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## Theoretical analysis of double-halide superexchange in layered solids of the compounds $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuBr}_4$ with $n=3$ and 4

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Recently, interlayer exchange-coupling constants in solids of compounds  $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuBr}_4$ , with  $n=3$  and 4, have been measured by Drumheller *et al.* Following our earlier theoretical analysis of such compounds with Cl instead of Br for  $n=2-5$ , and one ClBr mixed compound for  $n=2$ , we apply a four-center, six-electron model to calculate these coupling parameters, assuming a double-halide Cu-Br-Br-Cu superexchange unit. Excellent agreement with the experimental values is obtained. Nonlinearity of the superexchange bridge for  $n=4$  is found to be essential to obtain the correct value for the coupling parameter. We perform similar calculations on a layered structure with a Co-double-oxygen-Co bridge.

### I. INTRODUCTION

In recent years the magnetic ordering of Cu(II) spins in solids of compounds in the series  $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuX}$ , with  $X=\text{Cl}_4$  for  $n=2-5$  and also  $X=\text{Cl}_2\text{Br}_2$  for  $n=2$ , has been studied experimentally in detail.<sup>1-5</sup> The solids of these alkane diammonium copper complexes, called the ADA series for short, have "puckered"  $[\text{CuX}]^{2-}$  layers separated by organic chains. The Cu(II) cations in adjacent planes lie practically on top of each other ("eclipsed" structure) and are almost linearly bridged by two halogen ions. Only for  $X=\text{Cl}_4$  with  $n=4$  does the  $\text{Cu}_a-\text{Cl}_a-\text{Cl}_b-\text{Cu}_b$  interlayer chain show an essential nonlinearity. Further structural details can be found in the original literature.<sup>5</sup>

Owing to the large distances between the interlayer Cu(II) cations ( $>8 \text{ \AA}$ ), one expects their magnetic interactions to be very small. However, the experimental results of, e.g., Snively *et al.*<sup>2,4,5</sup> for a number of compounds in the ADA series, obtained on the basis of a high-temperature series expansion of the measured magnetic susceptibilities, have shown that the interlayer exchange-coupling constants  $J_{2h}$  are quite substantial, namely up to 30 K, for  $n=2$  and  $X=\text{Cl}_2\text{Br}_2$  (the subscript "2h" indicates the two-halide bridge). These authors also deduce from the experimental data that the halide-halide separation  $r$  is the appropriate parameter to describe the distance dependence of the exchange-coupling constant, i.e.,  $J_{2h} \propto r^{-n}$  with  $n \approx 10 \pm 2$  in the experimental range considered.

Later on, using a four-center, six-electron model (two electrons on each halogen, one on each Cu), Block and Jansen<sup>6</sup> obtained excellent agreement with experiment for the ADA series. Also for  $X=\text{Cl}_4$ , with  $n=4$ , the exchange-coupling constant was predicted correctly by taking the nonlinearity of the  $\text{Cu}_a-\text{Cl}_a-\text{Cl}_b-\text{Cu}_b$  bridge explicitly into account. The nonlinearity in this compound was found to be essential for obtaining the correct coupling constant and, moreover, for the fit in the power law  $J_{2h} \propto r^{-n}$ , suggested by Snively *et al.*<sup>5</sup>

Recently, using the same experimental technique, Snively *et al.*<sup>7</sup> have reported results for the relevant structural parameters and the exchange-coupling constants in two other compounds of the ADA series, i.e.,  $X=\text{Br}_4$  with  $n=3$  and 4 (see Table I). For  $n=4$ , a deviation from linearity is again observed, but its magnitude was not determined.

In order to show once more the capability of the model in accounting for long-range exchange interactions, calculations for  $J_{2h}$  were carried out for these compounds. Furthermore, we will discuss specifically the halide-halide distance power-law dependence as proposed by Snively *et al.*<sup>5,7</sup> In addition, attention will be paid to a quantitative model treatment of the interlayer exchange-coupling constant in the  $[\text{Co}(\text{PNO})_6](\text{NO}_3)_2$  complex ( $\text{P}=\text{C}_5\text{H}_5$ ).<sup>8</sup> Here, the superexchange path between the two Co cations is assumed to be primarily a Co-O-O-Co unit with a Co-Co distance of about 9.6 Å. The exchange-coupling constant is only of the order of  $-0.2 \text{ K}$ .<sup>8</sup> On the basis of the experimental data it has also been reasoned<sup>9</sup> that a third  $\text{O}^{2-}$  anion may be involved in the indirect coupling. The model calculation yields a very small value for  $|J_{2h}/k_B|$ ,  $<0.002 \text{ K}$ , and including a third intervening ligand, leads to, at most, a one-order-of-magnitude increase in this quantity.

