Lattice-Dimensionality Crossover Effects in Quasi-d-Dimensional Magnetic Materials

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We show that lattice-dimensionality crossover phenomena may be usefully analyzed by expansions in $R \equiv J'/J$, where J and J' are the interaction constants in d and $3-d$ lattice directions ($d=1$ or 2). The nature of the crossover phenomena is predicted to depend on the thermodynamic function considered, on sgnJ', and on sgn$J$. Comparison with experiment confirms our predictions, and we present the first unambiguous experimental demonstration of crossover in the ferromagnetic susceptibility.

Quasi-d-dimensional magnetic systems,[1] consisting of arrays of nearly isolated chains ($d \cong 1$) or layers ($d \cong 2$), can be described as having couplings J between z nearest neighbors in d lattice directions, and $J' \equiv RJ$ between z' nearest neighbors in the remaining $3-d$ directions.[2] If we replace quantum-mechanical spin operators by n-component unit vectors,[3] then we may take for the interaction Hamiltonian

$$\mathcal{H}(R) \equiv -J\sum_{\langle ij\rangle}{}^{(d)}\vec{S}_i^{(n)}\cdot\vec{S}_j^{(n)} - RJ\sum_{\langle ij\rangle}{}^{(3-d)}\vec{S}_i^{(n)}\cdot\vec{S}_j^{(n)}, \qquad (1)$$

where the angular brackets denote nearest-neighbor pairs of sites, and the first summation is over pairs of spins in d lattice directions while the second is over pairs of spins in the remaining $3-d$ lattice directions.

Intuitively, one expects such systems to be largely d dimensional in character for $T \gg T_c(R)$, since only as $T \to T_c(R)$ will the correlations arising from the weaker interaction J' become manifest. A crossover from d-dimensional to three-dimensional behavior "should" occur at some $T^\times(R)$. However some experiments show d-dimensional behavior even for T extremely close to T_c, while others show $d=3$ behavior well above T_c already. Here we seek to understand these data by examining general features of thermodynamic functions $f(R,T)$ as $T \to T_c(R)$; we show that the observability of a lattice-dimensionality crossover depends strongly on the function f, on sgnJ', and on sgn$J$. We also present new data that provide the first unambiguous demonstration of crossover in the ferromagnetic susceptibility.

(I) *Dependence on function $f(R, T)$.*—A necessary condition for detecting a crossover as $T \to T_c(R)$ is that deviations of a measured function $f(R,T)$ from $f(0,T)$ exceed the experimental resolution. Since $f(R,T)$ is analytic for $T \neq T_c(R)$, we may write $f(R,T) = f(0,T) + f^{(1)}(0,T)R + O(R^2)$, where $f^{(1)}(R,T) \equiv \partial f(R,T)/\partial R$. Then $\Delta f(R,T) \equiv [f(R,T) - f(0,T)]/f(0,T) = Rf^{(1)}(0,T)/f(0,T) + O(R^2)$; for sufficiently small R, we may truncate at $O(R)$, and solve for the temperature $T^\times(R)$ at which Δf becomes detectable. If $f(R,T)$ denotes either the magnetization $M(H,R,T)$ or the isothermal susceptibility $\bar{\chi}(H=0,R,T)$, then[2] $f^{(1)}(0,T) = z'(J/kT)f(0,T)\bar{\chi}(0,T)$, where $\bar{\chi} \equiv \chi/\chi_{\rm Curie} = \chi T/C$ (C is the Curie constant); hence[4]

$$\Delta f(R,T) = z'(J/kT)R\bar{\chi}(0,T) + O(R^2). \qquad (2)$$

For the specific heat $C_H(H=0,R,T)$, on the other hand, one has[2]

$$\Delta f(R,T) = O(R^2),$$

so that, for a given material, one would expect $T^\times(R)$ to be larger for M and $\bar{\chi}$ than for C_H.[5]

(II) *Dependence on* sgnJ'.—From (2) we see that sgnΔf = sgnJ', so that a ferromagnetic or antiferromagnetic interaction J' will result in an increase or decrease, respectively, of the function $f(R,T)$ with respect to $f(0,T)$. However for $C_H(R,T)$, Δf is independent of sgnJ'.

