

²¹D. F. Moore, M. R. Beasley, and J. M. Rowell, in Proceedings of the Fifteenth International Conference on Low Temperature Physics, Grenoble, France, August 24, 1978 (to be published).

²²P. B. Allen, W. E. Pickett, K.M. Ho, and M. L. Cohen, Phys. Rev. Lett. **40**, 1532 (1978).

²³L. L. Boyer, Bull. Am. Phys. Soc. **23**, 433 (1978), and Phys. Rev. B (to be published).

Temperature-Dependent Single-Ion Excitations in Anisotropic Paramagnets

M. E. Lines

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 1 December 1978)

By an exact calculation for an Ising chain it is established that single-ion (electronic) energy levels are temperature dependent in anisotropic paramagnets. The effect is produced by developing anisotropic spin-spin correlations and, in a more general context, is investigated using the correlated-effective-field statistical approximation. It should be directly observable by spectroscopic means in strongly anisotropic paramagnetic systems.

Most crystal-field-split electronic excitations involving magnetic ions in concentrated magnetic systems are dispersionless.¹ They can therefore be thought of as effective "single-ion" excitations. The exceptions are those which involve levels possessing nonzero matrix elements of exchange energy with thermally populated states.²⁻⁷ Although optical spectra dominantly contain modes in the latter category (at least in absorption) the gross effects of magnetic order upon them are in fact often well accounted for by simple (dispersionless) molecular-field theory,^{8,9} due presumably to the relative smallness of the relevant matrix elements for these cases. In this picture, the single-ion excitations are shifted or split by the internal molecular field in an ordered magnetic phase, but become temperature independent above the ordering temperature where this internal field averages to zero. To my knowledge this temperature independence for paramagnetic phases is still commonly assumed and no more accurate theoretical discussion has ever been presented. Experimental evidence for paramagnetic line shifts is scant, but I have found one paper¹⁰ which claims such an observation in $Dy_3Al_5O_{12}$.

In this Letter I establish by an exact calculation for an Ising linear-chain model that single-ion energy gaps can indeed be significantly temperature dependent in a disordered anisotropic magnetic system. In a more general context I note that the correlated-effective-field (CEF) theory of magnetism¹¹ suggests that this temperature dependence is present in all paramagnetic systems which possess uniaxial or lower magnetic anisotropy although the effect may be small

unless that anisotropy is marked. The effect is produced by developing anisotropic spin correlations as temperature is lowered and the CEF theory appears, by comparison with the exact results in the Ising chain limit, to be an adequate approximation in most physical situations.

Consider first a spin-1 closed Ising linear chain with single-ion anisotropy, described by the Hamiltonian

$$\mathcal{H} = \sum_{n=1}^N [D(S_n^z)^2 - 2JS_n^z S_{n+1}^z], \quad (1)$$

where spin quantum number $S=1$, number of spins $N \rightarrow \infty$, and $S_{N+1}^z \equiv S_1^z$. Regrouping the terms in the form

$$\mathcal{H} = \sum_{n=1}^N [\frac{1}{2}D(S_n^z)^2 + \frac{1}{2}D(S_{n+1}^z)^2 - 2JS_n^z S_{n+1}^z], \quad (2)$$

one notes that the partition function Z can be expressed in S^z representation as

$$Z = \text{tr} \prod_{n=1}^N V_n, \quad (3)$$

in which all the matrices V_n have an identical Hermitian form

$$V_n = V = \begin{pmatrix} e^{-\beta(D-2J)} & e^{-\beta D/2} & e^{-\beta(D+2J)} \\ e^{-\beta D/2} & 1 & e^{-\beta D/2} \\ e^{-\beta(D+2J)} & e^{-\beta D/2} & e^{-\beta(D-2J)} \end{pmatrix}, \quad (4)$$

where $\beta = 1/kT$ and the product \prod implies simple matrix multiplication.

By a unitary transformation $V' = \mathcal{S}^{-1}V\mathcal{S}$ the matrix V can be diagonalized in the form

$$V' = \begin{pmatrix} z & 0 & 0 \\ 0 & z_+ & 0 \\ 0 & 0 & z_- \end{pmatrix}, \quad (5)$$

where

$$z = 2e^{-\beta D} \sinh(2\beta J), \quad (6)$$

$$z_{\pm} = 2e^{-\beta D} \cosh(2\beta J) + 1 \pm \{ [2e^{-\beta D} \cosh(2\beta J) - 1]^2 + 8e^{-\beta D} \}^{1/2}. \quad (7)$$

Quite generally the largest eigenvalue is z_+ so that, for $N \rightarrow \infty$, we have

$$Z^{-1} \prod_{n=1}^N V_n = (z^N + z_+^N + z_-^N)^{-1} \begin{pmatrix} z^N & 0 & 0 \\ 0 & z_+^N & 0 \\ 0 & 0 & z_-^N \end{pmatrix} \rightarrow \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \rho_1'. \quad (8)$$

