

**Measurement and calculation of the superexchange interaction through
the two-halide bridge in the eclipsed layered compounds
[NH₃(CH₂)_nNH₃]CuX for $n = 2-5$ and $X = \text{Cl}_4$ and Cl_2Br_2**

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Magnetic susceptibility measurements on the eclipsed layered structure series of [NH₃(CH₂)_nNH₃]CuX ($n = 2, 3, 4,$ and 5 for $X = \text{Cl}_4$ and $n = 2$ for $X = \text{Cl}_2\text{Br}_2$) indicate that the interplanar superexchange interaction along the linear Cu-Cl-Cl-Cu path has a significantly stronger Cu-Cu distance dependence than that for the typical $M-X-M$ ($M = \text{Cu, Mn, Ni, Co; } X = \text{F, Cl}$) path, and a stronger power-law metal-metal distance dependence than previously expected for the two-halide bridge case. Furthermore, the evidence indicates a 10th-power dependence on the halide-halide separation, which appears to be the critical parameter for determining the strength of the two-halide superexchange. Previously unpublished data on the partially bromated compound is included. The results of a Rayleigh-Schrödinger perturbation calculation of the two-halide superexchange strength are presented and the calculated results are compared with experimental values.

I. INTRODUCTION

Much has been learned in recent years about the nature of magnetic superexchange through a single-halide anion.¹⁻³ Less thoroughly investigated, though, is superexchange through a two-halide bridge. We present here the first direct measurements of the superexchange strength-versus-distance relationship for the two-halide bridge, and discuss the ways in which these results differ from earlier expectations.

Most of the data concerning single-halide exchange have come from layered structures such as (C_nH_{2n+1}NH₃)₂CuCl₄ (*AA* series) or other related A_2MX_4 -type series, consisting of magnetically well isolated two-dimensional (2D) arrays of $M-X-M$ bridges. It has been found that the exchange strength varies with the $M-M$ distance d approximately as $J \propto d^\alpha$, where the parameter α has been variously estimated to be between -10 (Ref. 3) and the most recent value of -12 (Ref. 1). De Jongh and Block¹ have attempted to calculate this distance dependence using the perturbation approach of Jansen *et al.*,⁴ and have shown α to be -12 for Mn²⁺, Co²⁺, and Ni²⁺ over the experimental interionic distances.

In earlier attempts at exchange calculations⁵⁻¹⁰ and in the review articles^{11,12} which detail them more fully, the question of two anion superexchange is mentioned only in passing, typically with the remark that it will be similar in sign but weaker than the single-anion case. There are few previous quantitative calculations, the notable exceptions being the work of van Kalker *et al.*,¹³ and ter Maten and Jansen¹⁴

although they do not discuss the effect of the second anion in general. De Jongh and Miedema¹⁵ suggest the rule of thumb that J decreases by a factor of approximately 10^{-2} for each additional superexchange anion. We report here experimental and calculational results which show that, for the case of Cu-Cl-Cl-Cu, J shows a stronger power-law dependence on d than previously expected. Further, the data suggest that the Cl-Cl separation, d_{2h} , rather than the Cu-Cu distance, d_{out} , may in fact be the most appropriate parameter to consider for the strength of the two-halide superexchange.

In Sec. II we briefly review the characteristics of the alkanediammonium tetrachlorocuprate [NH₃(CH₂)_nNH₃]CuCl₄ (*ADA* series) compounds, and present the superexchange values determined from magnetization and susceptibility measurements. Also, the new results for the mixed halide compound EDA CuCl₂Br₂ (EDA: $n = 2$) are given. Results of a Rayleigh-Schrödinger perturbation calculation of the superexchange strengths are given in Sec. III. Section IV includes a discussion and comparison of the results.

II. EXPERIMENTAL RESULTS

The series of compounds of interest is similar to the well-studied *AA* series¹⁵ in that both have layers of puckered CuCl₄²⁻ planes separated by organic chains which can be used to vary the interplanar distance. The important difference appears in the relative location of the magnetic ions in adjacent layers. Neighboring planes in the *AA* series are staggered, so that each copper-halide octahedron in the quadratic

TABLE I. Data for the compounds $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuX}$ with $n=2, 3, 4$, and 5 for $X=\text{Cl}_4$ and with $n=2$ for $X=\text{Cl}_2\text{Br}_2$.

