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Theoretical analysis of double-halide superexchange in layered solids of the compounds $[\mathrm{NH_3(CH_2)}_n\mathrm{NH_3}]\mathrm{Cu}X$ for $X=\mathrm{Cl_4}$ with $n=2-5$ and for $X=\mathrm{Cl_2Br_2}$ with $n=2$

Ruud Block and Laurens Jansen
Institute of Theoretical Chemistry, University of Amsterdam, 166 Nieuwe Achtergracht, 1018 WV Amsterdam, The Netherlands

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A model analysis is undertaken of the recently measured exchange-coupling parameters J between copper ions in adjacent layers in solids of the series $[\mathrm{NH_3(CH_2)}_n\mathrm{NH_3}]\mathrm{Cu}X$, for $X=\mathrm{Cl_4}$ with $n=2-5$ and for $X=\mathrm{Cl_2Br_2}$ with $n=2$. The model is based on a four-center–six-electron description of the double-anion superexchange unit $\mathrm{Cu}_a \diagup \mathrm{Cl}_a \diagdown \mathrm{Cl}_b \diagup \mathrm{Cu}_b$ (for $n=2$, Br ions also are considered), where a and b denote adjacent layers, and where the two halogen ions lie between these layers. The orbitals of the six electrons are chosen to be of the $1s$ Slater type, with characteristic parameters λ. These values are taken over from previous work (one-anion bridge), except that for the Cu ion a small deviation is allowed for, namely $\lambda_{\mathrm{Cu}^{2+}}=1.00$, 0.97, and 0.94 a.u.$^{-1}$, keeping the λ ratio for all ions constant. Nonlinearity is neglected except for $n=4$, where the measured deviation is relatively large. First-order exchange perturbation theory is applied to evaluate the J's. It is found that the model yields quantitative agreement with experiment for the J ratios in the series, except for $n=4$. Further, for $\lambda_{\mathrm{Cu}^{2+}}=0.97$ a.u.$^{-1}$, quantitative agreement is obtained for the double-anion J values, again excepting $n=4$. In the latter case, taking nonlinearity of the bridge into account, the exchange coupling is found to be considerably suppressed, in agreement with experiment.

I. INTRODUCTION

Recently,[1-5] interesting results have been obtained on magnetic ordering of Cu II spins in solids of compounds of the series $[\mathrm{NH_3(CH_2)}_n\mathrm{NH_3}]\mathrm{Cu}X$, covering the range $n=2$, 3, 4, and 5 for $X=\mathrm{Cl_4}$, and $n=2$ for $X=\mathrm{Cl_2Br_2}$. The solids of those compounds, which we will collectively call ADA series, (alkane di-ammonium) have layers of "puckered" $\mathrm{CuCl_4}^{2-}$ planes separated by organic chains. This type of structure is also found with solids of compounds $[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH_3}]_2\mathrm{CuCl_4}$, collected under the name AA series (alkyl ammonium). The difference between these two series, which is important for their different magnetic behavior, is that in ADA adjacent layers of Cu II ions are practically on top of each other ("eclipsed" structure), whereas in the AA series the adjacent layers are "staggered." This opens the possibility that in ADA two neighboring copper ions in adjacent layers a and b can interact through superexchange via two chlorine atoms between them. The superexchange bridge $\mathrm{Cu}_a \diagup \mathrm{Cl}_a \diagdown \mathrm{Cl}_b \diagup \mathrm{Cu}_b$ is practically linear for $n=2$, 3, and 5, whereas the Cu_a-Cu_b-Cl_b angle in butane di-ammonium (BDA) turns out to be relatively large (see below). For $n=2$ and $X=\mathrm{Cl_2Br_2}$ the anions of the bridge are those of bromine. Since the smallest Cu-Cu distance between the layers is quite large (between ~ 8.1 Å for $n=2$ and ~ 11.5 Å for $n=5$), it is expected that the *inter*layer exchange effect will be very small. This is, however, in striking conflict with the experimental facts of Snively *et al.*[2,4,5] and, independently, von Känel,[3] who found substantial interlayer exchange-coupling constants J_{2h}/k (the subscript $2h$ denotes two halogen ions) for $n=2$ and 3. For $n=2$, together with $X=\mathrm{Cl_2Br_2}$, Snively *et al.* established that J_{2h}/k is even about (minus) twice as large as the *intra*layer coupling constant J_{intra}/k. The coupling through these two halogens is found to be antiferromagnetic (i.e., $J_{2h}<0$); that involving two Cu ions in the same plane (intralayer) is ferromagnetic (i.e., $J_{\mathrm{intra}}/k>0$). Snively *et al.* utilized high-temperature series expansions of the magnetic susceptibilities to calculate the exchange-coupling constants, whereas von Känel used critical-field data from temperatures below the critical point (linear magnetic birefringence, a magneto-optical effect) and applied a mean-field theory to obtain these constants. For further details we refer you to the original literature.

