Two-halide superexchange in $[NH_3(CH_2)_n NH_3]CuBr_4$ for $n = 3$ and 4

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High-temperature series expansions were applied to the magnetic susceptibility of the quasilayered "eclipsed" compounds $[NH_3(CH_2)_n NH_3]CuBr_4$ for $n = 3$ and 4 to determine the interplanar, J_{2h}, and intraplanar, J_{1h}, exchange and to test the predictions of the importance of the halide-halide separation in two-halide superexchange. The results are $J_{1h}/k_B = 26$ and 29 K, $J_{2h}/k_B = -26$ and -5 K, respectively, while transitions to long-range order are estimated to occur at 40 and 19 K. The strength of the exchange interaction as a function of halide separation through the linear two-bromine bridge between planes is shown to be $J \propto d^{-11 \pm 3}$ which agrees with the earlier results for the isostructural Cl_4 compounds.

Recent studies of the interplanar exchange in "eclipsed" layered compounds have shown that the superexchange through a linear two-halide bridge is surprisingly strong and that the halide-halide separation is the important parameter.[1] Typical examples of the eclipsed structure are members of the alkanediammonium series (ADA), $[NH_3(CH_2)_n NH_3]MX_4$ for $n = 2, 3, 4$, and 5 and $M = Cu$,[1-5] Mn,[6] Fe,[7] and Ni (Ref. 8) and $X = Cl$ and Br. They have been shown to be magnetically much less layeredlike owing to their eclipsed structure especially when compared with the well-studied "staggered" structure of the alkylammonium (AA) series, $(CH_{2n+1}NH_3)_2 CuCl_4$ (Refs. 9–11). Further, the superexchange through the linear two-halide bridge between the planes, J_{2h}, was found to behave as $J_{2h} \propto d_{2h}^{-10 \pm 2}$ when the halide was specifically chlorine.[1] Although a dichlorodibromo member of the group ($EDA\ CuCl_2Br_2$) has been studied,[1] no results for the pure bromides have been reported. To further test the effect of the interplanar halide separation we present data for the $n = 3$, PDA, and 4, BDA members of the pure bromide series.

These bromide compounds are isostructural with others of the ADA family. The layers consist of a puckered copper-bromine square planar lattice with the usual long and short $Cu^{2+}-Br^-$ bonds. Cu^{2+} ions lie nearly directly above one another in the so-called eclipsed arrangement allowing strong magnetic coupling via a two-halide bridge of the out-of-plane Br^- ligands. It was anticipated that replacement of Cl^- ions by Br^- ions would increase the interplanar exchange because of the increased overlap between Br^- anions.

Precession photographs indicate that the BDA $CuBr_4$ ($n = 4$) unit-cell dimensions are $a = 9.16$ Å, $b = 7.75$ Å, and $c = 7.84$ Å with $\beta = 103°$. The data are consistent with a monoclinic unit cell as found in the other $n = 4$ compound with a space group of $P2_1/c$. This leads to an interlayer separation of 8.92 Å. The cell dimensions for PDA $CuBr_4$ ($n = 3$) have

not been determined completely, however, the interlayer distance has been found to be approximately 8.60 Å. Thus the corresponding interlayer Br^--Br^- distances should be approximately 4.3 ± 0.1 and 3.8 ± 0.2 Å, respectively, assuming the bonds are nearly linear. The interlayer spacing does not increase as much as expected for BDA $CuBr_4$, indicating that the organic chain is probably buckled in a fashion similar to that described for BDA $CuCl_4$.[3] If this is the case then the Br^--Br^- distance for BDA $CuBr_4$ will be correspondingly larger than that given above. More accurate values must wait for better structural data.

Since large single crystals are not yet available the magnetic susceptibility measurements were taken on powdered samples. Figure 1 shows the results for PDA $CuBr_4$ (107.8 mg) and BDA $CuBr_4$ (94.9 mg). Susceptibility maxima occur at 44 and 19.5 K indicating that the transitions to long-range antiferromagnetic order occur at 40 ± 1 K for PDA $CuBr_4$ and 19 ± 1 K for BDA $CuBr_4$. To determine the intralayer and interlayer exchanges the high-temperature data were evaluated by using the high-temperature series expansion (HTSE) previously described.[1,2] The smooth curves through the data represent that HTSE with values of the exchange constants of $J_{1h}^{PDA}/K_B = 26 \pm 1$ K, $J_{2h}^{PDA}/k_B = -26 \pm 1$ K and $J_{1h}^{BDA}/k_B = 29 \pm 1$ K, $J_{2h}^{BDA}/k_B = -5 \pm 1$ K, where J_{1h} and J_{2h} are the intraplanar and interplanar exchanges, respectively, and k_B is the Boltzmann constant.

