Temperature Dependence of Short-Wavelength Magnon Frequencies: Relation to Heat Capacity*

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(Received 8 July 1969)

A relation between the temperature dependence of the energies of short-wavelength magnons and the heat capacity is presented. This relation, which has no adjustable parameters, is in perfect agreement with all available data for $T \lesssim 0.7T_N$. For NiF_2, agreement is up to T_N. The relation can be used to determine the magnon contributions to the heat capacity of magnetic solids.

RECENT experimental results on the temperature dependence of antiferromagnetic magnon frequencies have been obtained by neutron diffraction,[1–4] Raman scattering,[5–8] infrared absorption,[9,10] and from analysis of magnon induced sidebands on what otherwise would be weakly allowed optical transitions.[11] For the most part, the published theoretical approaches to this problem[12–17] have consisted of attempts to develop some type of self-consistent approach to treating the nonlinear terms that arise from expanding the Holstein-Primakoff transformation as a power series in the Bose operators. One exception to this general pattern has been the paper by Keffer and Loudon[16] in which the authors point out that a number of physical results can be understood by recognizing that although thermal effects can cause the angle between the instantaneous orientation of a given spin and its mean orientation to be quite large, the actual angle between the instantaneous orientations of adjacent spins can be smaller. The primary object of this paper is to point out that this fact also explains the observed temperature dependences of short-wavelength magnon frequencies. An heuristic argument based on this idea obtains a relation between these frequencies and the spin contribution to the heat capacity of the solid. This relation, having no adjustable parameters, is in amazingly good agreement with the available data. The secondary object of this paper is to suggest that the above relationship may be the best available method for obtaining a measure of the magnon contribution to the heat capacity. The main difficulties in obtaining this measure by direct application of heat-capacity techniques arise when one attempts to separate the magnon contributions from the lattice contributions.[18] For some of the more complicated materials, like the perovskites, for example, the lattice specific heat is too large a fraction of the total specific heat to be able to facilitate this separation at the present time.[19] On the other hand, these crystals are often the ones for which the magnon frequencies are most readily measured.

To understand the above-mentioned temperature dependence, we consider only the special case of an Heisenberg antiferromagnet. The argument to be presented can readily be generalized to more complex Hamiltonians. The present Hamiltonian has the form

$$\mathcal{H} = J \sum_{m(n),n} \mathbf{S}_n \cdot \mathbf{S}_{m(n)}, \tag{1}$$

where $m(n)$ is intended to indicate only the nearest neighbors of the spin S_n. On taking the commutation $[\mathcal{H},\mathbf{S}_n]$, one obtains the vector-operator equation

$$\dot{\mathbf{S}}_n = -2J\hbar^{-1}[\sum_{m(n)} \mathbf{S}_{m(n)}] \times \mathbf{S}_n. \tag{2}$$

Although this is not the most usual procedure, the spin-wave approximation can be introduced into Eq. (2) in order to obtain equations for the Bose operators of the form $\dot{a}(\mathbf{q}) \pm i\omega(\mathbf{q})a(\mathbf{q}) = 0$. The $\omega(q)$ depend on both J and

$$\gamma(\mathbf{q}) = \sum_{m(n)} \exp[i\mathbf{q} \cdot (\mathbf{R}_{m(n)} - \mathbf{R}_n)],$$

where $\mathbf{R}_{m(n)} - \mathbf{R}_n$ is the displacement vector connecting n and $m(n)$. For short wavelengths, $1 \gg |\gamma(\mathbf{q})| > 0$. In the spin-wave approximation at $T = 0$, the condition on q that $|\gamma(\mathbf{q})| = 0$ leads to

$$\omega(\mathbf{q}) = 2J\hbar^{-1}\langle \sum_{m(n)} S_{m(n)} \rangle = 2rJ\hbar^{-1}S,$$

* Work supported in part by the Advanced Research Projects Agency, the National Aeronautics and Space Administration, and by the Division of Engineering and Applied Physics, Harvard University.

