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Contribution from the Istituto di Teoria e Struttura Elettronica e Comportamento Spettrochimico
dei Composti di Coordinazione del CNR, Area della Ricerca di Roma, 00016 Monterotondo Stazione, Italy

Zero-Field Magnetic Susceptibility Study of the Magnetic Phase Transition in the Two-Dimensional Ionic Ferromagnet Bis(benzylammonium) Tetrabromochromate(II), $(C_6H_5CH_2NH_3)_2CrBr_4$[1]

Carlo Bellitto,* Pasquale Filaci, and Salvatore Patrizio

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Bis(benzylammonium) tetrabromochromate(II), $(C_6H_5CH_2NH_3)_2CrBr_4$, has been synthesized and characterized. The compound is a new example of the two-dimensional (2-D) ionic ferromagnet adopting a layered perovskite structure. The three-dimensional magnetic order, T_c, has been determined by ac magnetic susceptibility measurements, and it has been found to be 52.0 ± 1 K. The observed Curie temperature is 15 K higher than that found in the corresponding bis(benzylammonium) tetrachlorochromate(II). The static magnetic susceptibility above the Curie temperature has been fitted to a high-temperature series expansion for a square 2-D Heisenberg lattice to give the near-neighbor exchange constant $J/k = 13.1$ K and $g = 2.00$. The critical behavior of the title compound has been studied by magnetization and ac magnetic susceptibility measurements. The critical exponent β, which describes the temperature dependence of the reduced magnetization, is 0.23 in the temperature range $8 \le T \le 39$ K and ca. 0.50 as T_c is approached. The critical exponent γ, describing the divergence of the initial susceptibility, is not unique in the temperature range studied, thus suggesting there is a crossover from 2-D to 3-D behavior.

Introduction

Recently, we have synthesized and studied several organic-intercalated tetrachlorochromate(II) salts of the type $(RNH_3)_2CrCl_4$, where R is an alkyl group, and we have found that they order ferromagnetically between 37 and 42 K.[2] These compounds are interesting mainly for the following reasons: (i) They are some of the few examples of ionic insulators that show ferromagnetic interactions.[3] (ii) They have a layered-perovskite crystal structure, and their ferromagnetic properties are essentially two-dimensional (2-D).[2,4] (iii) They are transparent in the visible region except for two very intense and narrow spin-forbidden absorption bands that have been shown to be exciton-magnon combination bands.[5,6]

With the aim of finding and characterizing new ferromagnets, we thought it was worthwhile to study the corresponding bromide derivatives. Several tetrabromochromate(II) salts have been reported previously, but the magnetic properties were not studied in detail.[7]

In this paper we report the synthesis of the title compound and present a magnetic study of this compound by static and dynamic magnetic susceptibility measurements.

Experimental Section

Elemental analyses were performed by Malissa & Reuter Mikroanalytische Laboratorium, Elbach, West Germany. Benzylammonium bromide was prepared by direct reaction of benzylamine in ethanol and HBr gas. On cooling, a white microcrystalline product separated. The compound was recrystallized from the same solvent. Since the Cr(II) compound is very sensitive to air and moisture, the synthesis and all the manipulations were carried out by Schlenk techniques under O_2-free nitrogen.[8] All reactions involving noxious reagents (benzylamine) or corrosive and irritant substances such as hydrogen bromide and glacial acetic acid must be carried out in a well-ventilated fume hood.

Preparation. To a hot solution of Cr(II) in glacial acetic acid, prepared by passing HBr gas through a suspension of finely divided electrolytic Cr metal, was slowly added a stoichiometric quantity of benzylammonium bromide in the same solvent. On cooling, yellow plates of bis(benzylammonium) tetrabromochromate(II) were isolated. anal. Calcd for $C_{14}H_{20}N_2CrBr_4$: C, 28.61; H, 3.40; N, 4.76; Cr, 8.85; Br, 54.38. Found: C, 28.32; H, 3.42; N, 4.68; Cr, 8.65; Br, 54.08.

X-ray Powder Diffraction. The polycrystalline sample was sealed under N_2 in a Lindemann tube, i.d. 0.3 mm, and diffraction patterns were collected with a Philips Debye–Scherrer camera (Ni-filtered Cu Kα radiation).