On the theoretical side, following previous model calculations of the exchange-coupling constants in collinear *single*-anion exchange units in some $3d$-metal compounds,[6] similar calculations involving *two* intervening diamagnetic units were carried out by van Kalkeren and us.[7] In the description of magnetic ordering in the manganese pyrites $\mathrm{Mn}X_2$ (X=S, Se, and Te), it was found that two "molecular anions" $X_2{}^{2-}$ must be taken along in the superexchange unit for a pair of Mn ions in order to explain, in the model concerned, the observed different magnetic structures at low temperatures. Furthermore, in a preliminary attempt to analyze the magnetic structures and transition temperatures of the solid Eu monochalcogenides, even an extension to *three* intervening anions has been considered.[8] The model, applied in the above-mentioned analyses, will shortly be outlined in the following section. For a review and a number of applications (e.g., crystal stability of rare-gas crystals, crystal stability and elastic constants of ionic solids, stabilities of rare-gas halides, rotational barriers in simple molecules, hydrogen-bonding, and superexchange) we refer you to the literature.[9]

With respect to the systems under consideration here, Snively *et al.* in their latest paper[5] have tried to apply a similar model. Although their reported results are quantitatively disappointing, they still mention a reproduction of certain trends in some (distant-dependent) experimental results. The purpose of this paper is to present a consistent application of the above-mentioned model in the description of double-halide superexchange coupling and to show its ability to reproduce correctly the experimental facts in the ADA series.

II. FORMALISM

In the model used, we replace the open shell of each Cu II anion by one "effective" electron, the valence shell of each (Cl or Br) anion by two, spin-paired, "effective" electrons. The orbital functions of these electrons are assumed to be of the 1*s* Slater type, with characteristic parameter λ. The determination of the λ parameters for cations and anions will be discussed in Sec. III. The $\mathrm{Cu}_a \diagdown \mathrm{Cl}_a \diagup \mathrm{Cl}_b \diagdown \mathrm{Cu}_b$ bridge in the ADA series is thus represented by a four-center–six-electron model.

Using first-order exchange perturbation theory, the interaction energy for the interlayer two-halogen bridge is given by

$$E^{(1)}=(\Phi\sigma,\mathscr{V}\mathscr{A}_6\Phi\sigma)/(\Phi\sigma,\mathscr{A}_6\Phi\sigma)\ , \tag{1}$$

where Φ is the simple product of the orbital functions for the six electrons, σ is the total-spin function, distinguishing between σ_S for the two Cu spins antiparallel and σ_T for the two Cu spins parallel. Furthermore, $\mathscr{A}_6$ is the antisymmetrizer for the assembly of six electrons, and $\mathscr{V}$ is the *inter*atomic Coulomb interaction for two cations and two anions. Since $\mathscr{V}$ does not contain spin-dependent terms, we can at once integrate over spin space in (1). The interlayer exchange-coupling constant J_{2h} is then given by

$$2J_{2h}\equiv E_S^{(1)}-E_T^{(1)}=\frac{(\Phi,\mathscr{V}\mathscr{Q}_S\Phi)}{(\Phi,\mathscr{Q}_S\Phi)}-\frac{(\Phi,\mathscr{V}\mathscr{Q}_T\Phi)}{(\Phi,\mathscr{Q}_T\Phi)}\ , \tag{2}$$

