Magnetic Susceptibility of Quasi-One-Dimensional Ising Superantiferromagnets FeTAC and MCl₂ · 2NC₅H₅ (M = Co, Fe): Approximation with \( L \times \infty \) and \( L \times L \times \infty \) Chain Clusters

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Abstract—The temperature dependence of the zero-field susceptibilities of 2D and 3D Ising lattices with anisotropic coupling is analyzed. Infinite 2D and 3D lattices are approximated, respectively, by ensembles of independent \( L \times \infty \) and \( L \times L \times \infty \) chain clusters that are infinitely long in the strong-coupling (\( J \)) direction. This approach is used as a basis for a quantitative description of available experimental data on the magnetic susceptibilities of the 2D anisotropic Ising ferromagnet \([(\text{CH}_3)_2\text{NH}]\text{FeCl}_3 \cdot 2\text{H}_2\text{O} \) (FeTAC) and the quasi-one-dimensional 3D systems \( \text{CoCl}_2 \cdot 2\text{NC}_5\text{H}_5 \) and \( \text{FeCl}_2 \cdot 2\text{NC}_5\text{H}_5 \) in the entire experimental temperature range. A method is proposed for determining the relative interchain coupling strength \( J'/J \) from the maximum susceptibility value, which improves the accuracy of estimates for \( J'/J \) by more than an order of magnitude.

1. INTRODUCTION

Various currently known materials are Ising magnets \([1, 2]\). Even though the Ising coupling has an extremely simple form, the macroscopic properties of these materials, such as magnetic susceptibility, are very difficult to calculate. It should be noted that no rigorous closed-form expression for the longitudinal component of susceptibility has been obtained to this day even in exactly solvable Ising models. Moreover, there are reasons to believe that no such expression can be found in the class of differentially finite (holonomic) functions \([3–5]\) (see also \([6]\)).

The subject of this study is the magnetic susceptibility of quasi-one-dimensional Ising magnets. Systems of two types are considered: anisotropic square lattices with coupling constants \( J \) and \( J' \) such that \( |J'/J| \leq 1 \), and simple cubic lattices with dominant interaction along one axis represented by \( J \) and equal constants \( J' \) of interaction along the remaining two orthogonal axes.

Crystals of \([(\text{CH}_3)_2\text{NH}]\text{FeCl}_3 \cdot 2\text{H}_2\text{O} \) (FeTAC) have a 2D magnetic lattice consisting of bonded spin chains lying in a plane \([7–10]\). In crystals of \( \text{CoCl}_2 \cdot 2\text{NC}_5\text{H}_5 \) \([11–14]\) and \( \text{FeCl}_2 \cdot 2\text{NC}_5\text{H}_5 \) \([15–17]\), chains of magnetic ions are bonded into 3D systems. All of these materials are typical quasi-1D Ising superantiferromagnets that can be modeled by effective spin-1/2 Hamiltonians (with \( J > 0 \) and \( J' < 0 \)). As temperature decreases, ferromagnetically ordered spin chains become antiferromagnetically ordered. Their magnetic susceptibilities have distinct maxima at temperatures \( T_{\text{max}} \) above the respective critical points \( T_c \). The phase transition manifests itself in the susceptibility curve as an inflection point where the tangent line to the curve is infinitely steep (in the ideal case).

The susceptibility of a 2D Ising lattice was calculated in \([18]\) for the entire temperature range (in theory, from zero to infinity). The approximation used in that study (decoupling of many-spin correlation functions) is accurate within 0.35% in the isotropic model. However, the analysis presented below shows that the error in the coordinates of the susceptibility maximum amounts to tens of percent even for \( J'/J = -0.1 \) (\( J > 0 \)). Therefore, this approximation cannot be applied to quasi-1D systems in practical calculations.

The results obtained for 3D systems are even less accurate. The most reliable calculations of susceptibility for such systems make use of power series expansions. For the zero-field longitudinal susceptibility of the isotropic simple cubic Ising lattice, high-temperature expansions to the 25th- and even 32th-order terms were obtained in \([19, 20]\) and \([21]\), respectively. However, analogous expansions for anisotropic lattices are known only to the 10th- or 11th-order terms (see \([22]\) and \([23]\), respectively). Moreover, partial sums of the series rapidly diverge with increasing lattice anisotropy. In what follows, it is demonstrated that the available high-temperature series expansions of superantiferromagnetic susceptibility \([24]\) result in unacceptably large errors for \( |J'/J| = 10^{-2} \) (even after their conver-
ence is improved by Padé–Borel resummation). Note that interpretation of the experimental data discussed here requires modeling with an even smaller value of this parameter.

In this paper, susceptibilities are calculated by using cluster simulation. It is well known [25–27] that various characteristics calculated by this method (including susceptibility) converge to their values for an infinite system at an exponential rate with increasing cluster size everywhere in the parameter space except for a narrow critical region. However, this region cannot be resolved by modern experimental methods for the quasi-1D materials discussed here.