Magnetic Susceptibility Measurements. (a) Static magnetic susceptibility measurements in the temperature range 4.2–250 K were performed by using a Faraday apparatus described elsewhere.[9a] The polycrystalline sample was placed inside a quartz sphere, sealed under N_2, with a drop of glue, and suspended by a fine silica wire from a Sartorius electronic vacuum microbalance. The magnetic field and the gradient were supplied by two superconducting solenoids. The magnetization measurements were made at field strengths up to 5 T. Temperature measurements were based on a calibrated Au, 0.03% atomic Fe vs. chromel thermocouple in a liquid-He bath and on gallium arsenide diode.

(b) The ac magnetic susceptibility was measured in the temperature range 4.2–100 K with a mutual inductance setup described in ref 9b. The frequency of the ac field was 198 Hz. The absolute susceptibility calibration was made by reference to a standard sample of $Hg(Co(NCS)_4)$. The measurements reported below were corrected for diamagnetism as calculated from the known diamagnetic susceptibility of the constituents of $(C_6H_5CH_2NH_3)_2CrBr_4$; we used the value of -2.73×10^{-4} emu/mol. A correction for the diamagnetic effect of the sample holder was also applied. Another correction to the data arises from the temperature-independent susceptibility χ_{tip}. This correction was calculated from the usual expression by assuming that, with O_h symmetry for Cr(II) ($S = 2$), the ^5D splits to yield the ^5E_g ground state:

$$\chi_{tip} = 4N_a\mu_B^2/10Dq$$

where 10Dq = 9200 cm^{-1} from the electronic spectrum.

Results

Bis(benzylammonium) tetrabromochromate(II), $(C_6H_5CH_2NH_3)_2CrBr_4$, has been synthesized for the first time and by a more convenient method by using an apparatus described previously.[10] Tetrabromochromate(II) complexes have been previously synthesized by mixing stoichiometric quantities of $CrBr_2$ and the appropriate alkylammonium bromide.[7] We have found that finely divided electrolytic chromium metal dissolves in glacial acetic acid, when HBr gas is passed through the solvent under reflux. The stoichiometric addition of the benzylammonium bromide to the

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Table I. Powder X-ray Diffraction Data[a]

h	*k*	*l*	$\sin^2 \theta$ (obsd)	intens	$\sin^2 \theta$ (calcd)
0	0	4	0.009 021	vs	0.009 019
			0.009 354		
			0.016 812		
1	1	1	0.019 610	vs	0.020 286
0	0	6	0.020 097	vs	0.020 293
1	1	2	0.021 720	w	0.021 977
1	1	3	0.024 069		
			0.024 742	s	0.024 796
1	1	4	0.028 24	w	0.025 742
1	1	5	0.033 68	s	0.033 815
0	0	8	0.037 73	m	0.036 077
2	0	0			0.039 480
			0.039 918	m	
1	1	6			0.040 016
1	1	7	0.046 478	s	0.047 344
2	0	4			0.047 499
0	2	4	0.048 707	s	0.049 429
			0.053 31	w	
0	0	10	0.056 598		0.056 371
2	0	6	0.060 380	s	0.058 773
0	2	6			0.060 703
1	1	9	0.067 42		0.065 383
2	0	8	0.069 85		0.074 557
2	2	0	0.077 14	s	0.078 890
2	2	2			0.081 145
0	0	12	0.080 43	s	0.081 874
2	2	3	0.083 298	m	0.083 963

[a] Unit-cell parameters are given in the text.

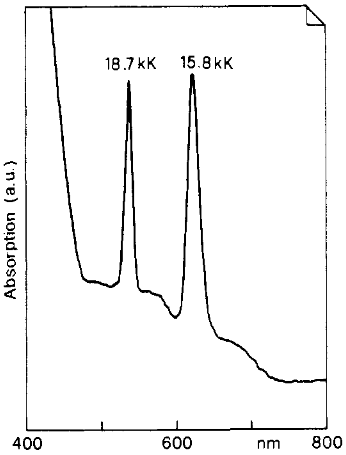

Figure 1. Room-temperature diffuse reflectance spectrum of $(C_6H_5CH_2NH_3)_2CrBr_4$.

solution then gave yellow plates on cooling. The compound has been characterized by elemental analysis and X-ray powder diffraction. The X-ray powder photographs could be indexed in the space group *Cmca* (D_{2h}^{18}), the same as that of the corresponding tetrachlorochromate(II) salts.[2] The results are reported in Table I. The values of the unit-cell parameters, obtained by the least-squares method, are $a = 7.8_6$ Å, $b = 7.6_7$ Å, and $c = 32.4_7$ Å. Attempts to determine the crystal structure by the single-crystal diffraction method failed due to the fact that the crystals under X-ray exposure were reduced to powder.

