usually assumed, B is then isotropic. We can express the net hyperfine field as $H_{para} = (A^{\parallel} + nB)m_{spin}$ and $H_{AF} = (A^{\parallel} - n\mathrm{B})m_{spin}$ for the paramagnetic and antiferromagnetically ordered state, respectively, where $A^{\parallel}$ is the easy axis component of the Cu on-site hyperfine coupling tensor, n is the number of nearest neighbor Cu ions around a Cu ion and m_{spin} is the effective spin moment.

A set of both the measurements of paramagnetic hyperfine coupling (i.e., K-χ plot) and antiferromagnetically ordered frequency gives us $2nBm_{spin}$ from the difference between the two-hyperfine fields. The ordered moment m_{spin} can be known from the neutron experiments and n is also known from the crystal structure, then leaving the value of B.

We have made such a set of measurements for CuO [11] and $YBa_2Cu_3O_6$ [13], and taken data from the literature of $CuGeO_3$ [9]. We have not had paramagnetic data of La_2CuO_4 and Nd_2CuO_4 yet, then we just assume the same value of $A^{\parallel} = -22$ kG/μ_B for those as that observed in $YBa_2Cu_3O_6$. We estimate the ambiguity caused by the present assumption to be ± 20 kG/μ_B.

In summary. we find the bond angle dependences of J and B in antiferromagnetic cuprates with the bond angle ranging from 98 to 180 degree. Both the bond angle dependences show an expected trend that becomes larger for larger bond angle. But we also find an unexpected behavior that B shows the dependence steeper than J. This suggests that the STH may include an unknown microscopic mechanism.

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