where the subscripts S and T refer to the singlet and triplet spin states of the two cations, respectively. The projectors $\mathscr{Q}_S$ and $\mathscr{Q}_T$ are found to be, employing the method of double-coset decomposition[10] of the antisymmetrizer $\mathscr{A}_6$, and using inversion symmetry of the two-cation–two-anion bridge,[11]

$$\begin{aligned}\mathscr{Q}_S=(I+P_{14}P_{25}P_{36})[I&-2(P_{13}+P_{14}+P_{34})+P_{36}+P_{13}P_{46}+2P_{14}P_{23}\\&+4P_{16}P_{23}+P_{14}P_{23}P_{56}+2(P_{134}+P_{143}-P_{136}-P_{163})\\&-4(P_{23}P_{146}+P_{23}P_{164})+P_{1346}+2P_{1364}+P_{1643}]\ ,\end{aligned} \tag{3}$$

and

$$\begin{aligned}\mathscr{Q}_T=(I-P_{14}P_{25}P_{36})[I&-2(P_{13}+P_{14}+P_{34})-P_{36}+P_{13}P_{46}\\&+2(P_{14}P_{23}+P_{134}+P_{143}+P_{136}+P_{163})-P_{14}P_{23}P_{56}\\&-P_{1346}-2P_{1364}-P_{1643}]\ ,\end{aligned} \tag{4}$$

where the electrons on the two halogens are numbered 1,2 and 4,5, respectively, and those on the two cations are numbered 3 and 6. In (3) and (4), P_{ij} stands for a permutation of electrons i and j, etc.

If we know the parameters for Cu^{2+} and Cl^-, Br^- (Sec. III), then we can evaluate J_{2h} for arbitrary (though inversion symmetric) configurations of the complex of two cations and two anions, i.e., for the superexchange unit considered in the ADA series.

III. DETERMINATION OF THE SLATER PARAMETERS

The method for the determination of the parameters in the 1s Slater functions $\lambda^{3/2}\pi^{-1/2}\exp(-\lambda r)$ for the cation and anion "effective" orbitals has been described in detail in Ref. 6. There, the model was applied to the 180° (single-halide) superexchange in some 3d-metal fluorides. Prime importance was given to establishing the *ratios* of the various λ parameters. The necessity of assigning absolute values was deliberately postponed. Following earlier work by Jansen and co-workers, the λ values, *relative* to one another, were obtained by comparing the diamagnetic susceptibilities of the *valence* shells. For the ions of interest in the present paper it was found that $\lambda_{Cu^{2+}}/\lambda_{F^-}=0.90$ and $\lambda_{Cl^-}/\lambda_{F^-}=0.63$, yielding the ratio $\lambda_{Cl^-}/\lambda_{Cu^{2+}}=0.70$. Later on, the ratio $\lambda_{Cl^-}/\lambda_{Br^-}$ of the orbital-extension parameters of the doubly filled effective orbitals representing the valence shells of the Cl and Br ions was used[12] in a (model) calculation of the coupling constant in the two-dimensional antiferromagnet $(C_3H_7NH_3)_2MnBr_4$.

Again taking recourse to SCF calculations for the $\langle r^2\rangle$ values from each shell of electrons on the ions, according to Herman and Skillman,[13] it was found that $\lambda_{Cl^-}/\lambda_{Br^-}=1.13$. In Table I we give the values for the quantities $\langle r^2\rangle$, in a.u.^{2}, summed both over all electrons and those for the valence shells only.