Electronic Spectra. The diffuse electronic reflectance spectrum of the title compound, reported in Figure 1, is characterized by two sharp spin-forbidden bands in the visible region at 18.700 and 15.800 cm^{-1} and by a broad band in the near-IR region, with a maximum at 9200 cm^{-1}. This is characteristic of a six-coordinated Cr(II) complex, thus confirming that we are in the presence of layers of octahedral $[CrBr_6]^{2-}$ linked into a square array by sharing equatorial bromide ions.[11] The most remarkable feature of the optical spectrum is represented by the two intense narrow spin-forbidden bands, observed previously in the corresponding tetrachlorochromate(II) compounds and assigned as "hot exciton–magnon" combination bands.[5] These bands appear at the same frequency as observed in tetrachlorochromate(II) complexes, suggesting that we are in the presence of pure spin-flip transitions.

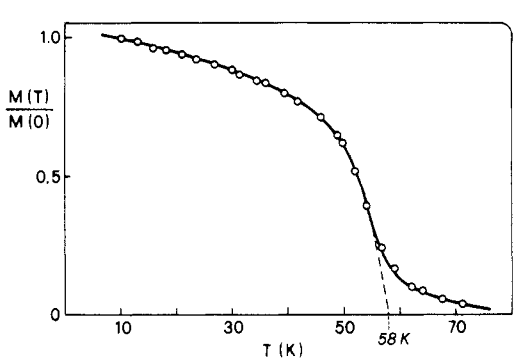

Figure 2. Reduced magnetization vs. temperature plot for $(C_6H_5CH_2NH_3)_2CrBr_4$.

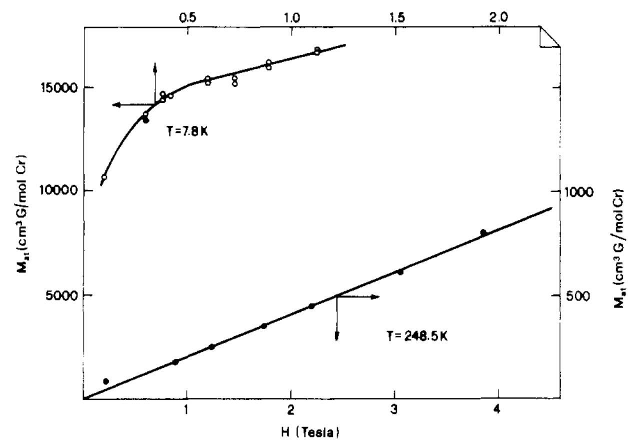

Figure 3. Magnetization vs. field plot at 8 K (well below T_c) and at 249 K (well above T_c).

Magnetic Properties. (a) High-Temperature Susceptibility. From ca. 100 K to room temperature the magnetic susceptibility follows the Curie–Weiss law: $\chi = C/(T - \Theta)$ with Curie C and Weiss Θ constants of 3.67 emu K/mol and 77 K, respectively. The positive value of Θ indicates predominant ferromagnetic exchange interactions. From the Curie constant, the corresponding effective moment μ_{eff} is 5.4 μ_B, well above the spin-only value, i.e. 4.90 μ_B for the Cr(II) ion (high-spin d^4 configuration). The experimental data above 50 K were analyzed in terms of the high-temperature series expansion method for an $S = 2$, 2-D square Heisenberg ferromagnet as modified by Lines[12] with the exchange Hamiltonian $H = -J\hat{S}_1 \cdot \hat{S}_2$:

$$Ng^2\mu_B{}^2/\chi = \tfrac{1}{2}k_BT + J(-4 + 9x - 9.072x^2 + 55.728x^3 - 160.704x^4 + 116.604x^5) \quad (1)$$

where $x = J/k_BT$ and g is the Landé factor. The best values of the nearest-neighbor ferromagnetic exchange constant J/k_B and of g were found to be $J/k_B = 13.1$ K and $g = 2.00$.[1]