### II. FORMALISM

In the model applied, the open shell of each paramagnetic Cu(II) cation is replaced by one "effective" electron, the valence shell of the diamagnetic halogen ions by two spin-paired "effective" electrons. The orbitals of these electrons are described by 1s Slater functions with specific orbital parameters. The superexchange paths in the ADA compounds and in the cobalt complex are thus represented by a four-center, six-electron unit. First-order exchange perturbation theory leads to the following expression for the interaction energy:

$$E_{\sigma}^{(1)} = (\phi\sigma, \mathcal{V} \mathcal{A}_6 \phi\sigma) / (\phi\sigma, \mathcal{A}_6 \phi\sigma), \quad (1)$$

TABLE I. Experimental and calculated exchange-coupling constants  $J_{2h}$  together with some relevant structural parameters. The calculated  $J_{2h}$  were obtained by applying a four-center, six-electron model using the (rounded-off) experimental structural data. For the calculated  $J_{2h}$  of ethane diammonium (EDA)  $\text{CuCl}_2\text{Br}_2$ , we refer to Ref. 6; for the experimental results, to Refs. 5 and 7. Further,  $R$  is the cation-cation distance,  $r$  is the anion-anion distance, and  $\theta$  is the angle  $\text{Cu}_a\text{—Cu}_b\text{—Br}_b$ .

	$n$	$R$ (Å)	$r$ (Å)	$J_{2h}/k_B$ (K)		
				Expt.	Calc.	
				$\theta=0^\circ$	$\theta=20^\circ$	
EDA $\text{CuCl}_2\text{Br}_2$	2	$\approx 8.3 \pm 0.2$	$\approx 3.7 \pm 0.2$	$-31 \pm 1.0$	$-28.5$	
PDA $\text{CuBr}_4$	3	$\approx 8.6$	$\approx 3.8 \pm 0.2$	$-26 \pm 1$	$-17.4$	
BDA $\text{CuBr}_4$	4	8.92	$\approx 4.3 \pm 0.1$	$-5 \pm 1$	$-12.1$	$-4.2$

where  $\phi$  is the simple product of the orbital functions for the six electrons,  $\sigma$  is the total-spin function (triplet or singlet),  $\mathcal{A}_6$  denotes the total antisymmetrizer, and  $\mathcal{V}$  represents the interatomic Coulomb interaction. Since  $\mathcal{V}$  does not contain spin variables, integration over spin space in (1) yields

$$E_\sigma^{(1)} = (\phi, \mathcal{V} \mathcal{D}_\sigma \phi) / (\phi, \mathcal{D}_\sigma \phi),$$

where  $\mathcal{D}_\sigma$  is the projector in orbital space for the triplet ( $S=1$ ) or singlet ( $S=0$ ) spin state of the form (including inversion symmetry)<sup>6</sup>

$$\mathcal{D}_{S=1} = (I - P_{14}P_{25}P_{36}) [I - 2(P_{13} + P_{14} + P_{34}) - P_{36} + P_{13}P_{46} + 2(P_{14}P_{23} + P_{134} + P_{143} + P_{136} + P_{163}) - P_{14}P_{23}P_{56} - P_{1346} - 2P_{1364} - P_{1643}], \quad (2)$$

$$\mathcal{D}_{S=0} = (I + P_{14}P_{25}P_{36}) [I - 2(P_{13} + P_{14} + P_{34}) + P_{36} + P_{13}P_{46} + 2P_{14}P_{23} + 4P_{16}P_{23} + P_{14}P_{23}P_{56} + 2(P_{134} + P_{143} - P_{136} - P_{163}) - 4(P_{23}P_{146} + P_{23}P_{164}) + P_{1346} + 2P_{1364} + P_{1643}]. \quad (3)$$

In Eqs. (2) and (3) the electrons on the two halogens are labeled 1,2 and 4,5, respectively, and those on the cations 3 and 6;  $P_{ij}$  stands for the permutation of the indices  $i$  and  $j$ . The exchange-coupling constant  $J_{2h}$  is simply given by

$$2J_{2h} = (E_{S=0}^{(1)} - E_{S=1}^{(1)}) / n^2,$$

$n$  being the number of unpaired electrons on the actual cations. For further details we refer the reader to the text of Ref. 6 and to references included in that paper.