The procedure described above leaves only one parameter to be chosen so as to yield, aside from a qualitative reproduction of the trends in the experimental data, also a best quantitative agreement between theory and experiment. The specific choice $\lambda_{F^-}=1.11$ a.u.$^{-1}$ (and, thus, $\lambda_{Cu^{2+}}=1.00$ a.u.$^{-1}$) in Ref. 6 leads to quite close agreement with the available experimental data for the compounds considered. However, it has to be emphasized that this assignment is directly connected with the application of the model to a three-center—four-electron superexchange unit. Keeping the ratios fixed, the calculated exchange-coupling constants depend strongly on the choice of the parameters. As a consequence, it is to be expected that in the present case, dealing with an application of the model to a four-center—six-electron system, slightly different absolute values may be found in order to obtain *quantitative* agreement with experiment. Nevertheless, the capability of the model in the description of the *qualitative* features in the ADA series must already be shown when the assigned λ values from Ref. 6 are used. For example, the *ratios* between the experimental coupling constants J_{2h}/k have to be predicted correctly and independently with respect to small variations in the absolute values of the orbital parameters.

In the present calculations we have taken three sets of parameters for the Cu, Cl, and Br ions, keeping their ratios fixed, with $\lambda_{Cu^{2+}}=1.00$, 0.97, and 0.94 a.u.$^{-1}$, respectively. The first set, directly adopted from Ref. 6, already leads to correct qualitative predictions in the series under consideration. The second set will be found to also yield correct quantitative results for J_{2h}/k and has further been used in the evaluation of the distant dependence of the coupling constants.

IV. NUMERICAL RESULTS AND DISCUSSION

On the basis of the parametrization method outlined in Sec. III, we can now calculate the double-anion superexchange constant J_{2h} for solids of different compounds of the ADA series, applying Eqs. (2)—(4). In doing so we allow, as mentioned, for some freedom in the Slater parameter $\lambda_{Cu^{2+}}$, in varying this quantity between 1.00 a.u.$^{-1}$ (as deduced from single-anion exchange) and 0.94 a.u.$^{-1}$. However, as imposed by the model, we keep the ratios $\lambda_{Cl^-}/\lambda_{Cu^{2+}}$ and $\lambda_{Cl^-}/\lambda_{Br^-}$ fixed at 0.70 and 1.13, respectively. The results for J_{2h}/k (K) are

TABLE I. Values for $\langle r^2\rangle$ in a.u.^{2}.

	Cl^-	Br^-	$\lambda_{Cl^-}/\lambda_{Br^-}$
$\sum_{tot}\langle r^2\rangle$	28.05	40.71	
$\sum_{\text{valence shell}}\langle r^2\rangle$	26.38	33.50	1.13

TABLE II. Values of J_{2h}/k (K) assuming linear bridges for all compounds of the ADA series considered plus their ratios, omitting BDA $CuCl_4$, as a function of $\lambda_{Cu^{2+}}$ (between 1.00 and 0.94 a.u.$^{-1}$). As input data for the calculations experimental values for the halogen-halogen and copper-copper distances have been used (Ref. 5).

		$-J_{2h}/k$ (K)					
Halogens		Br	Cl				
n		2	2	3	4	5	Ratio
Experiment		31 ± 1	13.7	2	0.16	0.04	100:43-46:6-7 : - : 0
$\lambda_{Cu^{2+}}$	1.00	19.3	8.8	1.4	1.8	0.01	100: 46 : 7 : - : 0
(a.u.$^{-1}$)	0.97	28.5	13.4	2.4	2.9	0.02	100: 47 : 8 : - : 0
	0.94	41.2	20.3	3.9	4.8	0.05	100: 49 : 9 : - : 0

given in Table II, assuming a linear $Cu_a \diagup Cl_a \diagdown Cl_b \diagup Cu_b$ bridge for all compounds; a and b denote adjacent layers.

As input data for the calculations we have used the experimental values for the halogen-halogen and copper-copper distances (r and R, respectively) as given by Snively, Tuthill, and Drumheller.[5] For what follows we denote this paper by STD. The experimental values for J_{2h}/k mentioned in the table are those listed in STD. The ratios of the J values are also given, omitting BDA $CuCl_4$.