The diagonal elements of this matrix make up, by definition, the one-spin Boltzmann distribution for the problem. Transforming back (i.e., forming the product $\delta\rho_1' S^{-1}$) to the S^z representation we find the one-spin density matrix

$$\rho_1 = N_+^{-2} \begin{pmatrix} \theta_+^2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \theta_+^2 \end{pmatrix}, \quad (9)$$

in which

$$\theta_+ = \frac{1}{4} e^{\beta D/2} [z_+ - 2] \quad (10)$$

and

$$N_+^{-2} (2\theta_+^2 + 1) = 1. \quad (11)$$

Writing this matrix as $\exp(-\beta\mathcal{H}_i)$ for the i th spin, we find the single-ion energy levels E_m ($m = 0, \pm 1$) in the form

$$E_0 = 0, \quad (12)$$

$$E_{\pm 1} = E_{-1} = -2kT \ln \left[\frac{1}{4} e^{\beta D/2} \left(2e^{-\beta D} \cosh(2\beta J) - 1 + \{ [2e^{-\beta D} \cosh(2\beta J) - 1]^2 + 8e^{-\beta D} \}^{1/2} \right) \right]. \quad (13)$$

Since $\langle \pm 1 | S^z | 0 \rangle = 0$ the excitation $E_{\pm 1} - E_0$ is dispersionless. The significant observation is that it is also temperature dependent. At high temperatures $T \rightarrow \infty$, one readily verifies the expected (random phase) limit $E_{\pm 1} - E_0 \rightarrow D$. At low temperatures, anisotropic spin correlations develop $\langle S_n^x S_{n+1}^x \rangle \neq 0$, $\langle S_n^x S_{n+1}^y \rangle = \langle S_n^y S_{n+1}^y \rangle = 0$ and, unless $D > 0$ and $D \geq 2|J|$, they finally saturate as $T \rightarrow 0$ to produce the low-temperature limiting form $E_{\pm 1} - E_0 \rightarrow D - 4|J|$. If $D > 0$ and $D > 2|J|$, the exchange interactions are not strong enough to overcome the effects of the crystal field (which favors the $S^z = 0$ local state) in the low-temperature limit, and the zz correlations pass through a maximum with decreasing temperature to vanish again as $T \rightarrow 0$. The corresponding $T \rightarrow 0$ energy gap is $E_{\pm 1} - E_0 = D$. The two qualitatively different situations are exemplified by Figs. 1 and 2, where we compute the energy gap numerically from (12) and (13) for the cases $D = 10k$, $J = 2k$ and $D = 10k$, $J = 10k$, respectively.

Having established the existence of temperature-dependent single-ion energy gaps by exact calculation for one particular example, we now examine the phenomenon in a more general con-

text. Since the effect is clearly absent in the random-phase approximation, it is necessary to go to an approximation which at very least takes some cognizance of the existence of static (i.e., equal-time) fluctuation phenomena. One such ap-

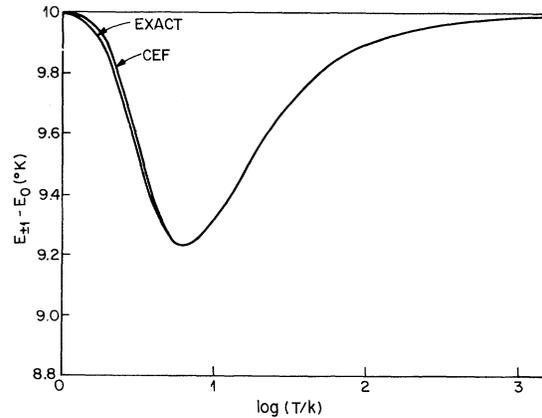


FIG. 1. The single-ion excitation between the $S^z = 0$ and $S^z = \pm 1$ states as a function of temperature for the Ising chain of Eq. (1) with $D = 10k$ and $J = 2k$.