(III) *Dependence on* sgn$J$.—The function $\bar{\chi}(R=0,T)$ in (2) depends strongly on sgn$J$. For $J>0$, $\bar{\chi}(0,T)$ diverges at some $T_c(0)$ which, for small R, should be only slightly smaller than $T_c(R)$, so that the fractional deviation $\Delta f(R,T)$ will become very large as $T \to T_c(R)$.[6] For $J<0$, however, $\bar{\chi}(R=0,T)$ remains finite and small-valued for all T; replacing $\bar{\chi}$ in (2) by the "upper bound" $\bar{\chi} = T/2\theta$ [$\theta \equiv zS(S+1)J/3k$], we get $\Delta f < [3z'/2zS(S+1)]R$. Thus $\Delta\bar{\chi} \cong R$, so that for $R \lesssim 10^{-2}$, it will be virtually impossible to detect a crossover in $\bar{\chi}$ or M.

Although these results are, strictly speaking, valid only for the classical Hamiltonian (1), we expect them to be qualitatively correct also for quantum systems.[4,5] We now show that this analysis provides a useful framework within which to explain the following hitherto unclear experimental results on quasi-d dimensional materials.

(a) χ for $J<0$ ($d\cong 1$ or 2): Although many experiments exist on $d\cong 1$ and $d\cong 2$ antiferromagnets, with $10^{-6}<|R|<10^{-2}$, lattice-dimensionality crossovers have not been detected in $\bar{\chi}$. For example, (i) for K_2CoF_4 and Rb_2CoF_4 ($d\cong 2$, $n\cong 1$), good agreement between $\bar{\chi}$ and $d=2$ theory has been found for $0<T<1.5T_c$ (thus *including* T_c)[1,7]; (ii) for K_2MnF_4 and Rb_2MnF_4 ($d\cong 2$, $n\cong 3$), $\chi_\parallel$ and $\chi_\perp$ are well-described at low T by spin-wave theory for a $d=2$ antiferromagnet with small spin-space anisotropy.[1,8] For $T\gtrsim T_c$, the data agree with high-T series for $d=2$, $n=3$.[1]

(b) χ for $J>0$ ($d\cong 2$): Contrariwise, χ data on the $d\cong 2$ Heisenberg ferromagnets $(C_lH_{2l+1}NH_3)_2CuCl_4$ ($l=1,2,\ldots,10$) exhibit clear lattice-dimensionality crossover as $T\to T_c(R)^+$, even though $|R|$ is as small as 10^{-4}–10^{-6}.[1,9-11] For example, Fig. 1 displays $\bar{\chi}_\parallel$ for $l=1$ ($R_1\cong +5.5\times10^{-5}$), $l=2$ ($R_2\cong -8\times10^{-4}$), and $l=3$ ($R_3\cong -6\times10^{-5}$). Also included are very recent data[12] on K_2CuF_4 ($R\cong +2.1\times10^{-4}$).[13] For $t\equiv kT/J>0.8$, all data are found to agree with high-T series ($d=2$, $n=3$).[14] For lower t, the series prediction becomes increasingly unreliable; however, the data for $l=1$–3 still coincide for $t\gtrsim 0.40$, and the data for $l=1$, 3 for $t\gtrsim 0.26$. In accord with point (II) above, the deviations for materials with $J'>0$ and with $J'<0$ are upward and downward, respectively. To test (2) quantitatively, we relate the temperature $t_2^\times\cong 0.40$ at which $\bar{\chi}$ for $l=2$ deviates from the common $l=1$, 3 curves ($R_1\cong|R_3|\cong 0.07\times|R_2|$), and the temperature $t_1^\times\cong 0.255$ at which the $l=1$, 3 curves deviate from each other. If $\Delta f(R,T)$ has about the same value when we perceive a deviation in Fig. 1, then from (2)

$$|R_1|\bar{\chi}(R=0,t_1^\times)/t_1^\times=|R_2|\bar{\chi}(R=0,t_2^\times)/t_2^\times. \qquad (3)$$

