Magnetism in one dimension

Crystals whose magnetic ions are arranged in separated chains have magnetic properties that indicate nearly ideal one-dimensional rather than three-dimensional behavior.

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"How," Aristotle asked, "*can a line or plane be animate? The supposition surpasses the power of our senses.*"

Not just biological phenomena but most physical phenomena as well become drastically altered or impossible in spaces of fewer than three dimensions. As is well known, the cooperative behavior of many-body systems depends very strongly on the coordination of the closely interacting particles and therefore on the number of spatial dimensions. As we shall see, not only does an examination of physics in fewer than three dimensions illuminate the familiar world of three dimensions, there are also real systems whose structure effectively reduces their dimensionality and for which, therefore, low-dimensional physics is a prerequisite. As a consequence, a considerable effort has been expended in explaining the properties of lower-dimensional and, especially, linear systems. During the last decade there has been a veritable explosion in the "one-dimensional" literature.[1] In this article we would like to discuss in the context of magnetism some of the motivating factors for this explosion and the progress that has been achieved so far.

For physicists, especially after the advent of modern quantum and statistical mechanics, the primary attraction of a one-dimensional space has been that a number of important many-body problems that seem impossibly complicated in three dimensions become tractable in one dimension. Indeed, as we shall discuss later, exact, closed form, results have been obtained for the static and dynamic properties of a number of systems described by simple one-dimensional model Hamiltonians. Two further developments, one experimental, one theoretical, in the past decade have made "one-dimensional physics" even more interesting and useful.

It has, first, become clear that there are in Nature a remarkably large number of materials whose properties are, in some sense, dominated by one-dimensional effects. These generally consist of long molecular chains whose central atoms interact readily along the chain, but which are effectively insulated from each other by side groups or intercalated molecules.

Second, in the theory of the phase transitions, especially since the development of the Renormalization Group Approach, it has become fully appreciated that spatial dimensionality plays a crucial role in the behavior of fluctuations from equilibrium. In general, as the spatial dimensionality of a physical system is decreased, fluctuation effects become relatively more important. This simply reflects the fact that the number of paths between two elements decreases dramatically as the dimensionality decreases. The extreme limit occurs in one dimension where there is only a single path between any two atoms in a chain, so that a fluctuation at any one site destroys the order between two halves of the system. It is therefore impossible to maintain any long-range order in the system at a temperature above absolute zero.

In this article we review some of the recent developments in the area of one-dimensional physics, especially on the experimental side. Our discussion will be almost exclusively in the context of magnetism. The reasons for restricting this article primarily to magnetic phenomena are threefold. Firstly, magnetic problems in general provide the simplest examples of one-dimensional cooperative phenomena; secondly, and concomitant with this, is the fact that many aspects of one-dimensional magnets are now very well understood, whereas both experiments and theory of, for example, one-dimensional conductors, are much more complex and much less developed. Thirdly, from our own parochial point of view, we believe that recent one-dimensional magnetic experiments provide particularly elegant illustrations of physics in one dimension.

One-dimensional materials

Before launching into a detailed review of the theory, especially the exact results, let us first discuss real one-dimensional materials—their crystal structures and their general magnetic behavior. The best one-dimensional magnets, or at least, the best understood ones are all transition-metal insulators with obvious, well-separated, linear chains. We show in figure 1 the crystal structure of perhaps the most ideal one-dimensional material, $(CD_3)_4\,NMnCl_3$, tetramethyl ammonium manganese chloride (called "TMMC"). Here the magnetism is associated with the Mn^{++} ion.

The Mn^{++} ion has a half-filled 3d shell, that is, a $3d^5$ configuration, so that according to Hund's rules, the lowest multiplet has $L = 0$ and $S = 5/2$. Transition-metal insulators are now sufficiently well understood that by knowing the magnetic ion and the crystal structure we may infer a surprisingly large amount about the probable magnetic behavior. For Mn^{++}, since the orbital angular momentum is zero, we expect the interatomic exchange, whether direct or mediated by intervening ions, to be isotropic. That is, for any two Mn^{++} ions the exchange Hamiltonian will be just $\mathcal{H}_{ij} = -2J\,\mathbf{S}_i\cdot\mathbf{S}_j$. In an insulator the Mn^{++} electrons are well localized, so that the direct exchange is usually quite small even for nearest neighbors in the crystal. The magnetic interaction then occurs via the intervening ions, a process given the general name "superexchange,"

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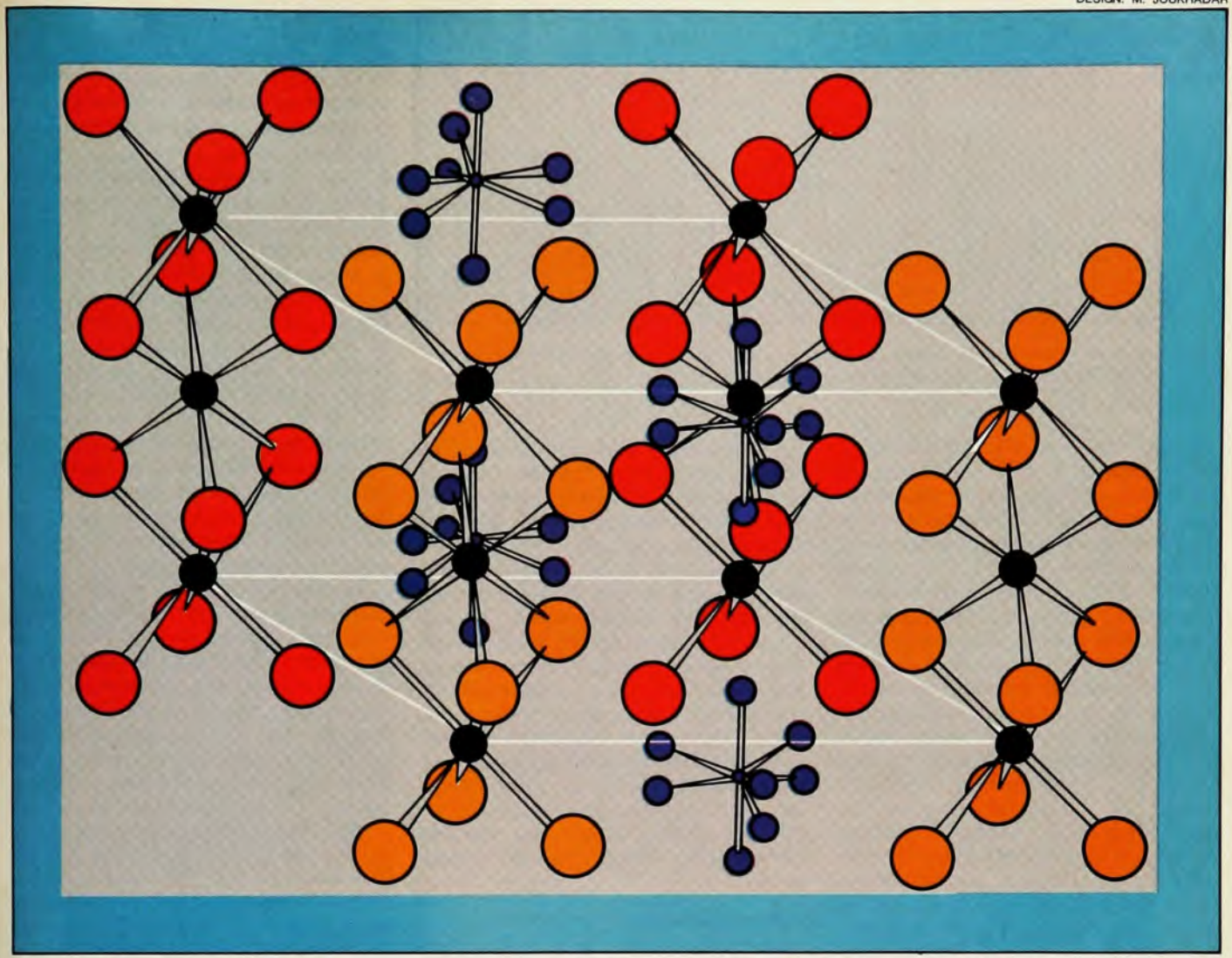


