Criticism of the Use of the Ising Model to describe Linear Chains of Antiferromagnetically Coupled Copper(II) Ions

By RICHARD W. JOTHAM

(*The Kesteven College of Education, Stoke Rochford, Lincolnshire*)

Summary Major disadvantages of the use of the anisotropic Ising model to describe strong antiferromagnetic coupling in infinite linear chains of copper(II) ions are discussed with particular reference to cupric oxalate.

EXAMINATION of the several recent reviews on antiferromagnetically coupled Cu^{II} ions reveals that the Ising model has been fairly generally accepted as the most convenient basis for the interpretation of infinite linear-chain systems.[1] This model involves the simplification of the effective spin-exchange Hamiltonian [equation (1)] by setting $\gamma = 0$.[2]

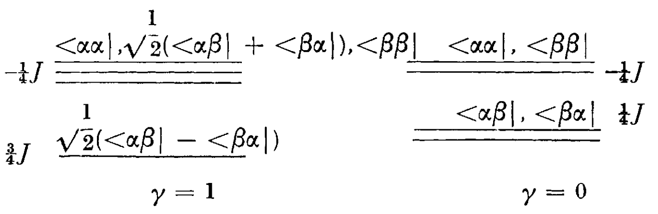
$$\mathcal{H} = -J[S_{i(z)}\cdot S_{j(z)} + \gamma(S_{i(x)}\cdot S_{j(x)} + S_{i(y)}\cdot S_{j(y)})] \qquad (1)$$

This practice considerably simplifies the sums—indeed it is the only way that analytical equations for the magnetic susceptibility have been obtained[3]—but it contrasts dramatically with the methods used for finite polynuclear systems (the Heisenberg model) in which γ is set equal to unity. Few workers appear to have appreciated what a drastic simplification is involved in the use of the Ising model for the accidental reason that most of the systems so-far described are only weakly coupled. Contrast, however, the predictions of the two models for a Cu^{II} dimer.

TABLE. *Magnetic data for copper*(II) *dicarboxylates*[a]

Compound	Ref.	Dimer model $-J$ (cm^{-1})	$10^6\sigma$	Heisenberg model $-J$ (cm^{-1})	$10^6\sigma$	[Equations (3) and (4)] $-J$ (cm^{-1})	Ising model $10^6\sigma$	[Equation (3)] $-J$ (cm^{-1})	$10^6\sigma$
Cupric oxalate,$0{\cdot}3H_2O$ ..	6(a)	379·5	173	357·5	13	451·8	594	411·9	81
Cupric oxalate	6(c)	330·6	212	321·7	5	451·8	596	354·8	103
Cupric malonate,$2{\cdot}5H_2O$ ..	6(a)	8·3	103	10·8	150	13·0	103	4·4	103
	6(b)	−1·7	125	6·3	228	−2·7	125	−0·9	125
Cupric malonate	6(a)	60·6	62	35·8	58	114·7	46	40·8	38
Cupric glutarate	6(a)	328·0	15	314·6	225	493·5	478	355·7	129
	6(b)	324·5	17	301·6	234	451·8	582	353·0	131
Cupric succinate,$2H_2O$ ..	6(a)	329·0	8	318·8	234	497·7	511	362·8	137
	6(b)	329·2	16	314·6	222	493·6	515	361·3	122
Cupric succinate	6(a)	337·8	23	328·5	213	507·4	494	369·9	107
	6(b)	332·2	19	311·5	230	472·7	558	362·4	124

[a] $g = 2{\cdot}16$, $10^6N\alpha = 75$ per mole Cu (cgsu), σ = standard deviation of calculated and experimental susceptibility values per mole Cu (cgsu). Temperature 75—380 K, $10^6 \times$ susceptibility: oxalates 480—620, malonates 1300—6100, others 100—850 per mole Cu (cgsu).



The striking difference in this case arises from the integral $<\alpha\beta|\mathcal{H}|\beta\alpha>$ which has the value $\frac{1}{2}\gamma J$. Calculated susceptibility/temperature curves for the two cases differ grossly in form and only the Heisenberg model is adequate for the description of experimental data on these compounds.

Machine calculations on chains with up to 11 members have been carried out by Bonner and Fisher[4] using different values of γ in equation (1). This is a much neglected paper, for it shows that the predictions of the Ising and Heisenberg models do not converge significantly as chain-length increases and, secondly, it provides empirical data for the approximate description of infinite linear chains with the preferred model of Heisenberg. We have fitted these data [modified to be consistent with equation (1)] to the polynomial expression given in equation (2). The agreement is better than 1% over the whole range studied by these workers and the equation therefore provides a convenient basis for the interpretation of appropriate experimental data. (*N.b.* this expression cannot be used for ferromagnetic coupling.)