[1] P. Martel, R. A. Cowley, and R. H. W. Stevenson, J. Appl. Phys. **39**, 1116 (1968).
[2] T. Riste and A. Wanic, J. Phys. Chem. Solids **17**, 318 (1961).
[3] T. Oguchi and A. Honma, J. Phys. Soc. Japan **16**, 79 (1961).
[4] K. C. Turberfield, A. Okazaki, and R. H. W. Stevenson, Proc. Phys. Soc. (London) **85**, 743 (1965).
[5] P. A. Fleury, Phys. Rev. **180**, 591 (1969).
[6] P. Moch, G. Parisot, R. E. Dietz, and H. J. Guggenheim, Phys. Rev. Letters **21**, 1596 (1968).
[7] A. Oseroff and P. S. Pershan, Phys. Rev. Letters **21**, 1593 (1968).
[8] P. A. Fleury, S. P. S. Porto, L. E. Cheesman, and H. J. Guggenheim, Phys. Rev. Letters **17**, 84 (1966).
[9] I. Silvera and J. W. Halley, Phys. Rev. **149**, 415 (1966).
[10] J. W. Halley and I. Silvera, Phys. Rev. Letters **15**, 654 (1965).
[11] R. L. Green, D. D. Sell, W. M. Yen, A. L. Schawlow, and R. M. White, Phys. Rev. Letters **15**, 656 (1965).
[12] Ojiro Nagai, Phys. Rev. **180**, 557 (1969).
[13] G. G. Low, Proc. Phys. Soc. (London) **82**, 992 (1963).
[14] M. Bloch, Phys. Rev. Letters **9**, 286 (1962); J. Appl. Phys. **34**, 1151 (1963).
[15] J. Kanamori and M. Tachiki, J. Phys. Soc. Japan **17**, 1384 (1962).
[16] F. Keffer and R. Loudon, J. Appl. Phys. Suppl. **32**, 2 (1961).
[17] T. Oguchi and A. Honma, J. Phys. Soc. Japan **16**, 79 (1961).
[18] D. T. Teaney, in *Critical Phenomena, Proceedings of a Conference Held in Washington, D. C., April, 1965*, edited by M. S. Green and J. V. Sensers (Natl. Bur. Std. Misc. Publ. 273, 1966).
[19] D. T. Teaney (private communication).

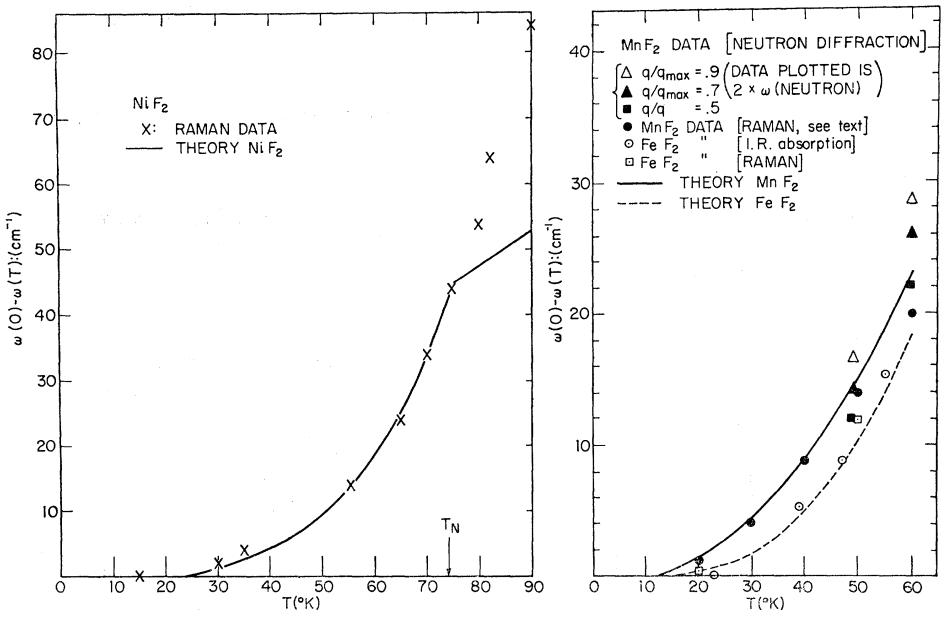

FIG. 1. (a) Comparison between the Raman data of Fleury (Ref. 5) and the relation given by Eq. (3). (b) Comparisons between available data and Eq. (3) for MnF_2 and FeF_2. See the text for explicit discussion of the data.