Crystal structure of TMMC. The crystal consists of chains of linked $MnCl_3^-$ ions separated by $(CD_3)_4N^+$ groups. The chains form a hexagonal array which is slightly distorted at low temperatures. The spin is associated with the manganese ion (black circles), and the antiferromagnetic spin-spin interaction is mediated by the chlorine ions (large orange circles). The $(CD_3)_4N^+$ groups are disordered. Figure 1

and tends to line up the spins in opposing directions, making the material antiferromagnetic. For simple geometrical configurations it is possible to deduce both the sign and the general order of magnitude of the exchange energy; these follow from quantum-chemistry considerations and from empirical trends.[2]

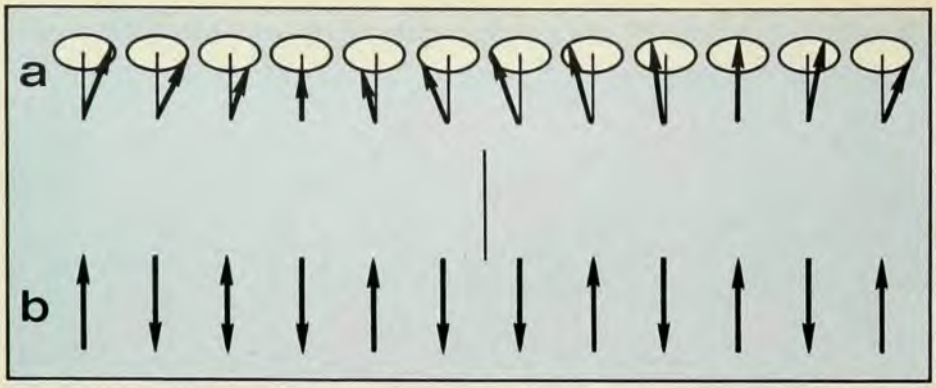
Let us apply these considerations explicitly to TMMC as an example. From figure 1, it is evident that the Mn^{++} ions are located in continuous one dimensional $MnCl_3$ chains; the separation between Mn^{++} ions along the chain axis is 3.25 Å. These chains of spins are kept well separated by the intervening $(CD_3)_4N^+$ complexes so that the separation between chains is 9.15 Å. This ratio of distances, 3:1, might not initially seem very large. However, superchange, which involves the overlap of the tails of the wave functions, falls off exponentially with distance. Thus the anisotropy is in fact quite large and, indeed, the exchange between chains is orders of magnitude smaller than the in-chain interaction. More detailed quantum-chemistry considerations also allow us to conclude that along the chains the coupling will be strong and antiferromagnetic between nearest neighbors and very much weaker between second neighbors. Thus TMMC should be a nearly ideal one-dimensional, antiferromagnetic material. We will discuss the corrections to the simple nearest-neighbor isotropic Hamiltonian later in this article.

Although the above structural reasoning provides an important first step, we would like in addition a simple experimental test that would enable us to decide how closely a real material approaches ideal one-dimensionality. The best empirical criterion turns out to rest on the most salient feature of one-dimensional magnets—the absence of long-range order at finite temperatures. For three-dimensional systems a magnetic phase transition typically occurs at temperatures comparable with the interaction energy divided by Boltzmann's constant, k. Explicitly, for a magnet with exchange energy $-2J\mathbf{S}_i\cdot\mathbf{S}_j$ between Z nearest neighbors, the mean-field ordering temperature is found to be

$$T_{MF} = \frac{2}{3} Z \frac{|J|}{k} S(S+1).$$

To estimate T_{MF}, we must first determine the exchange constant J using, for example, high temperature susceptibility measurements. The susceptibility itself should, of course, exhibit behavior characteristic of one-dimensional fluctuation. A variety of techniques including specific heat or magnetic susceptibility measurements, nuclear magnetic resonance, electron spin resonance and neutron diffraction can serve to determine the transition temperature T_N (N for Néel). If one then finds that the actual phase transition temperature is a factor of 10 to 100 less than the mean-field ordering temperature this result automatically suggests that one-dimensional behavior is predominant.

Let us apply these ideas to TMMC as an example. Experimental measurements show that the susceptibility increases slowly with decreasing temperature, reaches a maximum at around 50 K



Excitations in one-dimensional chains: (a) spin-wave excitation in a Heisenberg ferromagnetic chain, (b) spin-flip excitation in an Ising antiferromagnetic chain. Figure 2

and then begins to decrease gradually. Below about 20 K the susceptibility becomes somewhat anisotropic, that is the response to a field is different for the field along and perpendicular to the chain axis. We argued above that TMMC should correspond closely to a nearest-neighbor Heisenberg antiferromagnet in one dimension, with spin $5/2$. The system is, of course, quantum mechanical rather than classical in nature. However, in magnetism the relative importance of quantum effects is given by the ratio of $S(S+1)$ to S^2. The intrinsic quantum effects thus scale as $1/S$. For a spin of $5/2$, $1/S$ is small enough that a classical approximation appears reasonable. Michael Fisher[4] has found an exact solution for the susceptibility in the classical approximation. Fisher's classical theory with $J = -6.3$ K fits the experimental data very well, thus giving credibility to our heuristic arguments; at the minimum, this agreement shows that the correlations are predominantly one-dimensional.

Now what about the ordering temperature? More accurate theory for the susceptibility that takes explicit account of the spin quantum number gives $J = -6.47 \pm 0.013$ K. With this value for J the transition temperature should be $T_{MF} = 76$ K. In fact, the actual three dimensional ordering temperature as determined by a variety of techniques is 0.85 K; so that T_N/T_{MF} is approximately 10^{-2}. Thus TMMC does appear to be a very good candidate for nearly ideal one-dimensional behavior. To study the dimensionality directly one would like to probe the explicit spin correlations within and between the Mn^{++} chains. It turns out this is possible experimentally using neutron-scattering techniques. We shall discuss this in detail later.

From analyses of the same type, many materials approaching ideal one dimensionality have been discovered. We list a number of these in the table. With these one-dimensional systems one may now begin exploring experimentally statics and dynamics in a one-dimensional world. Before proceeding with our discussion of these experiments let us first pause to review the theory of linear magnets with special emphasis on exact results; of course, we will also want to identify the important theoretical issues.

Theoretical results

In discussing the theory of one-dimensional magnetism, we must begin with the Hamiltonian. For simplicity we consider a chain of spins with only nearest neighbor exchange, for which the Hamiltonian is:

$$\mathcal{H} = -2J \sum_i [\alpha S_i^z S_{i+1}^z + \beta(S_i^x S_{i+1}^x + S_i^y S_{i+1}^y)]$$

There are three cases of particular interest.

▸ $\alpha = 0$, $\beta = 1$: in this case only the transverse components of the spins are coupled; here the spins will tend to lie in the x-y plane but with no preferred direction on that plane. This is referred to as the "XY model."

▸ $\alpha = 1$, $\beta = 0$: in that case only the z components of the spins are coupled; clearly in any ordered state the spins will point along the z axis; this is referred to as the "Ising model."

▸ $\alpha = \beta = 1$; this is, of course, just the familiar Heisenberg model; no preferred direction in space is selected. For $J < 0$ the exchange is *antiferromagnetic*, that is, successive spins along the chain will tend to align antiparallel to each other. For $J > 0$ the exchange is *ferromagnetic* so that successive spins tend to align parallel to each other. We emphasize that both the XY model and the Heisenberg model have a continuous symmetry, in both cases a rotational symmetry. As we shall see, this continuous symmetry and the consequent broken symmetry in any ordered phase have important consequences for the instantaneous and dynamic fluctuation behavior.

As we have already emphasized, a one-dimensional system cannot sustain a long-range ordered state at finite temperatures. This may be understood easily for the Ising case. Suppose we have a completely aligned one-dimensional magnet. The cost in energy of flipping one section is simply $4JS^2$; however, this flip can occur at any of N places (see figure 2). The associated entropy is $kT \ln N$, and the net change in the free energy is $\Delta F = 4JS^2 - kT \ln N$, which is less than zero for $N > e^{+4JS^2/kT}$. It is evident that as N becomes infinite, such spontaneous flips will occur at all finite temperatures, and correspondingly the Ising chain will not sustain long-range order. For chains with continuous symmetry, absence of long-range order can also be simply demonstrated by considering their dynamics at finite temperatures.