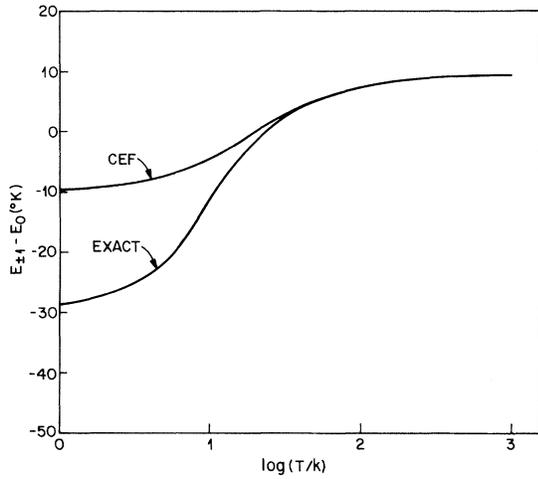


FIG. 2. As in Fig. 1, but for parameter values $D = 10k$ and $J = 10k$.

proximation is the CEF scheme set out in Ref. 11. For a many-body Hamiltonian

$$\mathcal{H} = \sum_i \mathcal{H}_i - \sum_i \sum_j \sum_\lambda J_{ij}^\lambda S_i^\lambda S_j^\lambda \quad (14)$$

in which \mathcal{H}_i defines the isolated-ion crystal-field energy levels, the equations of motion for the spin components S_i^μ ($\mu = x, y, z$) at the i th site involve effective-field operators $h^\lambda = \sum_j 2J_{ij}^\lambda S_j^\lambda$, where $\mu \neq \lambda$. In augmenting the random-phase approximation $h^\lambda \approx h_{\text{RPA}}^\lambda = \sum_j 2J_{ij}^\lambda \langle S_j^\lambda \rangle$, the CEF reads

$$\dot{h}^\lambda \approx h_{\text{CEF}}^\lambda = \sum_j 2J_{ij}^\lambda [\langle S_j^\lambda \rangle + \alpha^\lambda (S_i^\lambda - \langle S_i^\lambda \rangle)], \quad (15)$$

including a measure α of the instantaneous correlation between \vec{S}_i and its neighbors \vec{S}_j . These parameters α^λ are temperature dependent and can be determined completely by use of the fluctuations theorem. The resulting CEF equations of motion can be determined formally, i.e., $\dot{S}_i^\mu = (i/\hbar)[\mathcal{H}_i(\text{eff}), S_i^\mu]$ from an effective single-ion Hamiltonian $\mathcal{H}_i(\text{eff})$. In a paramagnetic phase and in the absence of an applied field, this Hamiltonian takes the form¹¹

$$\mathcal{H}_i^0(\text{eff}) = \mathcal{H}_i - \sum_j \sum_\lambda J_{ij}^\lambda \alpha^\lambda (S_i^\lambda)^2. \quad (16)$$

Clearly in the high-symmetry situation with $J_{ij}^\lambda = J_{ij}$ and $\alpha^\lambda = \alpha$ ($\lambda = x, y, z$) the last term in Eq. (16) reduces to $-\sum_j J_{ij} \alpha S(S+1)$, a trivial constant and, regardless of the temperature dependence of the ensuing spin correlations α , the crystal-field energy gaps will be temperature independent and just those of the isolated-ion Hamiltonian \mathcal{H}_i . More generally, however, the eigenlevels of $\mathcal{H}_i^0(\text{eff})$ will differ from those of \mathcal{H}_i in

a physically significant way, and the energy gaps will be temperature dependent. For single-ion excitations, as defined earlier, these temperature-dependent gaps will represent actual dispersionless excitations of the many-body system. For others the eigenfunctions and eigenlevels of (16) serve only as an effective-field basis for the description of wave-vector-dependent propagating excitations. Even here, however, a neglect of the last term in Eq. (16), i.e., the use of RPA, may produce serious errors in the predicted temperature dependence of the resulting mode dispersion.

Finally, we use the CEF theory in the Ising linear-chain context of Eq. (1) to examine its reliability. For this case only α^z is nonzero. It is given by

$$\alpha^z = -t_z + (1 + t_z^2)^{1/2}, \quad (17)$$

where

$$t_z = \frac{kT[1 + 2 \exp(-E/kT)]}{8J \exp(-E/kT)}, \quad (18)$$

and

$$E = D - 2\alpha^2 J \quad (19)$$

is the energy separation $E_{\pm 1} - E_0$. The numerical results for $D = 10k$, and $J = 2k$ and $10k$ are also plotted in Figs. 1 and 2. It is clear that CEF is essentially a weak-correlation theory. In Fig. 1, for which correlation $\alpha^z = \langle S_n^z S_{n+1}^z \rangle / \langle (S_n^z)^2 \rangle$ never exceeds values ~ 0.2 , the CEF approximation is quantitative. In Fig. 2 the CEF theory is quantitative at higher temperatures but, as a measure of temperature variation, is in error by a factor 2 as $T \rightarrow 0$. The error is about 16% at $\alpha^z = 0.5$. Since in three-dimensional paramagnets correlations ≥ 0.3 do not normally occur, the CEF approximation should be adequate for most real systems.