where r is the number of neighbors. This is just the frequency that would obtain from Eq. (2) if one considered each spin as independently precessing in an effective field

$$\mathbf{H}_{\text{eff}}^{(n)}=(g\beta)^{-1}2J\sum_{n}S_{m(n)}$$

and replaced $\mathbf{H}_{\text{eff}}^{(n)}$ by its mean value. We now argue that this picture of independently precessing spins is a good approximation to the short-wavelength magnons at all temperatures. Thus at some finite T, a spin $\mathbf{S}_n$ precesses in its own instantaneous field $\mathbf{H}_{\text{eff}}^{(n)}(t)$, where $\mathbf{H}_{\text{eff}}^{(n)}(t)$ obtains some extra time dependence (different from $T=0$) by virtue of the thermal excitation of low-energy long-wavelength magnons. Since only the low-frequency magnons are thermally excited at low temperature, the time dependence of $\mathbf{H}_{\text{eff}}^{(n)}(t)$ is slow compared to its own magnitude, i.e.,

$$\dot{H}_{\text{eff}}^{(n)}(t)\ll g\beta\hbar^{-1}|H_{\text{eff}}^{(n)}(t)|^2.$$

This situation is well known in nuclear-magnetic-resonance phenomena. The spin $\mathbf{S}_n$ follows the slow motion of $\mathbf{H}_{\text{eff}}^{(n)}(t)$ adiabatically and its direction is always quantized with respect to the instantaneous direction of $\mathbf{H}_{\text{eff}}^{(n)}(t)$. The excitation energy for this spin (and thus for the short-wavelength magnons) do not correspond to the mean value of $\mathbf{H}_{\text{eff}}^{(n)}(t)$ but rather to the mean value of its projection on the direction of $\mathbf{S}_n$. Thus, $\omega(q)|_T=g\beta\hbar^{-1}\langle\mathbf{H}_{\text{eff}}^{(n)}\cdot\mathbf{S}_n\rangle\times|S_n|^{-1}$. Substituting the above expressions for $\mathbf{H}_{\text{eff}}^{(n)}$ and taking proper account of the summation indices, one can show $g\beta\langle\mathbf{H}_{\text{eff}}^{(n)}\cdot\mathbf{S}_n\rangle=N^{-1}\langle\mathcal{H}\rangle$, where $\langle\mathcal{H}\rangle$ is just the expectation value of the Hamiltonian given by Eq. (1) and N is the number of spins one sums over. Taking $C_M(T)$ as the magnon contribution to the heat capacity (per spin), with $|S_n|=[S(S+1)]^{1/2}$, $\omega(q)|_{T=0}-\omega(q)|_T$ becomes

$$\omega(0)-\omega(T)=[S(S+1)]^{-1/2}\hbar^{-1}\int_0^T C_M(T')\,dT'. \quad (3)$$

We show below that Eq. (3) *quantitatively* relates the available heat-capacity data[20] and magnon-frequency data. Note that there are no adjustable parameters in Eq. (3). Strictly speaking, Eq. (3) should be valid at low temperatures and up to some fraction of the transition temperature. We show below, however, that it accurately satisfies the NiF_2 data up to the Néel temperature.

The most accurate measurements of a short-wavelength magnon frequency are probably Fleury's Raman scattering results on NiF_2.[5] The Raman scattering event that Fleury observes involves the simultaneous creation of two short-wavelength magnons which, because they are near each other, interact to yield a spectrum that has a peak at approximately $\omega(T)=2\omega(q)|_T-\omega(\text{interaction})$,[21] where $\omega(q)|_T$ represent the single-magnon energy near the Brillouin-zone boundary at temperature T. The crosses in Fig. 1 (taken from the solid line in Fig. 2 of Ref. 4) are $\omega(T=0)-\omega(T)$. Since the interaction energy is itself rather small, we assume here its temperature dependence is negligible. The solid curve

[20] J. W. Stout and E. Catalano, J. Chem. Phys. **23**, 2013 (1955).
[21] R. J. Elliott, M. F. Thorpe, G. F. Imbusch, R. Loudon, and J. B. Parkinson, Phys. Rev. Letters **21**, 147 (1968).

in Fig. 1 is

$$2\times(2)^{-1/2}\int_0^T C_M(T')\,dT',$$

where the values of $C_M(T')$ are taken from Ref. 20. The factor of 2 is from the two-magnon nature of the line and $(2)^{-1/2}=[S(S+1)]^{-1/2}$. Note once more that there are no adjustable parameters and the agreement is completely within the precision with which Fleury quotes the measured frequency shifts. The significance of this is further emphasized in Fleury's Fig. 2,[5] in which he plots one other theoretical result that might have had some relevance to the present problem.