The essential quantity that enters most important physical properties is the time-dependent two-spin correlation function at temperature T

$$\langle S_i^{\alpha}(0) S_{i+l}^{\alpha}(t) \rangle_T$$

which gives the probability that, given a spin at time 0, position i, pointing in direction α, then a spin at position $i + l$, some time t later, will also be pointing in direction α. Most often one deals with the space–time Fourier transform of the correlation function, $S^{\alpha\alpha}(\mathbf{q},\omega)$; for static properties one needs the spatial Fourier transform of the instantaneous correlations, $S^{\alpha\alpha}(\mathbf{q})$. The Fourier inversion theorem equates $S^{\alpha\alpha}(\mathbf{q})$ with the integral of $S^{\alpha\alpha}(\mathbf{q},\omega)$ over all energies or, equivalently, values of ω.

The most important feature in the static correlations is the rate at which they drop off with distance. For a system with long-range order, spins remain aligned to infinite distances, so that

$$\lim_{l \to \infty} \langle S_i^{\alpha}(0) S_{i+l}^{\alpha}(0) \rangle = \pm \langle S^{\alpha} \rangle^2.$$

Measured critical temperatures T_N and computed mean-field temperatures, T_{MF}

Crystals	S	T_N(K)	T_N/T_{MF}
$CuSO_4 \cdot 5H_2O$	1/2	1.4	0.02
$CuCl_2 2N \cdot C_5H_5$ (CPC)	1/2	1.1	0.08
α-Cu N Sal	1/2	.044	0.01
$CsNiCl_3$	1	4.6	0.13
$CsNiF_3$	1	2.6	0.08
$CsMnCl_3 \cdot 2H_2O$	5/2	4.9	0.12
$(CH_3)_4N \cdot MnCl_3$ (TMMC)	5/2	0.8	0.01

For the purpose of neutron studies the hydrogen-containing substances are often prepared in deuterated form.

For a one-dimensional chain with short-range order at finite temperatures one has typically

$$\langle S_i^{\alpha}(0) S_{i+l}^{\alpha}(0)\rangle \sim e^{-la/\xi}$$

where ξ is called the correlation length, and measures the range over which the spins are effectively ordered; the inverse correlation length, $1/\xi$, is generally denoted by κ. A similar definition for the correlation function holds in all dimensions. A second-order phase transition is characterized by a divergence of ξ. As we shall see, in one dimension even though there is no long-range order at finite temperatures, one often has $\xi \to \infty$ as $T \to 0$, so that $T = 0$ may be effectively a critical point.

Most of the peculiar features of linear magnets manifest themselves in $S(\mathbf{q})$ and, for dynamics, $S(\mathbf{q},\omega)$. Fortunately, these quantities are directly accessible experimentally with neutron-scattering techniques. In a neutron-scattering experiment in which one resolves both energy and momentum, one measures $S(\mathbf{q},\omega)$ directly. It is also possible to construct the neutron-scattering experiment in such a way that one integrates directly over ω while holding $\mathbf{q}$ constant. In that case, then, one measures the instantaneous structure factor $S(\mathbf{q})$ directly. In the classical limit the fluctuation–dissipation theorem together with the Kramers–Kronig relations leads to a simple relation between the correlation function and the susceptibility:

$$T\chi^{\alpha\alpha} = \sum_l \langle S_i^{\alpha}(0) S_{i+l}^{\alpha}(0)\rangle_T$$

The neutron-scattering results are thus related to susceptibility measurements as well as to the correlation function.

Classical systems

Not surprisingly, the problem is very much simpler if the spins are taken as *classical* variables. This might at first seem to be an academic exercise, since all real systems have quantum-mechanical spins. However, the results do provide useful intuitive guidance for the more difficult quantum calculations. More importantly, as we have already noted in the context of TMMC, many real one-dimensional systems have large spin quantum numbers so that the classical approximation may be valid down to quite low temperatures.

Let us consider first the instantaneous correlations. For simple Hamiltonians such as the Ising or Heisenberg models one finds that the correlations fall off exponentially with distance. For illustrative purposes we consider explicitly only the Heisenberg model, for which Fisher has found that

$$\langle \mathbf{S}_i \cdot \mathbf{S}_{i+l}\rangle = U^l S^2$$

$$\text{where } U = \coth\left[\frac{2JS^2}{kT}\right] - \frac{kT}{2JS^2}$$

It is apparent that $|U| < 1$ for $T > 0$ so that the correlations do indeed vanish as $l \to \infty$ for all finite temperatures. This illustrates directly the absence of long range order at all finite temperatures. The correlation length is given by

$$a/\xi = -\ln U$$

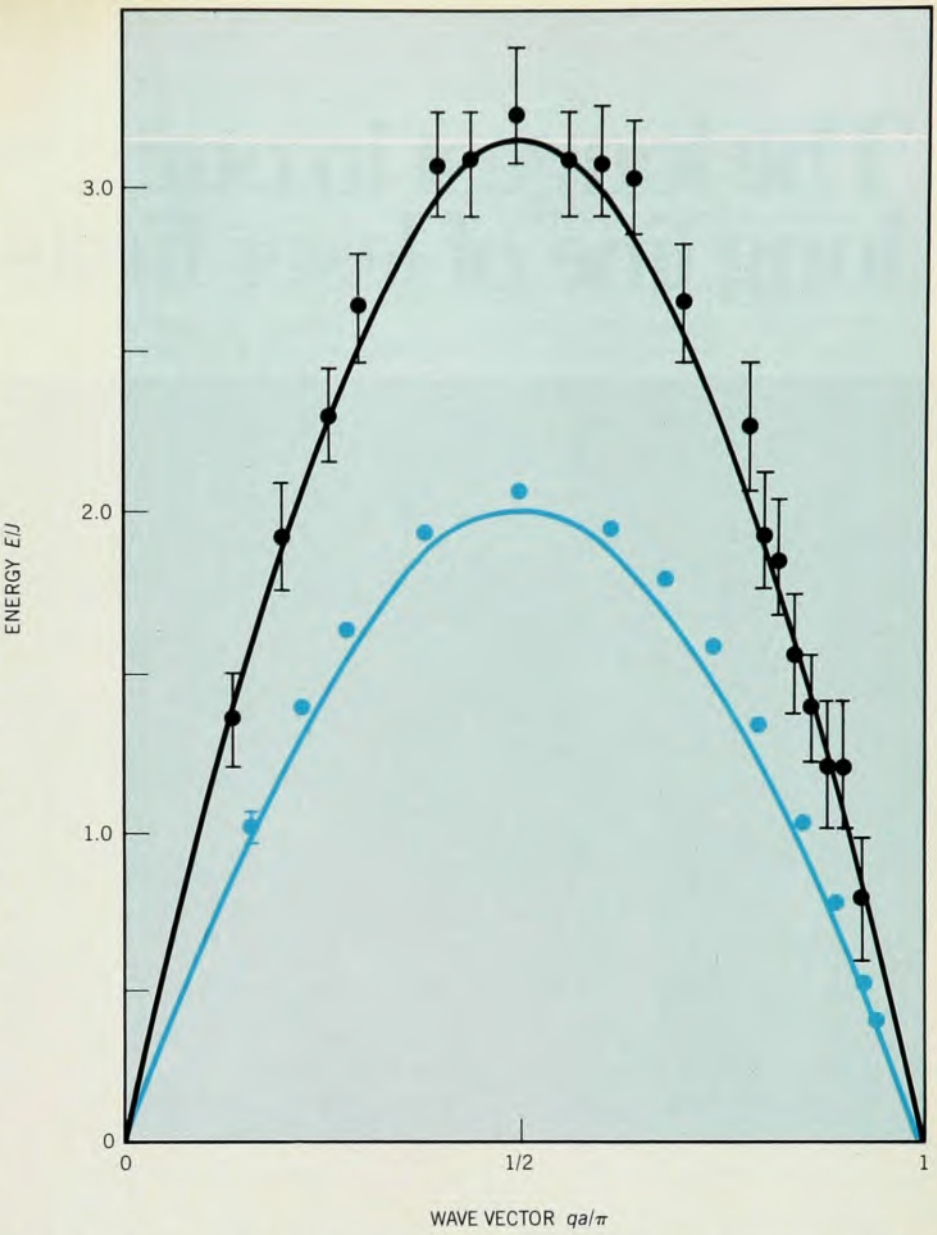
At low temperatures we see that the correlations diverge simply as $1/T$. We note that for a ferromagnet $\langle \mathbf{S}_i \cdot \mathbf{S}_{i+l}\rangle$ will always be positive whereas for an antiferromagnet it alternates in sign with l.