An explicit determination of the parameters  $\lambda$  in the Slater functions  $\psi = \lambda^{3/2} \pi^{-1/2} \exp(-\lambda r)$  has been given in Ref. 10. In that paper the model is applied to linear single-halide superexchange interactions in a series of 3d-metal fluorides. Following earlier work of Jansen and co-workers,<sup>11</sup> the  $\lambda$  values relative to one another were obtained by comparing the diamagnetic susceptibilities of the valence shells. Such a procedure leaves only one parameter to be chosen as to yield, apart from a reproduction of the experimental trends, also the best quantitative agreement between the model calculations and experimental data. The specific choice  $\lambda_{\text{F}^-} = 1.11$  a.u.<sup>-1</sup> in Ref. 10 is directly connected with the application of the model to a three-center, four-electron superexchange unit. Applying the model to a four-center, six-electron unit, keeping the *ratio's* between  $\lambda$  values fixed and lowering the orbital parameters from Ref. 10 by only 3%, Block and Jansen<sup>6</sup> found excellent agreement with the experimental data for the ADA series.

For the evaluation of the Slater parameter of the  $\text{O}^{2-}$  anion, we used the calculated diamagnetic susceptibility, proportional to the sum of  $\langle r^2 \rangle$  of this ion,<sup>12</sup> and the self-consistent-field results according to Herman and Skillman<sup>13</sup> for the relative contributions of the core and valence electrons (Table II of present paper). With the assignment of  $\lambda_{\text{F}^-}$  in Ref. 10, one obtains  $\lambda_{\text{O}^{2-}} = 0.91 \pm 0.02$  a.u.<sup>-1</sup> which leads in a three-center, four-electron model calculation for the linear  $\text{Ni—O—Ni}$  superexchange unit in solid NiO to excellent agreement with experiment:  $J_{\text{expt}}/k_B = -110 \pm 2$  K,<sup>14</sup>  $J_{\text{calc}}/k_B = -107$  K using  $\lambda_{\text{O}^{2-}} = 0.91$  a.u.<sup>-1</sup>. Regarding the application of the model to a four-center, six-electron unit we follow Ref. 6 by lowering the above value for  $\lambda_{\text{O}^{2-}}$  and the value for  $\lambda_{\text{Co}^{2+}}$  from Ref. 10 (1.02 a.u.<sup>-1</sup>) by 3% which yields  $\lambda_{\text{O}^{2-}} = 0.88$  a.u.<sup>-1</sup> and  $\lambda_{\text{Co}^{2+}} = 0.99$  a.u.<sup>-1</sup>.

TABLE II. Values for  $\langle r^2 \rangle$  in a.u.<sup>2</sup>.

	$\text{O}^{2-}$	$\text{F}^-$
$\sum_{\text{tot}} \langle r^2 \rangle$	22.35	10.60
$\sum_{\text{valence shell}} \langle r^2 \rangle$	22.24	10.52

### III. RESULTS AND DISCUSSION

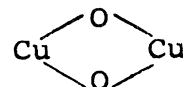
In Table I we have listed the values for the interlayer exchange-coupling constants  $J_{2h}$  in the ADA  $\text{CuBr}_4$  series for  $n=3$  and 4 as obtained from the model calculations assuming a linear superexchange unit. Also the result for the ADA  $\text{CuCl}_2\text{Br}_2$  with  $n=2$ , reported in earlier work,<sup>6</sup> and the experimental data, are presented in the table. Considering the inaccuracy in the available data for the distances  $R$  and  $r$ , i.e., the Cu-Cu and Br-Br separations, respectively, the agreement between the calculated and the experimental coupling constants for the linear compound with  $n=3$  is quite satisfactory. On the other hand, the assumption of linearity in the exchange path for the  $n=4$  compound yields an exchange-coupling constant which deviates much more from the observed value. However, if we take the nonlinearity in the butane diammonium (BDA)  $\text{CuBr}_4$  exchange path explicitly into account, i.e., adopting a  $\text{Cu}_a\text{—Cu}_b\text{—Br}_b$  angle  $\theta \approx 20^\circ$  as found in BDA  $\text{CuCl}_4$ ,<sup>6</sup> the model calculation again leads to quantitative agreement with experiment. Thus far, therefore, for all ADA compounds considered the model employed is found to accurately reproduce the experimental data.

An interesting feature of the observed coupling constants in the ADA compounds is the exchange-coupling—versus—distance relationships. As shown in Ref. 5 the data for the (nonlinear) BDA  $\text{CuCl}_4$  complex fail to coincide with the graphical plot of  $\ln |J_{2h}/k_B|$  vs  $\ln R$  obtained for the other (linear) ADA compounds. A plot of  $\ln |J_{2h}/k_B|$  vs  $\ln r$ , however, roughly shows a linear relation for all complexes. Therefore, Snively *et al.* proposed the halogen-halogen separation to be primarily responsible for the strength of the indirect exchange coupling between the copper ions. On the basis of their theoretical results, Block and Jansen deduced from the nonlinear behavior in BDA  $\text{CuCl}_4$  that its fit in the plot of  $\ln |J_{2h}/k_B|$  vs  $\ln r$  may possibly be accidental.