$[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuX}$	D_{out} (Å)	d_{2h} (Å)	T_C (K)	J_{1h}/k (K)	J_{2h}/k (K)	Ref.
$n=2, X=\text{Cl}_2\text{Br}_2$	$\approx 8.3 \pm 0.2$	$\approx 3.7 \pm 0.2$	≈ 45.0	15.0 ± 1.0	-31.0 ± 1.0	This work
$n=2, X=\text{Cl}_4$	8.11	3.63	31.5 ± 0.5	23.0	-13.7	a
			34.0 ± 1.0	20.0	-6 to -20	b
$n=3, X=\text{Cl}_4$	8.94		14.9 ± 0.2	16.5	-1.7	b
	9.12	4.60	13.5	15.4	0.0	c
				20	-2	This work
$n=4, X=\text{Cl}_4$	9.04	5.0	8.85 ± 0.2	13.0	-0.16	d
$n=5, X=\text{Cl}_4$	≈ 11.5	≈ 6.6	7.6 ± 0.2	14.1	-0.040	b

^aL. O. Snively, P. L. Seifert, K. Emerson, and J. E. Drumheller, Phys. Rev. B **20**, 2101 (1979).

^bH. von Känel, Physica (Utrecht) B **96**, 167 (1979).

^cD. W. Phelps, D. B. Losee, W. E. Hatfield, and D. J. Hodgson, Inorg. Chem. **15**, 3147 (1976).

^dL. O. Snively, K. Emerson, and J. E. Drumheller, Phys. Rev. B **23**, 6013 (1981).

net lies above a "hole" in the next plane. In the ADA series, on the other hand, the Cu^{2+} ions in adjacent layers lie nearly directly above one another ("eclipsed" structure), so that there may exist a significant superexchange path between them through the two intervening halides. For reference, Fig. 1 de-

picts the crystal structure for the unit cell of EDA with the large dashed circles around the interplanar Cl^- 's indicating the van der Waal radii which reflect their size. Figure 1 is drawn to scale for EDA while the $n > 2$ members of the series have larger interplanar separations.

Table I lists the measured values for the magnetic parameters for the ADA series as well as d_{out} and the interlayer anion-anion separation (d_{2h}). A brief discussion of each member of the series is given below with comments as to how the exchange values were found for each.

EDA CuCl_4 ($n=2$)

Our earlier work¹⁶ and independently that of von Känel¹⁷ reported the surprising result that the exchange through the two-halide bridge in EDA CuCl_4 . J_{2h}/k , instead of being weak as expected is very nearly equal to that of J_{1h}/k , the single-halide exchange in the $\text{Cu}-\text{Cl}-\text{Cu}$ planes, although opposite in sign. This represents an apparent violation of the rule of thumb indicating a reduction of the exchange by approximately 10^{-2} due to the extra anion, especially since the $\text{Cu}-\text{Cu}$ separation is much greater between layers than within a layer. As will be discussed in the Sec. IV, however, this is probably not an appropriate use of that rule. The two sets of data reported by the two different groups agree relatively well even though different techniques were used to determine the exchange values. For our calculations we used a high-temperature series expansion (HTSE) which included both the intraplane and the interplane exchange terms to fit the data. In contrast von Känel has used critical-field data from temperatures below the critical point, and calculated the exchange constants using mean-field theory. It is encouraging that the two methods produce similar results.