Since we have an exact result for the instantaneous correlations for all l, it is a straightforward exercise to calculate $S(q)$. For a simple antiferromagnet, the resulting expression has a series of Lorentzian peaks centered about $qa = \pi, 3\pi$, and so forth, with a width proportional to κ and height proportional to $\kappa^{-1} = \xi$.

Let us now consider the dynamics for classical spins with Heisenberg exchange. At $T = 0$ the spins will be perfectly aligned, for simplicity we take z as the spin direction. In this limit, the first excited states correspond to infinitely long-lived spin waves. The dispersion relation[5] for these spin waves can be simply calculated; for the antiferromagnet we have

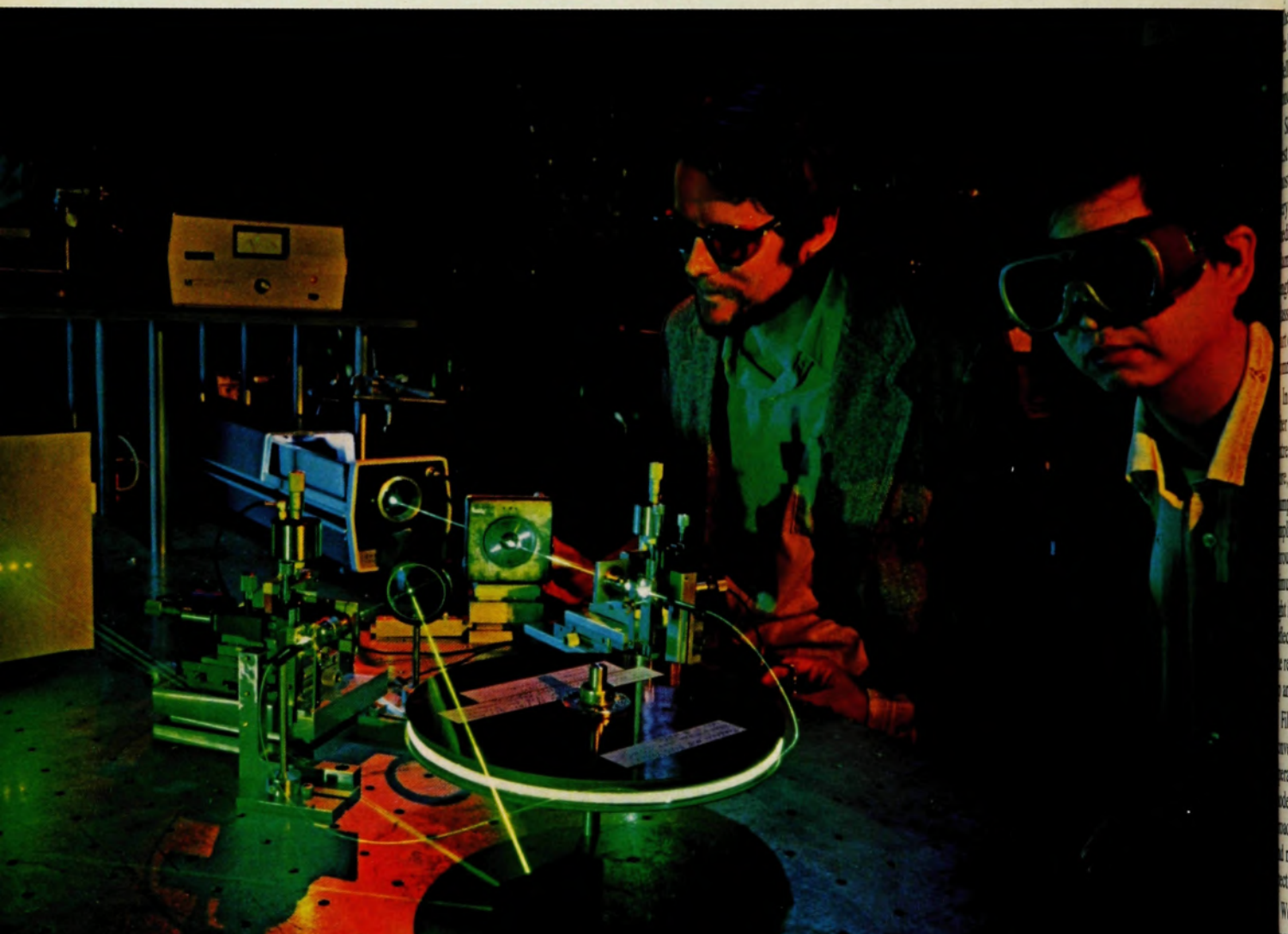
$$\hbar\omega(q) = 4|JS \sin q_z a|$$

The spin-wave excitations appear as poles in $S^{xx}(\mathbf{q},\omega)$ and $S^{yy}(\mathbf{q},\omega)$. Spin-wave excitations are illustrated figuratively in figure 2. Now what happens at finite temperatures? The system no longer has long-range order, so it is not correct to consider excitations out of a perfectly aligned ground state. One nevertheless might argue intuitively as follows: If we consider excitations with $q_z \gg \kappa$ then the



Excitation dispersion relations. For the classical chain (black) the excitations are simple spin waves with an infinite lifetime at $T = 0$; the experimental points are for TMMC with $|J|$ taken to be 6.47 K. For the spin-½ chain (color) the dispersion relation represents the threshold for spin excitations; the experimental points are for CPC with $|J|$ taken to be 13.4 K. Figure 3

The longest in our long line of laser firsts...



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Bell Labs scientists Roger Stolen and Chinlon Lin work with a fiber Raman laser, one of a new class of light sources that use optical fibers—up to a kilometer long—to produce tunable laser light. At left, the laser's output—which contains multiple Raman-shifted wavelengths—is taken off a beam splitter and dispersed by an external grating to show the broad range of wavelengths that can be tuned.

Bell Labs has developed some of the world's most transparent glass fibers to *carry* light for communications. We've also devised a way to make these highly transparent glass fibers *generate* light. In fact, they are the basis for a new class of tunable light sources called fiber Raman lasers. They're among the latest, and by far the longest, of many lasers invented at Bell Labs, beginning in 1957 with the conception of the laser itself.

Since the new fiber lasers work best at wavelengths at which they are most transparent, we can make them very long. The longest active lasing medium ever built, in fact, was a fiber Raman laser over a kilometer in length. Studying the ways light and glass interact over such distances is part of our research in lightwave communications.

In these new light sources, a glass fiber with high transparency and an extremely thin light-guiding region, or core, is excited by a pump laser. The pump light, interacting with the glass, amplifies light at different wavelengths through a phenomenon known as stimulated Raman scattering. This light is fed back into the fiber by a reflecting mirror. If gain exceeds loss, the repetitively amplified light builds up and "lasing" occurs.

Fiber Raman lasers have conversion efficiencies of about 50%, operate in pulsed and continuous wave modes, and are easily tunable over a broad wavelength range in the visible and near infrared regions of the spectrum.

We've used these lasers to measure the properties of fibers and devices for optical communications; and studies of the lasers themselves have revealed a wealth of information on frequency conversion, optical gain, and other phenomena. Such knowledge could lead to a new class of optoelectronic devices made from fibers, and better fibers for communications.

Looking back

These long lasers come from a long line of Bell Labs firsts:

1957: The basic principles of the laser, conceived by Charles Townes, a Bell Labs consultant, and Bell Labs scientist Arthur Schawlow. (They later received the basic laser patent.)