In order to investigate in more detail the dependence of the exchange-coupling constant with respect to the geometry of the exchange unit, we have carried out a number of model calculations, varying  $R$ ,  $r$ , and  $\theta$ . In Table III we have listed for different values of  $\theta$  the ratios  $J_\theta/J_{\theta=0^\circ}$  ( $J_\theta$  being the exchange-coupling constant  $J_{2h}$  for given  $\theta$ ) for  $R=8.6$  and  $8.9$  Å, respectively, with a

fixed cation-anion distance  $l$ . Although for the two values of  $R$ , the dependence on  $r$  is obviously different, the ratios are nevertheless nearly equal in the  $\theta$  range considered. Then, lowering, for  $R=8.9$  Å, the value for  $l$  from 2.4 to 2.3 Å, thus increasing  $r$ , the calculated  $J_{\theta=0^\circ}/k_B$  changes only from  $-11.3$  to  $-12.1$  K. Regarding the distance power law  $J_{2h} \propto r^{-n}$  with  $n=10 \pm 3$ , as proposed by Snively *et al.*,<sup>7</sup> this indicates an important influence of the cation-anion distance in the numerical calculations. Furthermore, the ratio  $J_\theta/J_{\theta=0^\circ}$  becomes significantly different with increasing  $\theta$ . For the latter distance parameters the model leads to  $(\partial \ln |J_{2h}/k_B| / \partial \ln r)_{R,l} = -9 \pm 0.6$  for  $\theta$  ranging from 0 to  $20^\circ$ .

From these results we can conclude that an accurate knowledge of the nonlinearity is extremely important for a correct quantitative model prediction. In the case of nonlinear exchange units, the angle  $\theta$  should be considered next to  $R$  or  $r$  as an essential parameter for the indirect interaction. In this context we note that also in double-oxygen-bridged copper systems of type



the exchange-coupling constants vary sensitively with respect to changes in the Cu—O—Cu angle.<sup>15</sup> In all model treatments or *ab initio* calculations, coupling constants turn out to be very dependent on the geometry of the superexchange unit.<sup>16,17</sup>

Regarding, finally, the indirect interaction between two Co ions via two oxygen ligands, in a bridge unit analogous to that in the ADA series, we have used the experimental interatomic separations  $R(\text{Co—Co})=9.6$  Å and  $r(\text{O—O})=5.5$  Å (Ref. 8) and a linear arrangement. The observed value for the exchange-coupling constant has been reported to be  $-0.22$  K obtained from a simple cubic  $XY$  ( $S=\frac{1}{2}$ ) antiferromagnetic fit of the magnetic susceptibility measurements.<sup>8</sup> The four-center, six-electron model calculation yields a very small value with  $|J_{2h}/k_B| < 0.002$  K with  $J_{2h}$  of correct sign. In the original literature on the  $[\text{Co}(\text{PNO})_6](\text{NO}_3)_2$  complex, it was proposed that an extra intervening oxygen of the  $\text{NO}_3^-$  ligands may possibly play a role in the superexchange

TABLE III. Ratios  $J_\theta/J_{\theta=0^\circ}$  for given  $\text{Cu}_a\text{—Cu}_b\text{—Br}_b$  angle ( $\theta$ ), where  $J_\theta$  is the interlayer exchange-coupling constant.  $R$  is the cation-cation distance and  $l$  is the cation-anion distance.

$\theta$ (deg)	$J_\theta/J_{\theta=0^\circ}$		
	$R=8.6$ Å $l=2.4$ Å	$R=8.9$ Å $l=2.4$ Å	$R=8.9$ Å $l=2.3$ Å
0	1.00	1.00	1.00
5	0.92	0.93	0.93
10	0.73	0.74	0.76
15	0.50	0.51	0.54
20	0.30	0.31	0.34
$J_{\theta=0^\circ}/k_B$ (K)	-17.4	-11.3	-12.1

mechanism.<sup>9</sup> We found that neither the inclusion of a third oxygen nor a 5% decrease of the orbital parameters resulted in an essential increase of the exchange-coupling constant. The effect of a third oxygen results in at most

one-order-of-magnitude larger value for  $|J_{2h}/k_B|$ . We note, however, that at such (both experimental and theoretical) extremely small values no great significance can be attached to their differences.

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