Equation (3) is roughly obeyed, since $R_1\bar{\chi}(0,t_1^\times)/t_1^\times\cong 0.13$ and $|R_2|\bar{\chi}(0,t_2^\times)/t_2^\times\cong 0.040$. The source of the discrepancy is that for $\bar{\chi}(0,t^\times)$ we have used the experimental values [$\bar{\chi}(0,t_1^\times)\simeq 600$, $\bar{\chi}(0,t_2^\times)\simeq 20$], which are largely affected by the small spin-space anisotropies; their influence is clearly evidenced by the curve for K_2CuF_4.[11] Noting from Fig. 1 that for $l=1$, the crossover occurs at $\bar{\chi}\cong 10^3$, we show in Fig. 2 that at *just* this value of $\bar{\chi}$ there occurs a "kink" in the log-log plot of $\bar{\chi}$ versus $1-T_c/T$, and the critical exponent γ changes from a $d=2$, $n=1$ value of 1.75 to a $d=3$, $n=1$ value of 1.25. (This kink cannot be due to a "smearing out"[15] of T_c since the error in T_c is negligible at the crossover point.)

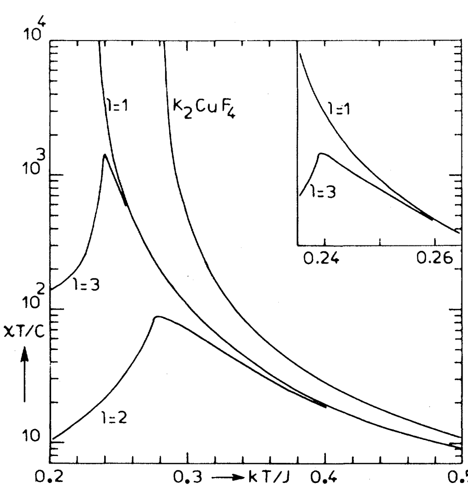

FIG. 1. $\bar{\chi}_\parallel$ corrected for demagnetizing effects, for $(C_lH_{2l+1}NH_3)_2CuCl_4$ ($l=1,2,3$) and for K_2CuF_4 (see Ref. 12).

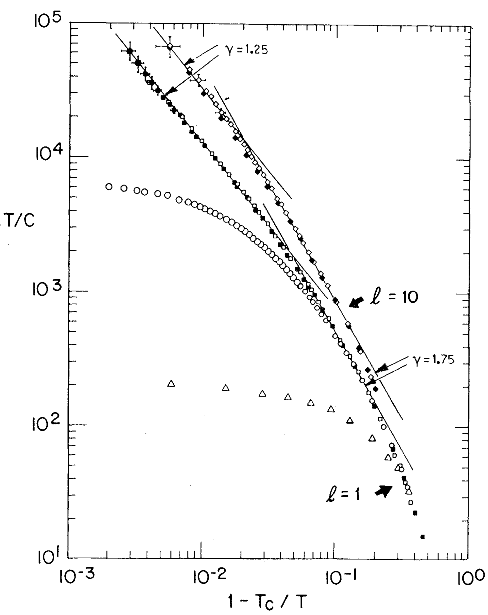

FIG. 2. $\bar{\chi}_\parallel$ for $l=1$ ($T_c=8.903\pm0.003$ K) and $l=10$ ($T_c=7.92\pm0.01$ K); the open and closed symbols indicate measurements made on two different samples of each material. The circles and triangles are data for the next-preferred and hard axes, respectively ($l=1$). Uncertainties in T_c and in demagnetizing corrections are indicated by horizontal and vertical bars, respectively.