1960: A laser capable of emitting a continuous beam of coherent light—using helium-neon gas; followed in 1962 by the basic visible light helium-neon laser. (More than 200,000 such lasers are now in use worldwide.) Also, a proposal for a semiconductor laser involving injection across a p-n junction to generate coherent light emitted parallel to the junction.

1961: The continuous wave solid-state laser (neodymium-doped calcium tungstate).

1964: The carbon dioxide laser (highest continuous wave power output system known to date); the neodymium-doped yttrium aluminum garnet laser; the continuously operating argon ion laser; the tunable optical parametric oscillator; and the synchronous mode-locking technique, a basic means for generating short and ultrashort pulses.

1967: The continuous wave helium-cadmium laser (utilizing the Penning ionization effect for high efficiency); such lasers are now used in high-speed graphics, biological and medical applications.

1969: The magnetically tunable spin-flip Raman infrared laser, used in high-resolution spectroscopy, and in pollution detection in both the atmosphere and the stratosphere.

1970: Semiconductor heterostructure lasers capable of continuous operation at room temperature.

1971: The distributed feedback laser, a mirror-free laser structure compatible with integrated optics.

1973: The tunable, continuous wave color-center laser.

1974: Optical pulses less than a trillionth of a second long.

1977: Long-life semiconductor lasers for communications. (Such lasers have performed reliably in the Bell System's lightwave communications installation in Chicago.)

Looking ahead

Today, besides our work with tunable fiber Raman lasers, we're using other lasers to unlock new regions of the spectrum in the near infrared (including tunable light sources for communications), the infrared, and the ultraviolet.

We're also looking to extend the tuning range of the free electron laser into the far infrared region—where no convenient sources of tunable radiation exist.

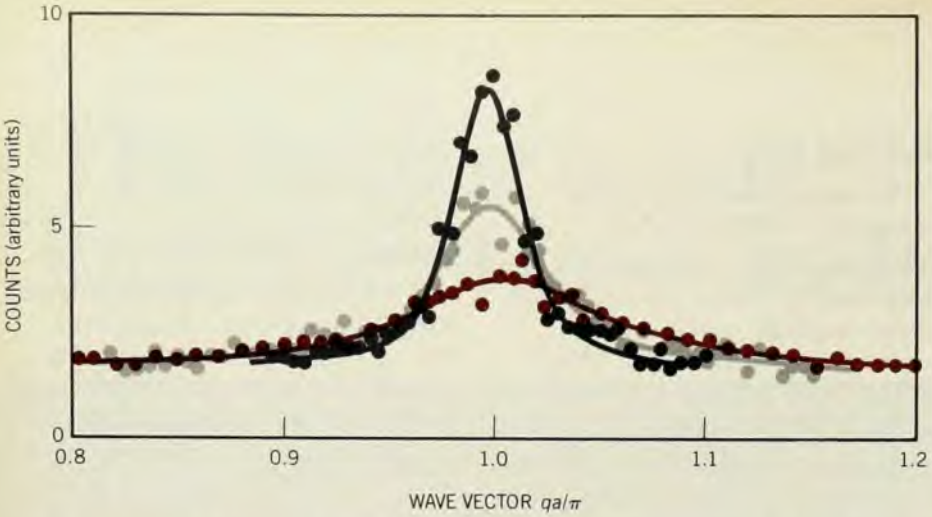
We're working on integrated optics—combinations of lightwave functions on a single chip.

Lasers are helping us understand ultrafast chemical and biological phenomena, such as the initial events in the process of human vision. By shedding new light on chemical reactions, atmospheric impurities, and microscopic defects in solids, lasers are helping us explore materials and processes useful for tomorrow's communications.

Also under investigation is the use of intense laser irradiation in the fabrication of semiconductor devices. The laser light can be used to heat selective areas of the semiconductor and anneal out defects or produce epitaxial crystalline growth. Laser annealing coupled with ion implantation may provide a unique tool for semiconductor processing.

We've played an important part in the discovery and development of the laser—an invention making dramatic improvements in the way our nation lives, works and communicates.

From Science: Service



Quasielastic neutron scattering spectra. Neutron intensity is plotted as a function of wave vector for scattering from instantaneous spin correlations in TMMC. at temperatures of 22 K (color), 12 K (grey) and 5.4 K (black). The peak intensity gives the structure factor $S(\pi/a)$ while the half-width at half-maximum gives the inverse correlation length. (From reference 9.) Figure 4

excitation can oscillate many times before leaving a region of correlated spins; thus we might still expect relatively sharp excitations. How sharp? We can use the dispersion relation to estimate the widths. Since q_z is quite well defined only to within a range of κ, we anticipate an energy smearing roughly on the order of

$$\Delta\omega(q) \sim \frac{d\omega(q)}{dq}\,\kappa \sim \frac{2kT}{S}\cos qa$$

An exact calculation gives a very similar result, but lacking the factor of cos qa; it is supported by the experiments in TMMC. Similar results to the above are obtained for the ferromagnet. As q passes from values much larger than κ to values smaller than κ we might naturally expect an evolution from propagating to overdamped to diffusive behavior for the spin excitations. As we shall see it is possible to test all of the above ideas in remarkable detail experimentally.

Quantum systems

Very much less is known about quantum systems. We confine our attentions here primarily to the $S = \frac{1}{2}$ Heisenberg antiferromagnet—a system with especially interesting dynamics, a few exact results, and at least one good experimental illustration. In 1931, Hans Bethe[6] found the ground-state eigenfunction for this system and showed that no long-range order exists even at 0 K. Various calculations suggest that at $T = 0$ the correlations drop off inversely with distance. In 1938 Lamek Hulthén derived[6] the ground-state energy

$$E = -N\,|J|\,(2\ln 2 - \tfrac{1}{2}) = -0.886N|J|$$

compared with $-0.5N|J|$ for the classical Néel antiferromagnetic ground state.

For the next two decades very little progress was made on this problem. Finally, in a celebrated paper published in 1962, Jaques des Cloizeaux and James J. Pearson[7] derived exactly the locus of the first excited states at $T = 0$. The dispersion relation is

$$\hbar\omega(q) = \pi|J\,\sin qa|$$

where again a is the separation between nearest-neighbor atoms along the chain. The first excited state has total spin 1 so these states represent triplet excitations out of the singlet ground state. This result is quite amazing for a number of reasons. Firstly, the classical theory, as we have seen, gives the identical analytic form for the dispersion relation but with the prefactor 2 instead of π. The similarity of the two results is shown clearly in figure 3. Secondly, the classical solution represents two-fold degenerate spin wave excitations, whereas the des Cloizeaux–Pearson states are triply degenerate. Thirdly, the classical Néel state spin waves have periodicity $-\pi/2 \le qa \le \pi/2$; this happens, of course, simply because in establishing a Néel ground state we have increased the real space periodicity from a to $2a$. On the other hand, the $S = \frac{1}{2}$ system does not have long-range order at $T = 0$ so that the real lattice remains periodic with the basic lattice constant. Accordingly we expect the excitations to exhibit a period of 2π instead of π in q-space. The states found by des Cloizeaux and Pearson, on the other hand, have a double periodicity like the classical states. The above raises the natural question: what connection do the des Cloizeaux–Pearson states have with real spin waves? Or, in other words, what are the eigenfunctions of these states and how will they manifest themselves in $S(q,\omega)$? In the classical case, $S(q,\omega)$ exhibits delta-function spin-wave peaks at $\omega(q)$. Will the same happen in the $S = \frac{1}{2}$ case for the des Cloizeaux–Pearson excitations? Unfortunately, theory has not yet succeeded in answering these questions, at least in any rigorous fashion, and we will have to appeal to experiment for answers.

Finally we consider briefly the exact results for the XY model. For *classical* spins there are exact solutions for the static correlations and for the long-wavelength in-plane and out-of-plane dynamics. The in-plane results for the classical XY ferromagnet are, in fact, identical to those of the Heisenberg antiferromagnet except for numerical prefactors and, of course, the phase factors.