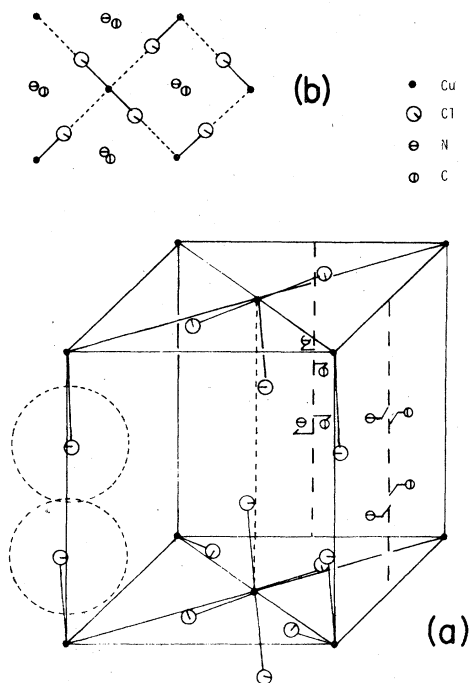


FIG. 1. (a) Unit cell of EDA CuCl_4 showing the positions of the ions (except hydrogens). Large circles on the left indicate approximate size of the Cl^- anions. Some of the $\text{Cu}-\text{Cl}$ bonds are included to help show the "puckering" of the layers. (b) Projection of the structure onto a plane to indicate the asymmetric $\text{Cu}-\text{Cl}$ bond lengths and to show the organic chain locations.

PDA CuCl_4 ($n = 3$)

The results for this compound come from three different sources. Phelps *et al.*¹⁸ have claimed that their data fit a strictly 2D ferromagnetic interaction thereby indicating that there is no interplane coupling. Von Känel¹⁷ on the other hand, using the critical-field approach, found significant interlayer coupling, as shown by his results in Table I. We therefore decided to fit the data of Phelps to our high-temperature expansions which include the out-of-plane exchange and found that indeed their data are consistent with a relatively strong interplane interaction. Thus we have chosen to use the value found by von Känel in the discussion which follows in Sec. IV.

BDA CuCl_4 ($n = 4$)

From our earlier work¹⁹ we have found that the interplanar interaction is weaker for BDA, though it is still not a good 2D ferromagnet when compared to many other layered structures. Because of the low value of the out-of-plane exchange and the limited number of terms in the high-temperature expansion used it was not possible to determine J_{2h}/k by that method. Instead the standard critical-field technique was used. As will be discussed in detail later, an unexpected modification of the crystal structure occurs in this compound which allows an interesting comparison to be made between the distance dependence of the exchange as a function of d_{out} and d_{2h} .

PentDA CuCl_4 ($n = 5$)

Because of the large interplane separation, this member is the best 2D ferromagnet of the series. The ratio of J_{2h} to J_{1h} is approximately 10^{-3} according to the critical-field results of von Känel.¹⁷ Unfortunately, the crystal structure of this compound is not well known so that only estimates of the various distances are used.

EDA CuCl_2Br_2 ($n = 2$)

The object in investigating this compound was to increase the interplane interaction by substituting the larger Br^- anions for the interlayer Cl^- ions. From previous experience with the mixed compounds of the AA series²⁰ and from the results of Willett²¹ and Witteveen²² it was expected that the Br^- anions take the interlayer locations leaving the Cl^- anions in the planes. The results seem to confirm this since J_{1h}/k is nearly the same as for the unbromated compounds while J_{2h}/k is considerably larger. These values were determined from the previously described^{16,23} HTSE used on data taken from a 0.068-g powdered sample of EDA CuCl_2Br_2 . Figure 2 shows the data plotted in the usual fashion of the reduced susceptibility versus

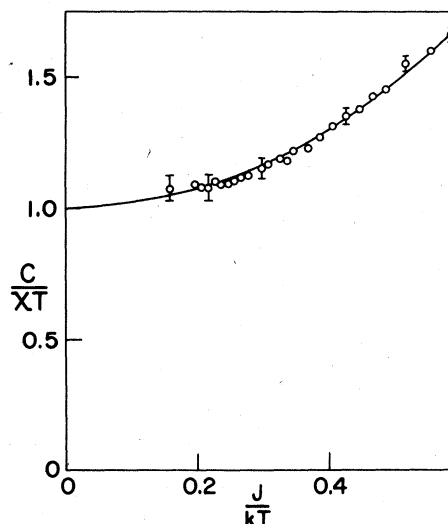


FIG. 2. Inverse susceptibility vs J/kT for EDA CuCl_2Br_2 . Solid curve represents the high-temperature series expansion for $J_{1h}/k = 15.0$ K and $J_{2h}/k = -31.0$ K.

the reduced temperature. The line through the data represents the calculated HTSE with $J_{1h}/k = 15.0 \pm 1.0$ K and $J_{2h}/k = -31.0 \pm 1.0$ K. This fit was the best obtainable and could not be rejected at the 99% confidence level. The fit shown used an average g value of 2.20. As was anticipated the bromides have significantly increased the interlayer exchange to the point that EDA CuCl_2Br_2 is better described as a linear-chain antiferromagnet with weaker ferromagnetic coupling between the chains. The transition temperature could not be determined from the powdered sample. It is estimated, however, to be between 40 and 45 K, based on the susceptibility maximum which occurs at 52 K.