(b) Low-Temperature Magnetization. The reduced magnetization m ($m = M(T)/M(0)$) vs. temperature plot for the title compound is shown in Figure 2. The curve shows rounding above the spontaneous ordering temperature T_c, which is characteristic of low-dimensional magnets. The external applied field, i.e. 920 Oe, introduces an uncertainty in the location of T_c. A reasonable estimate would be 58 K. We shall compare this value with that found by the ac mutual inductance technique (see below). The magnetization vs. field plots, at two different temperatures, have been recorded and are reported in Figure 3. The plot at $T =$

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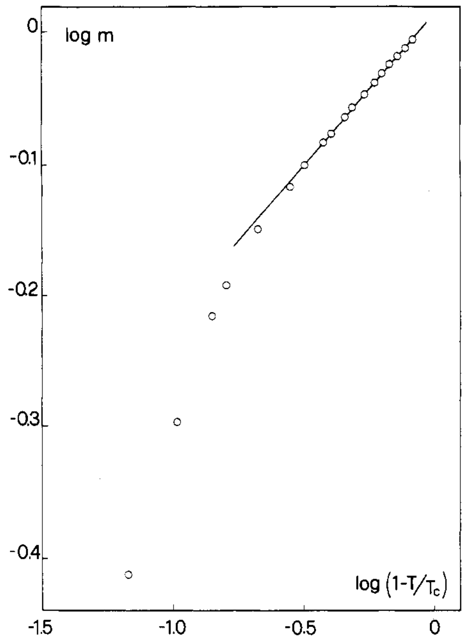

Figure 4. Logarithmic dependence of the reduced magnetization on reduced temperature $t_- = 1 - (T/T_c)$. Solid line is a least-squares fit.

249 K, well above T_c, confirms that all the spins are in the paramagnetic state. The experimental values fit the magnetization:

$$M = \frac{Ng^2\mu_B{}^2S(S+1)}{3k_B(T-\Theta)}H \qquad (2)$$

for $S = 2$, $g = 2.1$, and $\Theta = 77$ K. The second one, at $T = 7.8$ K, well below T_c, shows that the compound does not saturate completely at fields up to 1.5 T.

The spontaneous magnetization $M(0)$, at $T = 0$ K, has been approximated to M at $T = 4.2$ K and $H = 920$ Oe.

Critical Behavior of the Magnetization. The reduced spontaneous magnetization m can be fitted to a power law:

$$m = B(t_-)^\beta \qquad (3)$$

where $t_- = 1 - (T/T_c)$ and β is the critical exponent. A plot of log m vs. log t_- therefore has a gradient of β. The value of T_c was assumed to be 58 K, as estimated from Figure 2. Such a plot is shown in Figure 4. In this figure we can identify two straight lines: the first one of slope 0.23 for 39 K $\leq T \leq$ 8 K and the second one, less defined, of slope 0.5 as T_c as approached. A definite change of β is observed.

Zero-Field Susceptibility. The ac magnetic susceptibility (ν = 198 Hz) of the title compound is reported in Figure 5. The susceptibility features a sharp peak at 52 ± 1 K (no out-of phase χ'' was detected). One usually expects for a ferromagnet that the ac susceptibility remains constant below the ordering temperature T_c because of the demagnetizing effect and the initial $\chi_m{}^0$ goes to infinity. The susceptibility decreases steeply below T_c compared to what has been observed recently in the corresponding ferromagnetic bis(benzylammonium) tetrachlorochromate(II).[2b] A similar behavior has been observed in $NdH_{1.99}$, a ferromagnet with $T_c = 5.6$ K, and this has been ascribed to a single-domain powder sample or a multidomain sample with significant hysteresis.[13] Here, the decrease of the susceptibility is mainly due to the former effect. The divergence of the initial susceptibility in the high-temperature side of the susceptibility peak can be fitted to a function of the form[14,15]