These values clearly show that the "dimensionality" decreases as the interlayer separation increases. This is also evident from the decreased temperature of the susceptibility maximum. This behavior is shown more dramatically in Fig. 2, where the data are plotted as inverse reduced susceptibility versus reduced temperature. The BDA data more closely resemble the behavior of a square-planar Heisenberg ferromagnet, represented by the dashed line, whereas
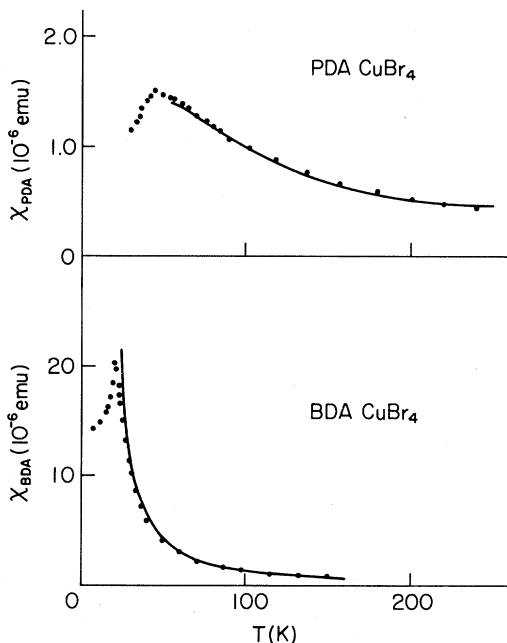
FIG. 1. Magnetic susceptibility vs temperature for BDA CuBr$_4$ (upper) and PDA CuBr$_4$ (lower). Solid lines through the data represent the high-temperature series expansion results with $J_{1h}^{BDA}/k_B = 29$ K, $J_{2h}^{BDA}/k_B = -5$ K and $J_{1h}^{PDA}/k_B = 26$ K, $J_{2h}^{PDA}/k_B = -26$ K. Not all data are shown.

the PDA data show entirely different, three-dimensional (3D)-like antiferromagnetic behavior. Again, the solid lines through the two sets of data are those given by the HTSE using the stated exchange constants.
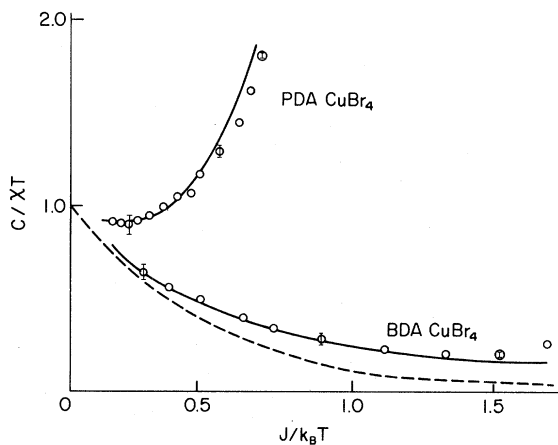
The principle reason for investigating the Br$_4$ com-

FIG. 2. Inverse reduced susceptibility vs inverse reduced temperature for PDA CuBr$_4$ (upper data points) and BDA CuBr$_4$ (lower data points). Solid curves represent high-temperature series expansions using the exchange values given in the text. Broken line represents 2D planar Heisenberg HTSE of Baker *et al.* C is the Curie constant.