From Table II it is seen that the ratios correctly reproduce the experimental results and vary very little between the three values for $\lambda_{Cu^{2+}}$. Furthermore, excellent absolute agreement exists for $\lambda_{Cu^{2+}}=0.97$ a.u.$^{-1}$, except for BDA $CuCl_4$, where the calculated value is substantially more negative than the observed one. STD already suggested that for this compound the nonlinearity of the two-halogen bridge must be taken into account. Using the crystal data given in Ref. 4 together with the Cu_a-Cl_a distance for EDA $CuCl_4$ by Tichy *et al.*[14] and its value for PDA $CuCl_4$ (i.e., $n=3$) given by Phelps *et al.*,[1] the very small change in this distance going from $n=2$ to 3 (from 4.378 to 4.373 a.u.) suggests that we may use for $n=4$ an average value of 4.375 a.u. for BDA $CuCl_4$. On this basis we calculate an angle $\theta=\angle Cu_a$-Cu_b-Cl_b of 20.8°. This angle is, for the three remaining compounds $n=2$, 3, 5, $X=Cl_4$, equal to 9°, 8°, and approximately 0° (the crystal data for the last compound is somewhat uncertain).

In order to analyze the effect of nonlinearity of the two-halogen bridge we have carried out some model calculations for BDA $CuCl_4$ varying the angle θ. In Table III we present the results of these

TABLE III. Values of J_{2h}/k (K) for BDA $CuCl_4$ as a function of $\theta=\angle Cu_a$-Cu_b-Cl_b in two cases. As input data for the calculations the experimental values for the chlorine-chlorine and copper-copper distances (Ref. 5) have been used in the first case (second column); those in the second case (third column) are the experimental value for the copper-copper distance and the value 4.375 a.u. for the copper-chlorine nearest-ion distance of the bridge (see text). $\lambda_{Cu^{2+}}=0.97$ a.u.$^{-1}$, $\lambda_{Cl^-}/\lambda_{Cu^{2+}}=0.70$. The values of J_{2h}/k in the second and third columns are, of course, the same for $\theta=20.8°$.

	$-J_{2h}/k$ (K)	
θ	$R=17.09$ a.u. $r=9.45$ a.u.	$R=17.09$ a.u. $l=4.375$ a.u.
0°	2.94	2.69
5°	2.75	
10°	2.24	1.95
15°	1.53	
20°	0.81	0.78
30°	0.02	0.18

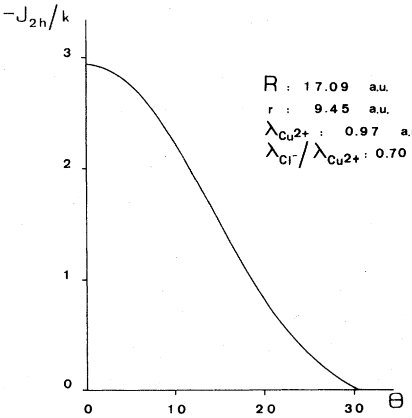

FIG. 1. Plot of J_{2h}/k for BDA $CuCl_4$ as a function of the angle θ according to the calculated data listed in the second column of Table III. The distances R and r are fixed at the experimental values (Ref. 5).

calculations of J_{2h}/k for BDA $CuCl_4$ as a function of θ for two different cases. In the first case the distance R between the copper ions and the distance r between the chlorines are fixed at their experimental values.[5] As a consequence, the distance l between the Cu-Cl nearest ions of the bridge varies with θ (a larger value of θ implies a larger value of l). For $\theta = 0°$, we thus find a value for J_{2h}/k already reported in Table II where a linear geometry was assumed with the experimental values for R and r as input data. The value of $\lambda_{Cu^{2+}}$ is 0.97 a.u.$^{-1}$. The second case concerns the situation of a θ variation where R is still fixed at the experimental value, but now together with a constant value for the distance l between the Cu-Cl nearest ions for which we take the above-mentioned value of 4.375 a.u. Here, the distance r between the chlorines varies with θ. The latter results, presented in the third column of Table III, will be further discussed below.

From the results obtained for the first case, i.e., varying θ with constant values for R and r, we conclude that the effect of nonlinearity in the two-halogen bridge on the value of J_{2h} is quite substantial. The calculated behavior of the exchange-coupling constant with the angle θ is shown in Fig. 1.