$$\chi_0 = \Gamma(t_+)^{-\gamma} \qquad (4)$$

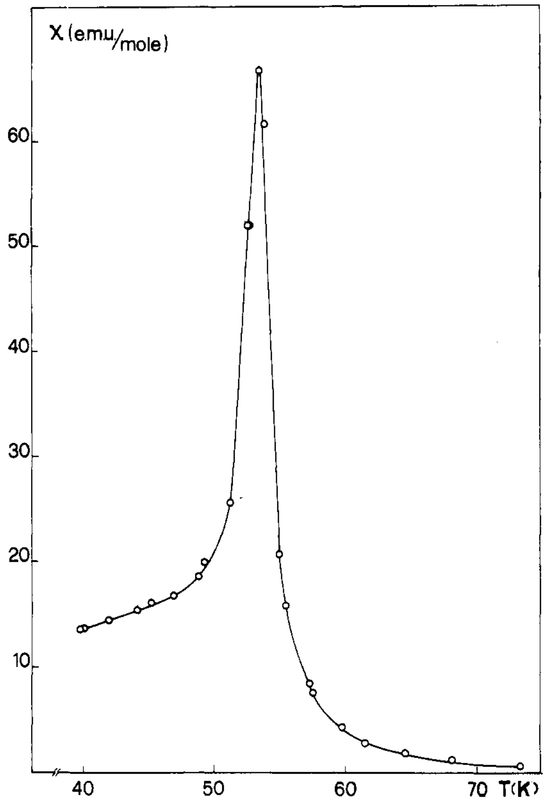

Figure 5. Ac magnetic susceptibility of $(C_6H_5CH_2NH_3)_2CrBr_4$ from 30 to 80 K.

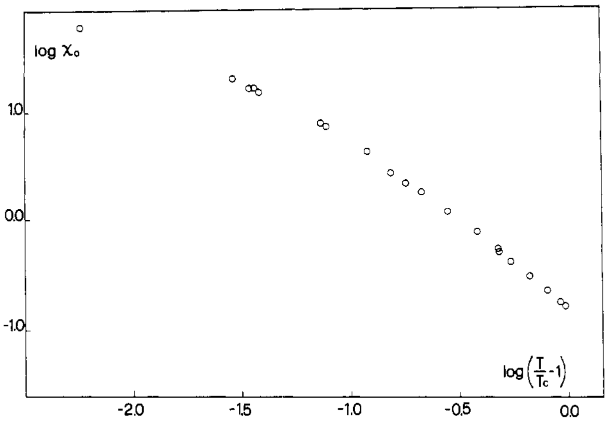

Figure 6. log–log plot of initial susceptibility χ the reduced temperature $t_+ = (T/T_c) - 1$.

where t_+ is the reduced temperature $(T - T_c)/T_c$ and γ is the critical exponent. The susceptibility has been plotted as log χ_0 as a function of log t_+, i.e. log $((T/T_c) - 1)$. T_c is the experimentally observed transition temperature. From Figure 6 a systematic decrease of γ on approaching T_c can be observed.

Discussion

Bis(benzylammonium) tetrabromochromate(II) has been synthesized and characterized. It crystallizes as yellow platelets, and although the complete crystal structure is unknown, the X-ray powder diffraction data suggest that the crystal structure is similar to that of the layered perovskite compounds of formula $(RNH_3)_2MX_4$ (R = alkyl group; M = Cd, Mn, Cu, X (halide)), where the full structure has been solved.[16] This crystal structure is also confirmed by the high-temperature magnetic susceptibility measurements and by electronic spectra. The susceptibility vs. temperature plot could in fact be fitted by a series-expansion

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Table II. Magnetic Parameters and Interlayer Spacings of $(RNH_3)_2CrX_4$ (R = Alkyl Group; X = Cl, Br)

compd	T_c/K^a	$(J/k_B)/K$	Θ/K	T_c/Θ	k_BT_c/J	interlayer spacing/Å	ref
$(CH_3NH_3)_2CrCl_4$	42.0	13.0	59	0.71	3.23	9.44	2b
$(C_2H_5NH_3)_2CrCl_4$	41.0	10.1	58	0.71	4.06	10.71	2b
$(C_3H_7NH_3)_2CrCl_4$	39.5	9.3	57	0.69	4.25	12.35	2b
$(C_6H_5CH_2NH_3)_2CrCl_4$	37.0	10.6	58	0.64	3.49	15.71	2b
$(C_6H_5CH_2NH_3)CrBr_4$	52.0	13.1	77	0.68	3.97	16.24	this work

[a] From SQUID and ac mutual inductance technique.