pounds was to further test the importance of the halide-halide separation for two-halide superexchange and to compare the behavior caused by the *inter-planar* Br$^-$ substitution to the previous results. Even though the unit-cell dimensions are not entirely complete, the interplanar spacings and the estimations of the halide-halide separations are adequate for this purpose. It is convenient to plot the results as the natural logarithm of J_{2h}/k_B versus the natural logarithm of d_{2h} as shown in Fig. 3. The slope of a line through the data is -11 ± 3, essentially the same as the value found for the CuCl$_4$ compounds.[1] Since the slope is calculated from only the three points for EDA CuCl$_2$Br$_2$, PDA CuBr$_4$, and BDA CuBr$_4$, the results are not as compelling as for the ADA CuCl$_4$ cases particularly since the points for EDA and PDA CuBr$_4$ lie very close together. Also, the buckling of the crystal structure in BDA probably leads to a weaker exchange interaction owing to a much less linear superexchange path. This causes the slope to be steeper than if the path was completely linear. Nevertheless it is apparent that the d_{2h}^{-11} behavior of the superexchange is equally as valid for the Br$^-$-Br$^-$ bridge as for the isostructural Cl$^-$ case.

A quantitative calculation of the Cu-Br-Br-Cu superexchange has been attempted using the four-center, four-electron Rayleigh-Schrödinger exchange calculation described in Ref. 1. The calculation does reproduce the correct sign for the exchange as well as a decrease in the magnitude of the exchange progressing from the mixed EDA CuCl$_2$Br$_2$ through BDA CuBr$_4$. However, since this calculation is valid only for a 180° path (fully linear bridge) it could not be used for BDA CuBr. Recently Jansen and Block[12] have completed the more appropriate four-center six-electron calculation and found excellent quantitative agreement with the experimental results on the ADA CuCl$_4$ series. A similar application of their calculations to the pure bromide compounds will be an interesting and a useful further test of the theory.
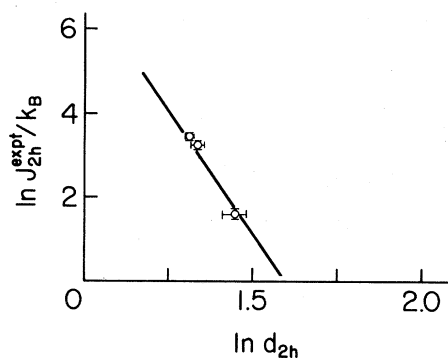

FIG. 3. Natural logarithm of the out-of-plane (two-halide) exchange vs the natural logarithm of the interhalide separation, d_{2h}, for EDA CuCl$_2$Br$_2$, PDA CuBr$_4$, and BDA CuBr$_4$. The slope of line through the data is -10 ± 3.

Measurements have also been made on EDA $CuBr_4$ ($n = 2$). Preliminary results of the analysis of these data indicate different behavior from the other members of the series possibly owing to the expected strong effect of the Br^- substitution. These data will be presented elsewhere, however, it is apparent that the much increased exchange coupling of the bromides is of considerable importance in this crystal and its magnetic behavior.

An interesting feature of the *intra*layer superexchange interaction is also revealed by comparison of the Cl_4 and Br_4 compounds. Since the Br^- provides a stronger superexchange path than the Cl^- there is expected to be increased *intra*layer exchange through the single-halide Jahn-Teller distorted path for this bromide series at similar intraplane Cu^{2+}-Cu^{2+} distances. However, the increase appears to be somewhat greater than that which is seen in the AA series when a comparison is made between the Cl_4 and Br_4 compounds.[10] In the AA series the intralayer exchange ratio between Br^- and Cl^- varies from about 1 to 1.3 for $n = 2-5$. This ratio is closer to 1.9–2 for the ADA series for the same values of n. The reason for this discrepancy is not obvious, but may be related to the fact that different HTSE were used in the two cases; those used to fit the AA series have ten terms[13] whereas those used for the ADA series have

only five. The fewer number of terms available for the ADA case limits applicability of the five-term expansion in the low-temperature range, but it does not limit its usefulness at higher temperatures. Unfortunately, there are few other analogous series for which a comparison of the single-halide "replacement ratio," can be made to see if there is a physical reason for the behavior seen in the AA and ADA compounds. A possible explanation may be that additional "buckling" of the Cu-Br layer causes a less linear Cu^{2+}-halide-Cu^{2+} exchange path, thus strongly affecting the behavior,[14] but unfortunately, this cannot be determined from only the cell dimensions. Calculations by Jansen and Block[15] indicate that the out-of-plane anions play an important role in the strength and sign of the in-plane exchange so it certainly may be important to consider a "coupling" between the two directions. A more careful study of these intralayer exchange effects will have to await a complete determination of the crystal structure.

ACKNOWLEDGMENTS

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