III. CALCULATION RESULTS

As indicated in the Introduction, there have been several attempts at calculating the superexchange strength in insulators, most notably the original work of Kramers⁵ and later that of Anderson⁶ and Goodenough.^{8,9} However, their calculations were at best semiquantitative and only useful in most cases for determining the sign of the exchange. Recently Jansen and co-workers,⁴ and independently Matsen and Klein²⁴ and their co-workers, have developed a method for calculating the superexchange interaction which seems to give remarkably good results when compared to the results of experiments. In view of that, we have followed the method of Jansen *et al.* to calculate the strength of the two-halide superexchange in the ADA series.

The basic approach is to use a Rayleigh-Schrödinger perturbation technique on an appropriate cluster of magnetic and diamagnetic ions. The

zeroth-order wave functions are those of the isolated ions and are represented by 1s Slater orbitals. Because these functions are not orthogonal, the exchange effect is seen in first order rather than third order as in the approach of Kramers. This greatly simplifies the calculation and also eliminates some of the errors associated with carrying the calculation to higher orders.⁴ Furthermore, the unfilled 3d shell of the magnetic ion is replaced by a single "effective" electron.

For the case of four electrons on four centers, the perturbing potential \mathcal{V} is taken to be

$$\mathcal{V} = e^2 \left[\frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \frac{1}{r_{12}} - \left(\frac{1}{r_{1b}} + \frac{1}{r_{2a}} + \frac{1}{r_{3a}} + \frac{1}{r_{4a}} + \frac{1}{r_{3b}} + \frac{1}{r_{4b}} + \frac{1}{r_{1z}} + \frac{1}{r_{1z'}} + \frac{1}{r_{2z}} + \frac{1}{r_{2z'}} \right) + \frac{1}{r_{ab}} + \frac{1}{r_{az}} + \frac{1}{r_{az'}} + \frac{1}{r_{bz}} + \frac{1}{r_{bz'}} \right],$$

where a and b refer to the two magnetic ions, each with one electron (subscripts 1 and 2), and z and z' refer to the centers of the diamagnetic ligand, which has two spin-paired electrons (subscripts 3 and 4). For the four-center case the ligand is represented as a molecular orbital. The zeroth-order wave functions

corresponding to the isolated ions are given by the 1s Slater orbitals:

$$a = (\lambda^3/\pi)^{1/2} \exp(-\lambda r_a), \quad z = (\mu^3/\pi)^{1/2} \exp(-\mu r_z), \\ b = (\lambda^3/\pi)^{1/2} \exp(-\lambda r_b), \quad z' = (\mu^3/\pi)^{1/2} \exp(-\mu r_{z'}).$$

We have constructed the molecular orbital (MO) of the diamagnetic ligand combination in three ways and have studied the effect of the different combinations. The three MO's are as follows:

$$\xi_{\pm}^{(1)} = ZK_1^{\pm} [z(3) \pm z'(3)][z'(4) \pm z'(4)],$$

$$\xi^{(2)} = ZK_2 [z(3)z'(4) + z'(3)z(4)],$$

$$\xi^{(3)} = ZK_3 [z(3)z(4) + z'(3)z'(4)].$$

where the ZK 's refer to the appropriate normalizing factors for each. The first MO is the usual formulation; both the bonding (+) and the antibonding (-) orbitals were used. We have called the second orbital "covalent" because it stresses the sharing of the electrons by both of the nuclei of the anions. The last orbital listed is referred to as 'ionic' since both electrons are preferentially placed either on z or on z' . The orbital extension parameters λ and μ are determined from self-consistent field (SCF) calculations of $\langle r^2 \rangle$ by Herman and Skillman,²⁵ using diamagnetic susceptibilities of the closed and open shells of the ions. We have used the same values for λ and μ as given by de Jongh and Block¹ for Cu and Cl, namely, $\lambda(\text{Cu}^{2+}) = 1.00 \text{ a.u.}^{-1}$, $\mu(\text{Cl}^-) = 0.70 \text{ a.u.}^{-1}$, and we