equation valid for a 2-D square Heisenberg ferromagnet.[12] The near-neighbor exchange constant is positive, and therefore the exchange is ferromagnetic. This can be explained by assuming the presence of distorted Cr(II) octahedra, due to the cooperative Jahn–Teller effect, in a way similar to that found in Rb_2CrCl_4.[17,18] In the latter, the $[CrCl_6]$ octahedra are tetragonally elongated and the four-fold axis of adjacent octahedra are along the [011] and $[0\bar{1}1]$ directions of the *Cmca* unit cell. The ferromagnetic exchange can be understood, because the Jahn–Teller effect constrains the unpaired e_g electron of Cr^{2+} to the d_{z^2} orbital and allows superexchange via bridging bromide anions between a half-filled d_{z^2} orbital on one Cr^{2+} ion and the empty $d_{x^2-y^2}$ orbital of its neighbors. This antiferrodistortive ordering of the elongated intraplanar Cl–Cr–Cl bond produces two sublattices with orthogonal single-ion anisotropies and gives an alternate canting of the spins with respect to the easy [110] direction. The incomplete saturation observed in the magnetization vs. field curve may be an indication that a spin-canted structure is present. The value of the exchange constant J/k is comparable with that found in bis(methylammonium) tetrachlorochromate(II) and higher than that found in the corresponding bis(benzylammonium) tetrachlorochromate(II); see Table II. In the first term of these organic-intercalated salts, i.e. $(CH_3NH_3)_2CrCl_4$, the Cl–Cr···Cl bond angles within the basal plane are close to 180° (i.e. 166°);[4] therefore, a small antiferromagnetic contribution to the superexchange is present, because the half-filled d_{z^2} and the empty $d_{x^2-y^2}$ are not completely orthogonal. As previously reported,[2b] in $(C_6H_5CH_2NH_3)_2CrCl_4$ the J constant is lower compared with that in $(CH_3NH_3)_2CrCl_4$, thus suggesting that a more distorted crystal structure (e.g. with the octahedra tilted with respect to one another) is present.

To explain the observed higher value of J in the title compound we can assume that the crystal structure is the same as that of the corresponding tetrachlorochromate(II) and the ferromagnetic intralayer exchange contribution of the bromide ion is larger because of the larger extension of the bromide valence electron shell. The existence of a finite transition temperature T_c in 2-D Heisenberg ferromagnets can be explained if it recalled that the system is not ideal.[19] The interplanar exchange and the anisotropy are, in fact, essential for establishing long-range order. The apparent discrepancy in the determination of the Curie point from the Faraday method compared with that of the mutual-inductance techniques is due to that fact that an external applied field is used in the former. The Curie point is smeared out and the $M(T)$ curve shifts toward higher temperatures.

From Table II, an increase in T_c determined with the same technique is observed on moving from the chloride derivatives to the bromide one. The main contribution to the determination of the magnetic phase transition temperature T_c is J'/J, i.e. the ratio of the interplanar exchange J' to the intraplanar J. This can be ascribed to a better overlap and greater polarizability of the bromide ion, which results in a more effective –Cr–Br···Br–Cr– exchange. Indeed, if we compare the values of T_c and the intralayer exchange J values of $(CH_3NH_3)_2CrCl_4$ with those of the title compound, we conclude that J' in the latter should be definitely higher.

A quantitative contribution of the interplanar exchange constant J' and of the planar anisotropy can be ascertained only by a single-crystal magnetic measurements. A similar trend in the variation of T_c has also been observed recently in $Rb_2CrCl_xX_{4-x}$ ($x = 1, 2$; X = I, Br).[20] Finally, a brief comment on the critical properties is presented. The spontaneous magnetization obeys a power law over a wide range of temperatures, below T_c. The observed value of 0.23 lies between the predicted values for 2-D Ising (i.e. 0.125) and 3-D Ising (i.e. 0.312) models[21] and is similar to the values for 2-D XY compounds such as K_2CuF_4 (i.e. 0.22).[22] The fact that the critical exponent γ, obtained from the initial susceptibility vs. the reduced temperature t_+ plot, is not unique, suggests there is a crossover from 2-D to 3-D behavior.[21]

Further experiments are in progress in order to ascertain the nature of this crossover.

Registry No. $(C_6H_5CH_2NH_3)_2CrBr_4$, 102629-61-8.

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