Perhaps, the most famous exact result in one-dimensional magnetism is the calculation[8] by Elliott Lieb, Ted Shultz, and Daniel Mattis for the spin-$\frac{1}{2}$ XY magnet, in which the spin problem is mapped exactly into a fermion problem. Explicitly, these authors show that the spectrum of lowest-lying excited states is given by

$$\hbar\omega(q) = 2|J\,\sin qa|$$

in precise agreement with the classical spin wave. This result is, in some sense, even more surprising than the des Cloizeaux–Pearson result for the Heisenberg antiferromagnet. We should emphasize that the XY system also does not have long-range order at $T = 0$ K. Indeed, Barry McCoy has shown rigorously that the spin correlations drop off as $l^{-1/2}$ for large l at $T = 0$. The agreement between the Lieb, Shultz and Mattis calculation and the classical spin-wave result leads one to suspect that these XY excitations might just be simple spin waves. Unfortunately this turns out not to be the case. There is clearly much more work to be done on the spin-$\frac{1}{2}$ linear XY magnet. However, as far as we know, there are no good physical realizations of this system so we shall not discuss it further here.

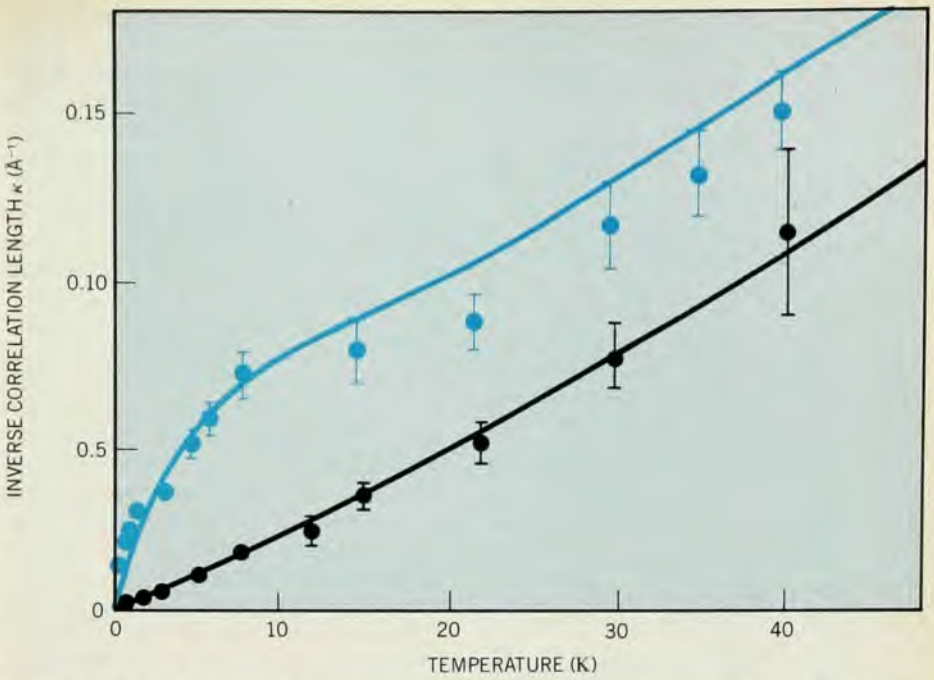
In the above discussion we have presented rather rapidly a potpourri of exact results for various linear spin systems. The essential features are as follows; in all cases there is no long-range order at finite temperatures due to the divergent thermal fluctuations. However, for *classical* systems the ground state at $T = 0$ has long-range order just as in three dimensions; further, the excitations at $T = 0$ are predicted to be just simple spin waves as in three dimensions. The behavior at finite temperatures even for classical systems is, however, quite different from three dimensions. In particular, we expect sharp spin-wave excitations even in the absence of long-range order provided that one is in the regime $q \gg \kappa$. The evolution of the dynamics as one goes from q much smaller than κ to much larger than κ will be of particular interest. The quantum spin-$\frac{1}{2}$ antiferromagnets are clearly much subtler than the classical models. Here, there is not a long-range ordered state even at $T = 0$. Nevertheless, one finds for the Heisenberg and XY antiferromagnets a locus of first excited states with q-dependence identical to that of the classical spin wave solutions. The

nature of these states and of the spin excitations as a whole remains an open question. Perhaps, it is a question best answered by experiment rather than by more exact results.

Experimental results

Let us now turn our attention back to real experimental systems in order to determine how relevant all of the above is to the physical world. Here we shall emphasize two of the materials listed in the table, namely, $(CD_3)_4NMnCl_3$, or TMMC, and $CuCl_2{\cdot}2NC_5D_5$, or CPC. These are, to a certain extent, physical realizations of the linear classical Heisenberg antiferromagnet and the linear spin-½ Heisenberg antiferromagnet. We begin our discussion with TMMC, which is in fact, the progenitor of modern one-dimensional experimental research. We have already discussed some of the evidence for the predominance of one-dimensional effects in TMMC. The system is, of course, quantum rather than truly classical in nature. However, as we said earlier for manganese $1/S$ is small enough that we can hope a classical theory will be adequate. We have already seen that the exact result for the susceptibility of a classical Heisenberg antiferromagnet describes the measured value in TMMC rather well.

To confirm the one-dimensional nature of the magnetism in TMMC directly we probe the spatial structure of the correlations using neutrons; that is, we measure $S(\mathbf{q})$. Figure 4 shows the results of measurements[9] of $S(\mathbf{q})$ with $\mathbf{q}$ scanned along q_z. As anticipated, one does indeed observe Lorentzian scattering centered about $q_z a = \pi$. This confirms that there are simple antiferromagnetic correlations along the chain. Measurements at fixed q_z with q_x and q_y varied show that the scattering is independent of q_x and q_y, that is, that one is observing *planes* of scattering rather than *peaks* as in a typical three-dimensional system. The neutrons are, of course, simply performing a spatial Fourier analysis of the instantaneous correlations. The fact that the cross section is planar in q-space means that the correlations are exclusively linear in real space; this result holds down to at least 0.9 K. One may now analyze the measurements quantitatively using our earlier results. The width of the peaks gives κ, the inverse correlation length; the peak height gives the value of $S(q)$ for $q = \pi$. The results of this analysis are shown in figure 5. From the figures it may be seen that both the inverse peak height and the inverse correlation length extrapolate to 0 at $T = 0$ K. This may be regarded as direct experimental proof that an idealized one-dimensional system will only admit a long-range ordered state at $T = 0$! The black line in figure 5 corresponds to the exact results discussed previously for the *classical* Heisenberg model. The agreement between theory and experiment is clearly very good.



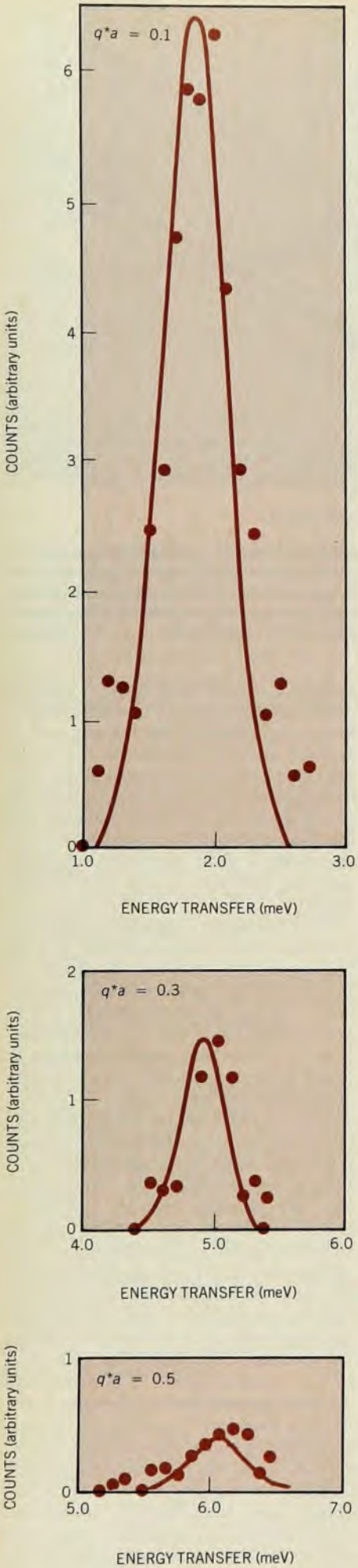
Inverse correlation length as a function of temperature for TMMC. The black curve shows the results of the classical theory discussed in the text with parameters appropriate for TMMC (a = 3.21 Å, $2JS^2$ = 135 K); the experimental points are the results of neutron scattering experiments such as those shown in figure 4. The colored curve and experimental points show the comparable results for TMMC doped with 15% of copper. (Adapted from reference 9.) Figure 5