The same crossover phenomenon is observed for $l=10$, but at a value of $\bar{\chi}$ about 10–20 times larger, in accord with the fact that $R_{10} \cong -3 \times 10^{-6}$ is smaller than R_1. The prediction that the crossover point for $\bar{\chi}$ is determined by the product $|R|\bar{\chi}(t^{\times})/t^{\times}$ is again roughly confirmed, since $|R_{10}|\bar{\chi}(t_{10}^{\times})/t_{10}^{\times} \cong 0.10$ [with $t_{10}^{\times} \cong 0.23$, $\bar{\chi}(t_{10}^{\times}) \cong 8000$].[1] A somewhat different analysis was given in Ref. 10.

(c) C_H ($d \cong 1, 2$): Clear evidence for lattice-dimensionality crossover is also found in C_H studies on $d \cong 1$ compounds[1] and $d \cong 2$ Heisenberg ferromagnetics,[10,16] since here the crossovers appear as small λ-type anomalies ($d=3$ divergences), superposed upon smooth, *nondivergent* contributions of the ideal ($R=0$) systems. Empirically, the energy stored in the λ anomaly is often small and decreases rapidly with $|R|$.[10,16] The prediction[5] [point (I) above] that $T^{\times}(R)$ will be larger for $\bar{\chi}$ than for C_H is confirmed, e.g., in the $l=2$ copper compound: Whereas $\bar{\chi}$ is affected for $T \lesssim 1.6T_c$ (Fig. 1), there is no effect of R on C_H for $T \gtrsim 1.2T_c$.[10]

(d) M for $J<0$ ($d \cong 1$): Magnetization data in fields up to saturation, and at temperatures above, at, and below $T_c(R)$ have recently been obtained[17] on $Mn(N_2H_5)_2(SO_4)_2$ ($d \cong 1$, $n \cong 3$, and $|R| \cong 10^{-2}$). For all T, agreement with the calculated $d=1$ behavior was found, there being no apparent indications of crossover.[17]

(e) M for $J>0$ ($d \cong 2$): By contrast, magnetization data for $T \leqslant T_c$ for $(C_2H_5NH_3)_2CuCl_4$ ($d \cong 2$, $n \cong 3$, and $R \cong -8 \times 10^{-4}$) show the characteristics expected for a $d=3$ ordered antiferromagnetic array of ferromagnetic layers.[18,9]

(f) $\tilde{M}_s$ for $J<0$ ($d \cong 2$): The spontaneous *staggered* magnetization, $\tilde{M}_s \equiv \tilde{M}(\tilde{H}=0, R, T)$,[2,4] for the antiferromagnets K_2NiF_4, and Rb_2MnF_4 ($d \cong 2$, $n \cong 3$) has been studied by NMR[19] in the spin-wave region and by neutron scattering[15,20-21] in the critical region. At all measured T, $d \cong 2$ behavior is observed, even though $T_c(R)$ was approached as closely as $1-T/T_c \cong 3.3 \times 10^{-4}$ for K_2NiF_4.[21] However, the "order" below $T_c(R)$ is definitely $d \cong 3$ (e.g., in the neutron experiments $\tilde{M}_s$ is derived from a $d=3$ *Bragg peak*). That, nevertheless, $\tilde{M}_s$ shows essentially a $d=2$ exponent ($\beta \simeq \frac{1}{8}$) can be understood from (1), realizing that $|R| \leqslant 10^{-6}$ for these materials. Very recently, $\tilde{\chi}$ for K_2XF_4 (X = Ni or Mn) has been measured for $T > T_c$,[22] and $d \cong 2$ behavior ($\gamma \simeq 1.75$) is observed down to $1-T_c/T \cong 0.01$, with no sign of crossover yet. Also, in K_2XF_4 small spin-space anisotropies (0.2–0.4%) cause the critical behavior of $\tilde{M}_s$ and $\tilde{\chi}$ to be $d \cong 2$ Isinglike. Comparing $\tilde{\chi}$ for K_2XF_4 with $\bar{\chi}$ for the $l=10$ Cu salt ($|R_{10}| \cong 3 \times 10^{-6}$, $1-T_c/T^{\times} \cong 0.02$), we expect from (2) the crossover for K_2XF_4 at still lower values of $1-T_c/T$, since, for K_2XF_4, (i) $|R|$ is probably smaller, and (ii) $|J|/kT_c$ is smaller ($\cong 1$ and $\frac{1}{5}$ for Ni^{2+} and Mn^{2+}, respectively, compared to 4 for Cu^{2+}). Clearly, for K_2XF_4, $d=3$ behavior for $\tilde{M}_s$ and $\tilde{\chi}$ can be expected only in an extremely narrow range around $T_c(R)$. Moreover, the range will be even narrower *below* than *above* $T_c(R)$, since $\tilde{\chi} = C_{\mathrm{sgn}(T-T_c)}(1-T_c/T)^{-1.75}$, with $C_-/C_+ = 0.0265$ for $d=2$, $n=1$.[23] If a $\tilde{\chi}$ crossover should occur at, say, $1-T_c/T \cong 10^{-3}$, one would expect an $\tilde{M}_s$ crossover at $1-T/T_c \cong 1.3 \times 10^{-4}$, which would explain why the observed $d \cong 2$ behavior of $\tilde{M}_s$ extends so close to T_c.