$$\chi'_M = \frac{Ng^2\beta^2}{|J|}(0{\cdot}092281 + 0{\cdot}18616P - 0{\cdot}20556P^2 + 0{\cdot}074679P^3 - 0{\cdot}0091808P^4) + N\alpha \qquad (2)$$

$$\text{where } P = kT/|J|$$

We have also checked this expression by computing susceptibility through random walks on very long chains of antiferromagnetically coupled Cu^{II} ions. Excellent agreement was obtained except near the absolute zero and the detailed results have been discussed elsewhere.[5]

We decided to test both the Ising and Heisenberg models on a series of compounds in which diverse structural types are observed, namely the copper(II) salts of $\alpha\omega$-dicarboxylic acids.[6] The ammonia complex of cupric oxalate has an infinite linear-chain structure[7] and its (graphically recorded) susceptibility data are very similar to the data for other cupric oxalate complexes. Conversely, copper malonate is virtually magnetically dilute, while later members of the series appear to be dimeric, like cupric succinate dihydrate.[8] A survey of representative compounds from our file of susceptibility data of over 400 Cu^{II} complexes had revealed that most of the likely linear systems may well have been of dubious purity owing to preparation by precipitation methods. Secondly, many of the structurally characterised infinite linear systems, like cupric benzoate trihydrate,[9] are so weakly coupled that the data cannot decisively distinguish between the various models. When the coupling is stronger, the predictions of the different models diverge rapidly. This is plain from the form of the analytical expressions given by Fisher for the Ising model,[3] which are given in equations (3) and (4). These equations have again been modified to be consistent with equation (1)—simple numerical factors may be noticed by other workers in this field.

$$\chi'_{\parallel} = (Ng^2\beta^2/4kT)\exp(J/2kT) + N\alpha \qquad (3)$$

$$\chi'_{\perp} = (Ng^2\beta^2/8kT)[(\tanh(K)/K) + \mathrm{sech}^2(K)] + N\alpha \qquad (4)$$
$$\text{where } K = |J|/4kT$$

Most of the divergence between the Ising and Heisenberg models may be traced to equation (4), from which it may be seen that the perpendicular component of the Ising susceptibility is independent of the sign but not the magnitude of the exchange integral. In particular, for a large $|J|$, it suggests a much larger average susceptibility than can be obtained from a corresponding Heisenberg equation, and this is precisely the defect implicit in the energy-level scheme for a dimer.

We examined the data for the copper(II) dicarboxylates using four models, namely equation (2), the weighted average of equations (3) and (4), equation (3) alone, and the corresponding equation for a dimer, (5). (All equations give the molar susceptibilities per Cu^{II} ion.)

$$\chi'_{M} = (Ng^2\beta^2/kT)[\exp(J/kT)/(1 + 3\exp(J/kT)]+N\alpha \qquad (5)$$

The results are shown in the Table. They confirm that only the dimer model is applicable to higher members of the series. Little can be said about the cupric malonates, but note the reasonable performance of the Ising model here. For the cupric oxalates, however, the results are quite striking. The dimer model is inappropriate, equation (3) gives a fair description but equation (2) gives remarkable agreement with data measured by different workers. These compounds are well-behaved Heisenberg infinite linear-chain antiferromagnets with moderately strong coupling, but they are very poorly described by the Ising model. We suggest that there must now be strong doubts concerning the use of the Ising model on experimental as well as the long-standing theoretical doubts. It seems appropriate to introduce the use of the data of Bonner and Fisher as a basis for the interpretation of experimental data on compounds of this type.[10]

The invaluable help of colleagues at the University of East Anglia in the provision of computing facilities is acknowledged.

(*Received*, 13*th December* 1972; *Com.* 2085.)

[1] P. W. Ball, *Co-ordination Chem. Rev.*, 1969, **4**, **361**; E. Sinn, *ibid.*, 1970, **5**, 313, and references cited therein.
[2] G. F. Newell and E. W. Montroll, *Rev. Mod. Phys.*, 1953, **25**, 353.
[3] M. E. Fisher, *J. Math. Phys.*, 1963, **4**, 124.
[4] J. C. Bonner and M. E. Fisher, *Phys. Rev.*, 1964, **135**A, 640.
[5] R. W. Jotham, *Phys. Stat. Solidi* (*b*), in the press.
[6] (a) L. Dubicki, C. M. Harris, E. Kokot, and R. L. Martin, *Inorg. Chem.*, 1966, **5**, 93; (b) B. N. Figgis and D. J. Martin, *Inorg. Chem.*, 1966, **5**, 100; (c) V. V. Zelentsov and T. G. Aminov, *Doklady Akad. Nauk S.S.S.R.*, 1964, **158**, 1393.
[7] L. Cavalca, A. C. Villa, A. G. Manfredotti, A. Mangia, and A. A. G. Tomlinson, *J. C. S. Dalton*, 1972, 391.
[8] B. H. O'Connor and E. N. Maslen, *Acta Cryst.*, 1966, **20**, 824.
[9] M. Inoue, S. Emori, and M. Kubo, *Inorg. Chem.*, 1968, **7**, 1427.
[10] S. Emori, M. Inoue, and M. Kubo, *Bull. Chem. Soc. Japan*, 1972, **45**, 2259.