From the figure we see that, after changing gradually in the beginning, J_{2h} rapidly decreases when θ becomes larger than, for example, 10°. For $\theta \approx 21°$, the value for $|J_{2h}/k|$ is found to be smaller than 0.8 K. Although this value is not yet as small as the absolute value of the observed one (0.16 K), the model correctly predicts the relatively large effect of nonlinearity in the two-halogen bridge.

A further aspect of the observed coupling constants in the ADA series under consideration, with $X = Cl_4$, concerns the exchange-versus-distance relationship. In a plot of $\ln|J_{2h}/k|$ versus the natural logarithm of the Cu_a-Cu_b distance, $\ln R$, STD show that, except for BDA $CuCl_4$, a straight line can be drawn through the experimental data with a slope of -16 ± 2. The failure of BDA $CuCl_4$ to coincide with this graphical picture of variation in R is then supposed to be explained by the assumption that it is the halogen-halogen separation r which is responsible for the strength of the indirect coupling, and not the Cu-Cu distance. The deviation ($\theta \approx 21°$) from linearity of the exchange path in this compound is, by STD, not expected to be responsible for the large reduction in the experimental data. In a similar plot of $\ln|J_{2h}/k|$, but now with respect to the natural logarithm of the chlorine-chlorine spacing, $\ln r$, all *four* data points turn out to lie nearly on a line with slope -10 ± 2. From this result STD conclude that the anion-anion overlap appears to be the primary parameter which determines the superexchange coupling.

Apart from the obvious fact that, regarding the large differences in the values of R and r in the compounds concerned, a "power-law" dependence is not expected to be applicable, we nevertheless wish to state the following points which result from the model calculations.

First of all, it has to be noted that in BDA $CuCl_4$, assuming the Cu_a-Cl_a distance l practically constant, the nonlinearity is directly connected with an increase of the distance r between the chlorine ions. Therefore, it is interesting to deduce from the data, listed in the third column of Table III, the correlation between J_{2h}/k and r. One readily verifies that in the range $0° < \theta < 20°$ we find a linear relationship between $\ln|J_{2h}/k|$ and $\ln r$ with a slope of -10.5 ± 0.5. Since, roughly speaking, both the geometries and the calculated exchange-coupling constants of PDA and BDA $CuCl_4$ are equal in the linear case ($\theta = 0°$), it then follows that BDA will closely coincide with the graphical presentation of STD, mentioned above, with slope -10 ± 2. However, extending the range in the variation of θ to 30° (Table III, third column), one finds in a similar plot of $\ln|J_{2h}/k|$ vs $\ln r$ a line with slope -12 ± 2. Hence, the rapid change in slope (and its deviation) possibly imply that the fit to the STD power law -10 ± 2 may be somewhat accidental. Note that the changes in r with θ are relatively small compared to those between the other members of the ADA series.

A last remark concerns the sensitivity in the model calculations for J_{2h}/k with respect to variations in l. As long as l is practically constant (as is the case in the compounds considered), the calculations support the conclusion of STD that the chlorine-chlorine distance appears to be a primary parameter in the exchange coupling. On the other hand, if the distance l is not fixed within a small range, the "power law" of J_{2h}/k with r does not fit at all the calculated results then obtained.

In summarizing, we have shown that a consistent application of the model leads to the following.

(1) Quantitative agreement with the experimental *ratios* of exchange-coupling constants J_{2h} in the ADA series, except for BDA, on the basis of orbital parameters taken from Ref. 6 (single-anion ex-

change).

(2) Quantitative agreement with the experimental values of the *coupling constants* separately, provided that the orbital parameters (still with fixed ratios) are lowered by 3%. Such a small change is expected from the beginning since the model is applied to a different type of superexchange unit compared to that of Ref. 6.

(3) Nearly-quantitative agreement with the experimental effect of nonlinearity in BDA $CuCl_4$ on the exchange-coupling constant.

(4) A quantitative explanation for the simultaneous fit of BDA $CuCl_4$ to the relationship $\ln|J_{2h}/k|$ vs $\ln r$ in the chlorine compounds considered by STD.

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