In an experimental context, what we have calculated is the *equilibrium* energy splitting. Experimental observations by spectroscopic methods¹² will, unless the excitation frequency is smaller than the spin relaxation rate, possess an exchange-induced line shape reflecting the probability distribution of spin correlations about their ensemble average. This line shape is determined by spin dynamics and we present no calculation of such details in this Letter. The energy shifts [e.g., of Eq. (19)] then represent the temperature variation of the center of area of the relevant lines. These will correspond fairly closely to the line peaks except in one inter-

esting limit—the near-neighbor Ising limit. Here eigenstates of S^z are eigenstates of the complete Hamiltonian and the predicted temperature variation will appear only as a weighted *intensity* average over a few temperature-independent lines [e.g., at energies D and $D \pm 4J$ for Eq. (1)] unless the excitation frequency is less than the spin relaxation rate.

In summary we find that single-ion paramagnetic excitations will be temperature dependent in anisotropic magnetic systems, the magnitude of the effect being proportional to the product of ground-state exchange and the degree of correlation anisotropy. The effect should therefore be completely absent for magnetic moments in a cubic environment (e.g., for systems like KNiF_3 , EuS , NiO , CoO , Pr_3Tl), should be present but small for S -state ions in a lower-symmetry environment (e.g., MnF_2 , KFeF_4 , BaMnF_4 , GdCl_3), and should be largest in highly anisotropic materials like K_2CoF_4 , Rb_2FeF_4 , CoCl_2 , RbFeCl_3 , CoF_2 , $\text{Dy}_3\text{Al}_5\text{O}_{12}$, and (double-hep) Pr.

¹M. E. Lines, Phys. Rev. B **11**, 1134 (1975), Eq. (3.16).

²Y. L. Wang and B. R. Cooper, Phys. Rev. **172**, 539 (1968), and **185**, 696 (1969).

³R. J. Birgeneau, in *Magnetism and Magnetic Materials—1972*, AIP Conference Proceedings No. 10, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1973), p. 1664.

⁴Y. Y. Hsieh, Phys. Rev. B **8**, 3459 (1973).

⁵M. E. Lines, J. Phys. C **7**, L287 (1974).

⁶W. J. L. Buyers, T. M. Holden, and A. Perreault, Phys. Rev. B **11**, 266 (1975).

⁷P. Bak, Phys. Rev. Lett. **34**, 1230 (1975).

⁸S. Sugano and Y. Tanabe, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. 1, Chap. 6.

⁹K. A. Wickersheim, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. 1, Chap. 7.

¹⁰A. H. Cooke, K. A. Gehring, M. J. M. Leask, D. Smith, and J. H. M. Thornley, Phys. Rev. Lett. **14**, 685 (1965).

¹¹M. E. Lines, Phys. Rev. B **9**, 3927 (1974).

¹²For example, by Raman scattering or by infrared or optic absorption or fluorescence.

First-Order Phase Transition and Critical Neutron Scattering in Chromium

Hiroshi Betsuyaku

Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan

(Received 21 August 1978)

The critical behavior of Cr near the first-order antiferromagnetic transition at 38.5°C has been studied by neutron scattering. This study reveals the existence of a sharp central peak at the satellite position in a narrow temperature range just above T_N . It exhibits a very singular temperature dependence such as the two-dimensional planar model predicts. Such unusual behavior supports the conjecture that the two-dimensional planar model is realized in the critical region of Cr.

Metallic chromium, Cr, is known to exhibit a very interesting itinerant antiferromagnetism, and many of its properties have been studied extensively.¹ An investigation of very pure, nearly strain-free Cr showed that the paramagnetic-antiferromagnetic phase transition at $T_N = 38.5^\circ\text{C}$ is of first order.² Despite numerous attempts based on the itinerant theory of magnetism to clarify the origin of this transition,^{3,4} no satisfactory explanation has been reported yet. However, only quite recently have Bak, Krinsky, and Mukamel (BKM)⁵ given arguments based on the renormalization-group theory that certain phase transitions which involve a doubling of the unit cell should be first order. Cr exhibits a transverse sinusoidal magnetic structure with

propagation vector $\vec{Q} = [Q\ 0\ 0]$. Accordingly, the order parameter appropriate for describing phase transition in Cr has twelve independent components. The Landau-Ginzburg-Wilson Hamiltonian for the system with twelve-component vector has no stable fixed point in the ϵ expansion, which has been asserted to explain the first-order nature of the transition in Cr. Nevertheless, their theory has the following defect: Cooling through T_N in zero magnetic field produces an "apparent cubic" state²; that is, the satellite reflection $\vec{q} = [\pm Q\ 0\ 0]$, $[0 \pm Q\ 0]$, and $[0\ 0 \pm Q]$ have equal intensity. The "apparent cubic" state cannot be interpreted unambiguously. For example, it may in fact be a "triple- \vec{Q} " state with three equal-amplitude \vec{Q} 's coexisting in every region of the crystal.