TABLE II. Experimental and calculated interplane superexchange values for the EDA series compounds. The orbital extension parameters used for the calculation were $\lambda(\text{Cu}^{2+}) = 1.0 \text{ a.u.}^{-1}$, $\mu(\text{Cl}^-) = 0.7 \text{ a.u.}^{-1}$, and $\mu(\text{Br}^-) = 0.6 \text{ a.u.}^{-1}$. The four calculated values for each compound correspond to the molecular orbitals (1) $a(1)b(1)[z(3) \pm z(4)]$ [two values for bonding (+) and antibonding (-)] (2) $a(1)b(2)[z(3)z'(4) + z'(3)z(4)]$, and (3) $a(1)b(2)[z(3)z(4) + z'(3)z'(4)]$. $1 \text{ a.u.} = 0.529 \text{ \AA}$.

$[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuCl}_x\text{Br}_y$	d_{out} (a.u.)	d_{2h} (a.u.)		J_{2h}^{calc}/k (K)	J_{2h}^{expt}/k (K)	
$n=2, x=2, y=2$	15.7	7.0	(1)	+	-198	-31
				-	-288	
			(2)		+ 23	
$n=2, x=4, y=0$	15.3	6.9	(3)		- 2.3	-13.7
			(1)	+	-176	
				-	-217	
$n=3, x=4, y=0$	17.1	8.7	(2)		-171	-1.6
			(1)	+	-195	
				-	-205	
$n=5, x=4, y=0$	21.0	12.5	(3)		- 0.15	-0.04
			(1)	+	-190	
				-	-182	
			(2)		-662	
			(3)		- 0.003	

have found $\mu(\text{Br}^-) = 0.60 \text{ a.u.}^{-1}$ using their technique.

The first-order exchange energy is given as usual by the difference between the singlet and triplet energies. The specific expression is

$$2J = \frac{1}{n^2} \left(\frac{\langle \phi_0 | \mathcal{O}_S \mathcal{U} | \phi_0 \rangle}{\langle \phi_0 | \mathcal{O}_S | \phi_0 \rangle} - \frac{\langle \phi_0 | \mathcal{O}_T \mathcal{U} | \phi_0 \rangle}{\langle \phi_0 | \mathcal{O}_T | \phi_0 \rangle} \right),$$

where ϕ_0 is a simple product function of the unperturbed wave functions, $\phi_0 = a(1)b(2)\xi^{(i)}(3,4)$, and $\mathcal{O}_{S,T}$ are the projection operators for the singlet or triplet state given by

$$\mathcal{O}_S = (I - P_{13} - P_{23} + P_{13,24})(I + P_{12}),$$

$$\mathcal{O}_T = (I - P_{13} - P_{23})(I - P_{12}).$$

P_{13} , etc., refer to the permutation operators which interchange electrons 1 and 3 and so forth. Finally, n is the number of unpaired electrons on the metal cation, which for Cu^{2+} is one.

Using this equation, we have calculated J_{2h} for each of the three molecular orbitals given earlier. The results are presented in Table II and they are discussed in more detail in the next section.

IV. DISCUSSION

As has been mentioned, the most interesting and initially surprising result of studying this series is the large interplane interaction which was found. The system effectively changes from a 1D antiferromagnet to a 3D antiferromagnet then to a 2D ferromagnet as first the anion is changed (Br^- to Cl^-) and then the interlayer distance is increased. Within the CuCl_4 series the two-halide and single-halide exchange strengths have a ratio which ranges from order unity to roughly 10^{-3} . A graphical view of this variation is obtained by plotting the natural logarithm of J_{2h} versus the natural logarithm of d_{out} , the interlayer Cu-Cu distance, as in Fig. 3(a). Except for BDA a straight line may be drawn through the data with a slope of -16 ± 2 . This value represents the first direct measurement of the exchange-versus-distance relationship for the linear two-halide bridge. Thus we find a considerably stronger dependence on the interlayer distance than that previously suggested from empirical evidence on single-halide exchange, namely, J_{1h} varies as d^{-12} .