We remind the reader that at low temperatures the classical theory predicts sharp spin-wave excitations, provided that q_z is much larger than κ. A series of scans at varying wave vector q_z are shown in figure 6. From the figure it is evident that $S(\mathbf{q},\omega)$ is indeed characterized by sharp excitations. The solid lines represent the predictions of simple spin-wave theory for $S(\mathbf{q},\omega)$ convoluted with the instrumental resolution function. Both the energies and the relative intensities, and hence eigenfunctions, are well accounted for. The experimental energies are plotted as a function of qa in figure 4 with $|J| = 6.47$ K. The predicted sine-wave dispersion curve is indeed obtained. There is, however, a small consistent discrepancy between the observed energies and the classical spin wave theory. Calculations by a variety of authors suggest that for $S = 5/2$ the classical spin wave energies should be renormalized by 7 to 8%. This brings theory and experiment into near perfect agreement.

But are these really perfectly well-defined excitations? From our heuristic discussion as well as the exact theory we expect that for $q_z \gg \kappa$ the spin waves will have an energy width of the order $\kappa d\omega/dq$ and that the line shape should evolve as q changes from large values to small. We show in figure 7 very high-resolution measurements of the magnetic scattering from TMMC. They show beautifully the evolution from propagating to diffusive behavior as q changes from greater than to less than κ.

In general, it is clear that most of the physics anticipated in an ideal linear system is found in TMMC. Further there is gratifying accord between experiment and classical spin theory. It is perhaps worth noting that the theory for the static correlations preceded the neutron experiments, whereas essentially all of the theory for the finite temperature dynamics followed the experiments. This represents a most gratifying symbiotic coupling between theory and experiment.

With this rather complete experimental picture of the classical (or rather, $S = 5/2$) one-dimensional Heisenberg model we would now like to proceed to the quantum limit. As we noted previously, a very good realization of the one-dimensional $S = 1/2$ Heisenberg antiferromagnet is found in the compound $CuCl_2{\cdot}2NC_5D_5$, dichloro-bis-pyridine copper II (CPC). The Cu^{++} ($3d^9$) has its orbital moment quenched by the crystal field so that one is left with a spin-½ system with Heisenberg exchange interactions. In this case one has strongly bonded $CuCl_2N^{--}$ chains similar to the $MnCl_3^-$ chains shown in figure 1. The chains are kept well separated by the large pyridine ions. From a combination of electron spin resonance, susceptibility and specific heat measurements one is able to conclude that the exchange is accurately isotropic, with $J/k = -13.4 \pm 0.2$ K. The mean-field ordering temperature for the spins in the chain is therefore $T_{MF} = 13.4$ K; the actual ordering temperature is $T_N = 1.14$ K. CPC is clearly less one-dimensional than TMMC; nevertheless, for $T > 1.14$ K one should see predominantly one-dimensional fluctuation behavior. Hence we should be able to address some of the



Spin wave peaks as a function of wave vector in TMMC. The solid lines are the prediction of a simple classical theory convoluted with the instrumental resolution. Neutron-scattering results are shown for several wave vectors near $\pi(q^* = q - \pi/a)$. Figure 6

issues raised by the theory for this quantum system.

Detailed neutron-scattering studies[11] in CPC have indeed demonstrated the existence of well-defined peaks in $S(q,\omega)$. We plot in figure 3 the peak energy in reduced units as a function of q. It is evident that the agreement with the des Cloizeaux–Pearson calculation is excellent. This represents one of those rare cases in physics where π is determined from an amplitude rather than a phase. (The explicit value obtained $\pi = 3.2 \pm 0.1$, is, however not overly impressive in its accuracy!) Yasuo Endoh and his coworkers also determined approximately the integrated intensity of the excitations in $S(q,\omega)$ and they found rather good agreement with the predictions of ordinary spin-wave theory. Thus the des Cloizeaux–Pearson excitations may be validly described as "spin waves." It should be noted however that the experimental intensity falls below the theoretical spin-wave value for qa near π.

There are still many unanswered questions for the quantum Heisenberg chain. Firstly, experiments indicate that the temperature evolution is quite similar for the des Cloizeaux–Pearson excitations and for classical spin waves; there is no theory for the quantum chain at finite temperatures. Secondly, no information is available on the instantaneous correlations at finite temperatures either from experiment or theory. The behavior of the $S = \frac{1}{2}$ Heisenberg antiferromagnet in a magnetic field is expected to be particularly interesting, and again there is very little experimental information. Finally, more recent theory[12] has suggested that the excitations in zero field should be extended in energy, with the des Cloizeaux–Pearson states representing the low-energy threshold; initial experiments appear to support this result, although there is a compelling need for improved experiments and theory. Clearly this still represents a rich problem for both theorists and experimentalists. At the same time, it is perhaps amazing that a mathematical exercise, the $S = \frac{1}{2}$ one-dimensional Heisenberg chain, begun by Bethe in 1931, has ended up being tested and elucidated in great detail by experiments on a real material, CPC.

In this discussion we have accentuated the role of neutron scattering, primarily because it is the only probe capable of giving information about the spin correlations over all distances and at all times, subject, of course, to resolution limitations. We should mention however that resonance techniques, both nmr and especially epr, also have yielded valuable information about one-dimensional Heisenberg spin dynamics. Both techniques probe the dynamics at very low energies, and therefore elucidate the dynamics for small q, most notably the long-time diffusive behavior. Unfortunately, the theory appropriate to these probes is rather complicated so we shall not discuss them further in this article.

For the one-dimensional Heisenberg systems, the experiments are quite advanced. It is therefore appropriate to ask what new issues might one consider addressing in one dimension. It turns out, of course, that there is a cornucopia of interesting, substantive problems. We shall first discuss one of these in detail and we shall then mention some other problems of future importance.

Disordered systems

For the past decade, a great deal of research has been carried out in disordered systems. Work has tended to focus on two separate physical aspects.

- The percolation problem—in this case, one has a sufficiently large number of broken bonds, or in the case of magnetism, missing spins, that the system is on the threshold of breaking up into a set of disconnected finite clusters.
- Random excitations—here one is interested in the nature of the excitations for systems with large fluctuations in the potential and/or in the transfer matrix elements. Each of these problems is easily studied in magnetic insulators by preparing appropriate substitutional alloys.

As for the pure systems, the mathematics connected with the cooperative behavior of disordered magnets becomes very much easier in one dimension; indeed in certain cases, exact results are obtainable. As an example we consider the problem of a one-dimensional magnetic binary alloy. We begin with the simplifying assumption that the spins may be treated as *classical* variables, and we assume nearest-neighbor Heisenberg exchange along the chain. The Hamiltonian is therefore

$$\mathcal{H} = \sum_i [p^2 J_{11} \mathbf{S}_i^{(1)} \cdot \mathbf{S}_{i+1}^{(1)} + p(1-p) J_{12} (\mathbf{S}_i^{(1)} \cdot \mathbf{S}_{i+1}^{(2)} + \mathbf{S}_i^{(2)} \cdot \mathbf{S}_{i+1}^{(1)}) + (1-p)^2 J_{22} \mathbf{S}_i^{(2)} \cdot \mathbf{S}_{i+1}^{(2)}]$$

where p is the probability that a site is occupied by a spin of species 1. Not surprisingly, the techniques developed by Fisher for the pure chain may be immediately taken over for the random chain. Gratifyingly, one may solve for the instantaneous correlations and hence the static thermodynamic properties exactly.[13] We shall not quote the general results here; we shall instead consider two limits of special physical interest. Firstly, we consider the percolation regime in which we have a small number of non-

magnetic impurities that is, $p \lesssim 1, J_{12} = J_{22} = 0$. It is obvious that the percolation threshold in one dimension occurs for p infinitesimally close to one, since a single impurity ($p = 1 - 1/N$) breaks the chain into two parts, destroying the infinite connectivity. By contrast, for a two-dimensional square lattice with nearest-neighbor bonds the site percolation threshold is $p_c = 0.59$. The thermodynamic behavior of magnets with $p \approx p_c$ at finite temperatures has recently been a subject of active research. However, our understanding of magnetism in this regime is still quite limited. A very interesting result suggested by experiments in two- and three-dimensional magnets is that the inverse correlation length at finite temperatures in percolation clusters with $p < p_c$ may be written