In view of the specific anisotropy to be modeled, chain clusters of infinite length in the direction of the dominant interaction \( J \) are used as subsystems \((L \times \infty \text{ strips and } L \times L \times \infty \text{ parallelepipeds for 2D and 3D systems, respectively})\). Undesirable surface effects are eliminated by setting periodic boundary conditions in the transverse directions for subsystems of both types. Furthermore, frustration is obviated by using chains of length \( L = 2, 4, \ldots \) (measured in units of the lattice constant), with the only exception of a single chain \((L = 1)\). Thus, the magnetic lattice of an \( (d-1) \times \infty \) superantiferromagnetic cluster \((d = 2 \text{ or } 3)\) consists of two identical interpenetrating sublattices with opposite magnetic moments.

In Section 2, formulas for susceptibilities are presented, including both general expressions well suited for computations and exact asymptotic ones. The cumbersome analytical formulas derived for few-chain subsystems are relegated to the Appendix. In Section 3, the strip width ensuring the accuracy required to calculate the susceptibility of FeTAC is determined. In Section 4, the corresponding calculated results are presented. Sections 5 and 6 contain results for 3D systems analogous to those presented in the preceding two sections. Section 7 summarizes the principal results of this study.

2. CALCULATION OF SUSCEPTIBILITIES

The anisotropic Ising Hamiltonian is written as

\[
H = -\frac{1}{2} \sum_{(i,j)} \sigma_i^x \sigma_j^x - \frac{1}{2} \sum_{[i,j]} \sigma_i^z \sigma_j^z, \tag{1}
\]

where the Pauli matrices \( \sigma_i^z \) are localized at the sites of a square or simple cubic lattice. The sums with \((i,j)\) and \([i,j]\) are taken over the nearest-neighbor pairs along the directions corresponding to \( J \) and \( J' \), respectively.

According to Kubo’s linear response theory [28, 29], the static zero-field susceptibility tensor is

\[
\chi_{\mu \nu} = -\beta \langle M_\mu \rangle \langle M_\nu \rangle + \int d\beta' \langle M_\mu (\beta') \rangle M_\nu (0), \tag{2}
\]

where \( \mu \) and \( \nu \) stand for \( x, y, \) or \( z \); \( \beta = 1/k_B T \) is the inverse temperature measured in energy units \((k_B \text{ is Boltzmann’s constant})\); angle brackets denote ensemble-averaged quantities; \( M_\mu \) is the projection of the magnetic moment of the system on the \( \mu \) axis; and \( M_\mu (\beta) = e^{\beta \mu H_M} e^{-\beta H} \) is a component of magnetization in the Matsubara representation.

Note that superantiferromagnets, being characterized by zero total spontaneous sublattice magnetizations, have zero magnetic moments in the absence of applied field: \( \langle M_\mu \rangle = 0 \). Therefore, the first term on the right-hand side of (2) vanishes under the conditions considered in this study.

The component of the magnetic moment parallel to the \( z \) axis is

\[
M_z = \frac{1}{2} g_B \mu_B \sum_{j=1}^N \sigma_j^z, \tag{3}
\]

where \( g_\parallel \) is the longitudinal \( g \) factor, \( \mu_B \) is the Bohr magneton, and \( N \) is the total number of particles in the system. Since \( M_z \) commutes with Hamiltonian (1) and \( \langle M_j \rangle = 0 \), the expression for the molar zero-field longitudinal (parallel) susceptibility obtained by substituting (3) into (2) is

\[
\chi_\parallel (T) \equiv \lim_{N \to \infty} \frac{N_A}{N} \chi_{zz} = \frac{N_A g_\parallel^2 \mu_B^2}{4 k_B T} \lim_{N \to \infty} \sum_{j=1}^N \langle \sigma_j^z \sigma_j^z \rangle_N, \tag{4}
\]

where \( N_A \) is Avogadro’s number and \( i_0 \) is any particular site in a uniform lattice \( \chi_{\parallel} \) is independent of its location. To evaluate the longitudinal susceptibility, one must calculate and add up all spin–spin correlation functions and take the infinite-lattice limit.

The longitudinal susceptibilities of single-, double-, and four-chain Ising models are known in analytical form (see Appendix). An analysis of these formulas shows that the predicted variation of the susceptibilities of superantiferromagnetic clusters with temperature is in qualitative agreement with experimental data. The susceptibility curve has a peak (see Fig. 1), and its magnitude indefinitely increases with lattice anisotropy. At temperatures below the maximum point, the susceptibility curve has an inflection point that approximately corresponds to the critical point of the entire system. The slope of the tangent line at the inflection point increases with the number of chains in a subsystem, approaching infinity.

For subsystems consisting of a larger number of chains, the susceptibility can be found only by numerical methods. One formula well suited for computing