We point out that the fit to power-law form is simply an approximation which allows us to compare our results with the work of others. It has been conjectured¹ that the true d dependence of J may be exponential in character ($\ln J \propto d$) so that the "effective exponent" $\partial(\ln J)/\partial(\ln d)$ is an increasing function of distance. We of course cannot distinguish between exponential and power-law behavior on the basis of our four data points.

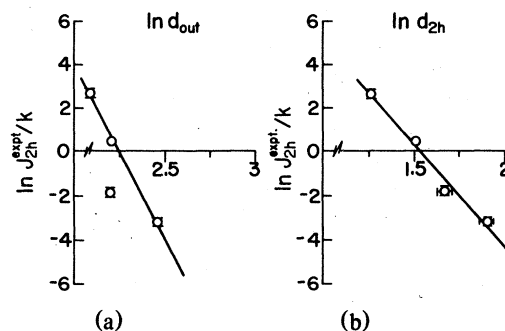


FIG. 3. (a) Natural logarithm of J_{2h} vs natural logarithm of d_{out} for the ADA CuCl_4 series. Slope of the line is 16 ± 2 . (b) $\ln J_{2h}$ vs $\ln d_{2h}$ for the same series. Slope of the line through the data is -10 ± 2 .

We consider next whether d_{out} is in fact the most fundamental parameter for the determination of J_{2h} for the two-halide exchange. Evidence that it is not is found in the failure of BDA to fall on the straight line of Fig. 3(a). As mentioned earlier, the crystal structure of BDA is different than expected in that its interlayer distance is the same as in PDA. It is believed¹⁹ that this is because the organic chain buckles. In addition, the adjacent layers are shifted by 13° in BDA which causes the Cl^- - Cl^- distance to be larger than for PDA while not changing the Cu^{2+} - Cu^{2+} distance. Whatever the reason for the buckling, the question must be asked why the magnetic interaction decreases as though the separation were larger.

One possible explanation is that the exchange path in BDA is not exactly linear because of the 13° shearing of the adjacent layers. There is evidence from the superexchange calculations of van Kalkeren *et al.*⁴ that the exchange does weaken in nonlinear exchange paths. However, it would not be expected to reduce the interaction by as large an amount as the data indicate.

A better explanation seems to be that it is not the cation distance that is critical to the strength of the superexchange, but rather the halide-halide separation, d_{2h} . Figure 3(b) shows a plot similar to that of Fig. 3(a) except that the abscissa is the Cl^- - Cl^- spacing. Notice that all four data points lie nearly on a line, indicating that in fact it may be the anion-anion overlap that is the primary parameter dictating the superexchange strength. Even though the layers shear in BDA, the Cu^{2+} octahedra retain their orientation with respect to the plane. Thus, d_{2h} increases in this compound compared to that value for PDA, whereas d_{out} does not. The fact that BDA shows, by still lying below the line, only slightly weaker exchange than its separation would indicate may be explained by its nonlinear exchange path, as suggested above.

Other authors have made brief mention of the importance of the anion-anion interaction. Von Känel¹⁷ has commented that the overlap of the Cl^- anions is crucial to the magnitude of the exchange for the ADA series. By comparing EDA with the compound KCuF_3 , he has argued that the exchange does decrease by 10^{-2} as an additional halide is inserted into the interlayer environment. However, reliable quantitative estimates are extremely difficult to make considering that not only does the anion change but the interlayer distances are significantly different. Therefore any conclusions based on a comparison to KCuF_3 should be viewed with extreme caution.

Evidence has been given by Algra *et al.*²⁶ that the anion-anion overlap is important in the Co-Cl-Cl-Co path in Cs_2CoCl_4 . However, that bridge is far from being linear, so that it is difficult to assign a specific path to the exchange. Accordingly, these workers have only made the claim that the anion-anion overlap plays a role in the overall exchange interaction and have presented no new quantitative estimates for its strength. Algra and co-workers²⁷ make a similar statement concerning the importance of the anion-anion overlap in the more nearly linear path of Co-O-O-Co in the compound $(\text{C}_5\text{H}_5\text{NO})_6\text{Co}(\text{ClO}_4)_2$. Unfortunately, in neither case are they able to demonstrate directly the effects of varying the anion-anion separation.