(g) M_s for $J>0$ ($d \cong 2$): Results for the spontaneous *direct* magnetization, $M_s \equiv M(H=0, R, T)$, are only available for K_2CuF_4.[24] In comparing with the other $d \cong 2$ Cu ferromagnets [see (b) above], we conclude from the fact that $R \cong 2.1 \times 10^{-4}$ that a crossover in $\bar{\chi}$ should occur at $t \cong 0.33$, corresponding to $1-T_c/T \cong 0.15$. This explains the $d \cong 3$ critical behavior observed for both $\bar{\chi}$[12] and M_s.[24]

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[3] The cases $n=1$, 2, 3, and ∞ correspond, respectively, to the $S=\frac{1}{2}$ Ising, $S=\infty$ planar, $S=\infty$ Heisenberg, and spherical models [H. E. Stanley, Phys. Rev. Lett. 20, 589 (1968)].

[4] Note from Ref. 2 that Eq. (2) remains valid with $f=\tilde{M}$ or $\tilde{\chi}$ (where the tilde denotes a staggered quantity) provided that $\bar{\chi}(0,T)$ in (1) is replaced by $\tilde{\chi}(0,T)$. Note also that Eq. (2) is not correct for quantum systems, and the errors in applying (2) to quantum systems may well be larger for $S=\frac{1}{2}$ materials than for, say, $S=\frac{5}{2}$ materials (here S denotes the spin quantum number). Certainly there is no reason *a priori* to suppose that the errors are worse for $\tilde{M}$ and $\tilde{\chi}$ than for M and χ.

[5] The absence of a term linear in R in the specific heat depends on a symmetry argument that is not valid for a quantum system. One might plausibly argue that the linear term will be small in quantum systems, especially for large S.

[6]The smaller the value of R, the closer one must approach $T_c(R)$ for Δf to become appreciable.

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[11]Only because the $l=1$, 2, 3 salts have about the same spin-space anisotropies (Refs. 1 and 10) (Ising anisotropy $R_A^{\mathrm{I}} \cong 0.02\%$, and XY anisotropy $R_A^{XY} \cong 0.3\%$) can we expect the difference in behavior to be solely due to the difference between R_1, R_2, and R_3. For K_2CuF_4, R_A^{I} is much smaller ($< 0.001\%$), but R_A^{XY} is much larger ($\cong 1\%$) (A. Dupas and J. P. Renard, to be published). Therefore the upward deviation of $\overline{\chi}_{\parallel}$ for K_2CuF_4 in Fig. 1 may be ascribed partly to the larger R_A^{XY}, in addition to the effect of the larger R. Further, in comparing compounds with different R_A^{I}, it is found (L. J. de Jongh, to be published) that $R_A^{\mathrm{I}} \cong 0.02\%$ is sufficient to make the critical behavior for $1-T_c/T \lesssim 0.25$ Ising-like ($l=1$ in Fig. 2). For the $l=10$ salt, $R_A^{\mathrm{I}} \cong 0.006\%$, and the Ising region starts at $1-T_c/T \approx 0.15$ (Fig. 2).

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