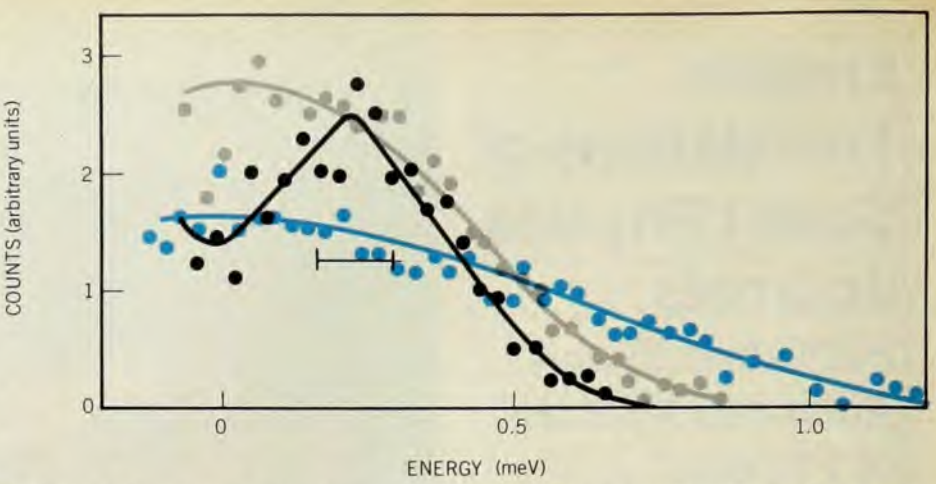
$$\kappa = \kappa_T + \kappa_G$$

where κ_T (T for thermal) is the inverse correlation length in the infinite network at temperature T and κ_G (G for geometrical) is the geometrical inverse correlation length characterizing the size of the percolation clusters. Thus at very high temperatures one expects $\kappa \simeq \kappa_T$ while at $T = 0, \kappa = \kappa_G$. Theory has not yet been able to provide a fundamental basis for this additive property of κ. It is therefore of interest to look at the results in one dimension. From the exact solution[12] we find for a linear magnet with non-magnetic impurities

$$\kappa_p(T) = \kappa_\infty(T) + (1 - p)/a$$

where κ_∞ is Fisher's value, given earlier, for the infinite chain and $(1 - p)$ is the concentration of impurities. It is clear that $a/(1 - p)$ is the mean size of the magnetic blocks in the random chain so that for this case κ_G, the reciprocal of the mean size is $(1 - p)/a$. Thus the heuristic formula suggested by experiments in two and three dimensions turns out to be an exact relationship in one dimension.

Let us now change our physical model from one with non-magnetic impurities to one with a small number of *weak links;* that is, we assume p is small and $J_{11} \gg J_{12}$. For simplicity we shall assume that the number of impurities is small enough that we can ignore disruptions of the chain due to pairs of impurities. It is clear that this model is a close analogue to the frequently used model of one-dimensional conducting chains with intermittent weak links. Let us now consider the probable behavior of such a system. At intermediate temperatures, that is, $kT \lesssim J_{11}S_1^2$, correlations will develop within the strongly coupled segments of the chain; however, for $J_{12}S_1S_2 \ll J_{11}S_1^2 \approx kT$ no information will be propagated through the weak links due to the large thermal disorder. Thus we may effectively take $J_{12} = 0$ and we expect percolation behavior as described above. Now suppose the temperature is lowered so that $J_{11}S_1^2 \gg kT \approx J_{12}S_1S_2$; in this temperature range the spins in the segments between the weak links will be strongly correlated and hence will respond like one rigid spin. Thus we now have defined a new one-dimensional problem with renormalized spins each coupled with energy $J_{12}S_1S_2$; we therefore expect to return to pure system behavior but with a much weaker interaction energy. As we discuss below this heuristic picture is confirmed by the exact results and by experiment.



High resolution scans of magnetic scattering in TMMC. The scattered intensity at $q^*a = \pi - qa = 0.015$, is shown for temperatures of 9.0 K (color), 4.3 K (grey), and 1.45 K (black); corresponding values of κa are 0.022π, 0.010π, and 0.0034π. Note the appearance of a well-defined peak when $q^* \gg \kappa$. The bar shows the experimental resolution. (Adapted from reference 10.) Figure 7

The above "weak-link" system may be realized in nature simply by doping TMMC with copper; that is, one prepares $(CD_3)_4N\ Mn_p\ Cu_{1-p}\ Cl_3$. As before the classical spin approximation should again be valid for Mn^{++}; however, for Cu^{++} we have $S = \frac{1}{2}$, so that the classical spin approximation will not be valid for the Cu^{++} links; however, we expect quantitative rather than qualitative changes in the behavior due to quantum effects. From measurements using epr and susceptibility techniques one may conclude that the ratio $J_{12}S_2/J_{11}S_1$, is about -0.04 for Cu-Mn and Mn-Mn, so that the link is indeed weak.

Recently, extensive neutron-scattering experiments performed on the TMMC: Cu system at Brookhaven and at Grenoble[14] have found quasielastic spectra $S(q_z)$ very similar to those of figure 4. The results are illustrated for TMMC doped with copper in figure 5. It is evident that the heuristic picture we gave above is, in fact, confirmed. For $T > 4$ K, the inverse correlation length in the doped samples is, to a first approximation, simply shifted uniformly by $1 - p$. At about 4 K there is a marked crossover, and the inverse correlation length begins to go to zero linearly, that is the correlation length diverges as $1/T$. Thus, at low temperatures the doped chain does indeed act like a renormalized system in which the manganese segments act like single spins and the divergence of the correlation length is controlled by the "weak links." The colored line in figure 5 represents the result of the exact solution to the classical random-chain Hamiltonian; once more, the agreement is very good.

Charge-transfer salts

Let us now discuss briefly a final topic of continuing importance in one-dimensional magnetism. One of the most interesting classes of one dimensional compounds is that of organic charge-transfer salts. These are systems composed of planar organic complexes that may typically have either strong electron acceptor or electron donor properties. These planar complexes tend to stack on top of each other, forming pseudo-one-dimensional compounds. The range of properties which they exhibit is quite remarkable. A subset of them do indeed seem to exhibit true one-dimensional behavior. However, in contrast to the transition-metal compounds we have focussed on, the relevant microscopic Hamiltonian may be quite complicated. Accordingly, both theory and experiment for these systems are much less developed than those we have discussed.

Partially because of the work on these organic charge-transfer salts a number of other one-dimensional theoretical and experimental issues have come to the fore. These include spin-dimerization and magnetic-field driven commensurate–incommensurate transitions in the spin-$\frac{1}{2}$ antiferromagnetic chain. As we noted above, *disorder* has important effects on one-dimensional chains and especially on the nature of the cross-over from one-dimensional to three-dimensional behavior. We have shown that for simple site disorder, theory and experiment are in good accord; however, more complicated disorder seems to occur in the organic salts, and much work remains to be done before we can claim a full understanding. All of these phenomena are

currently the subject of much active research, and we can foresee much progress in the near future.

Epilogue

There are, of course, many aspects of one-dimensional magnetism that we have not discussed here. We hope that we have, nevertheless, succeeded in communicating the basic flavor of these studies. Because of the low dimensionality, fluctuation effects are essentially everything. In spite of this, in certain regimes, one observes well defined excitations, while in others disorder prevails. Studies of one-dimensional systems are characterized by a rich coupling between theory and experiment because certain idealized models are exactly soluble, and because Nature offers us real physical systems that correspond remarkably closely to these idealized models.

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