The data from EDA CuCl_2Br_2 seem to suggest that the superexchange through a two-halide bridge can be stronger than that for the single-halide case. We caution, however, that such a conclusion is probably erroneous. The ferromagnetic superexchange within the Cu^{2+} planes of the series is in fact anomalous, since experimental and theoretical evidence indicates that 180° superexchange interactions are antiferromagnetic. Kugel' and Khomskii²⁸ have shown that the ferromagnetic interaction in those planes is due to the Jahn-Teller distortion of the Cu-Cl bonds. Recall that this asymmetry was pictured in Fig. 1. Without the distortion the expected value for J has been estimated to be on the order of -200 K, using a single-halide calculation similar to that described in Sec. III.

The results of our calculation provide additional qualitative support for the importance of the two-halide overlap to the strength of the superexchange. Table II presents the results obtained from the model calculations along with the extension parameters used and the appropriate distances for EDA, PDA, PentDA, and for the mixed chloride-bromide EDA. We have not found J_{2h} for BDA, since the calculation is only valid for a 180° exchange path, and the bridge is not sufficiently linear in this compound. For no member of the series are the calculated values of the exchange in agreement with the experimental results. We focus attention, however, on the results for the "ionic" orbital, noting that they best reproduce

several important *qualitative* features of the series. First, the exchange constant for the Br^- ion is larger than that for the Cl^- ion by a ratio of 2.1:1 while the ratio for the measured values is 2.3:1. Second, the exchange does decrease in the correct way in going through the series from EDA to PentDA [as shown in Fig. 4(a)]. The format of Fig. 4(a) is the same as the previous ln-ln plot of the exchange values versus distances (Fig. 3). The slope of the line in Fig. 4(a) is approximately -19 , which is relatively far from that found from the data for the Cu^{2+} - Cu^{2+} separation. Contrariwise, the slope of the line through the data in Fig. 4(b) for the Cl^- - Cl^- distance is approximately -10 , which agrees well with the value (-10 ± 2) for the slope of the line for the experimental data in Fig. 3(b). It is encouraging that the results for the "ionic" orbital reproduce the experimental distance dependence to a rather surprising accuracy even though the actual values differ by an order of magnitude. Further, these initial results support the idea that it is the anion-anion overlap which is the critical parameter in the two-halide exchange.

The calculated results are clearly unacceptable for the usual molecular orbital and for the "covalent" orbital. We believe that this indicates that the anions are not bonding to each other in the way we suggested earlier,¹⁶ namely that they are not behaving as a single large superexchange anion. Instead, the fact that the ionic orbital is most successful in giving the correct distance dependence suggests that a four-center, six-electron cluster should be considered. As noted above, the ionic orbital tends to localize both electrons on either one or the other anion. In a four-center, six-electron cluster each anion would be represented by its own localized pair of electrons, making the separation of the anions more complete.

In summary, we have presented the first direct measurement of the linear two-halide superexchange

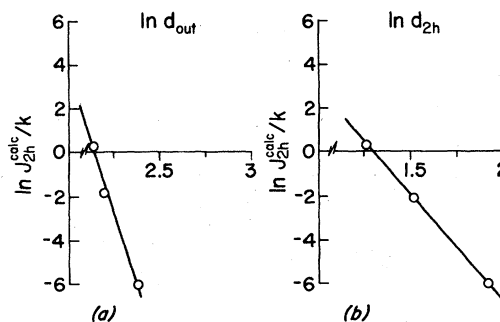


FIG. 4. (a) Natural logarithm of the calculated J_{2h} vs natural logarithm of d_{out} for the ADA CuCl_4 series. Slope of the line is -19 . (b) $\ln J_{2h}$ vs $\ln d_{2h}$ for the same series. Slope of the line through the points is -10 .

bridge in a series of transition-metal compounds. From the analysis we show that the previously suggested distance dependence of the exchange should be modified. We further present the results of a model calculation which qualitatively reproduces that important feature of the two-halide superexchange. Both the experimental and theoretical results indicate that the exchange is most properly described as a

function of the anion-anion overlap and goes approximately as the 10th power of that distance.

ACKNOWLEDGMENTS

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