Although there are Raman data on pure MnF_2,[7] it is not nearly precise enough to test Eq. (3). The best temperature data for our purposes are those of Moch *et al.*[6] on the two-magnon impurity scattering in Ni:MnF_2. In our own laboratory we have demonstrated that the ratio of the frequencies for the impurity scattering to the pure crystal scattering is independent of temperature over the range Moch *et al.*[6] measure. Thus, in Fig. 1(b) the solid circles represent $1-[\omega(T)/\omega(0)]$, as measured by Moch *et al.* for the Ni:Mn line, multiplied by the zero-temperature two-magnon frequency for pure MnF_2. The open and closed triangles, and the solid square, are one-magnon neutron-diffraction data.[4] For convenience, twice the neutron energy shift is plotted. The solid line is

$$2\times(\tfrac{5}{2}\times\tfrac{7}{2})^{-1/2}\int_0^T C_M(T')\,dT$$

as obtained from Ref. 20.

The Raman data for FeF_2 are not sufficiently accurate for our purposes. The open squares in Fig. 1(b) are two frequencies taken from Fleury *et al.*[8]; however, if all of their frequency determinations were plotted, the scatter would suggest serious discrepancies. On inspection of their data, however, this scatter is really within their uncertainties. The infrared absorption data are Silvera and Halley[9,10] are very precise and their data are indicated by the open circles in Fig. 1(b). The dashed line is

$$2(2\times3)^{-1/2}\int_0^T C_M(T')\,dT'$$

corresponding to a two-magnon spectrum, spin of 2.

The salt CoF_2 is much more complicated than the other three fluorides because of the particular properties of the Co^{++} ion. In any event, Fig. 2 demonstrates the situation for two neutron-diffraction peaks in CoF_2. The (0,0,1.5) and the (−0.5, 0, 1) magnons are indicated by

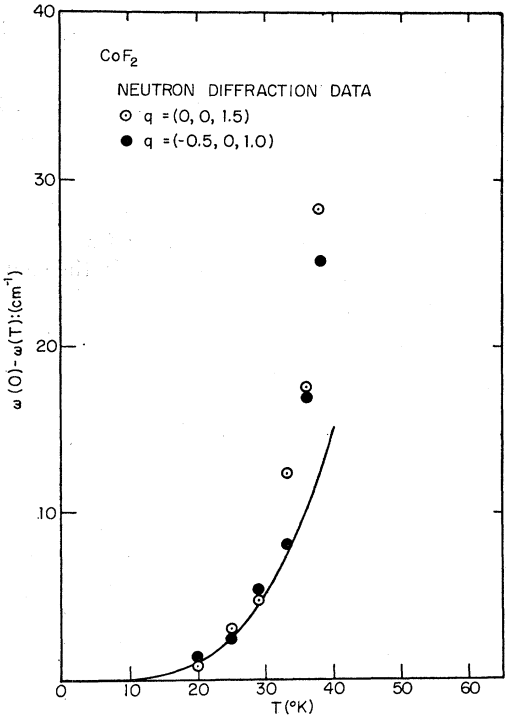

FIG. 2. Comparison between neutron diffraction data for CoF_2 and Eq. (3). The effective spin $S=\frac{1}{2}$ is arbitrarily chosen as giving the best fit to the data.

open and closed circles, respectively. The solid curve is

$$(\tfrac{1}{2}\times\tfrac{3}{2})^{-1/2}\int_0^T C_M(T')\,dT',$$

corresponding to a one-magnon event and an effective spin of $\frac{1}{2}$. The use of an effective spin of $\frac{1}{2}$ is questionable, and for present purposes in CoF_2, we must take it as an adjustable parameter.

In view of the increased linewidth of all of magnon spectra as one approaches the Néel temperature, the agreement between Eq. (3) and the available data is quite good. The NiF_2 data in Fig. 1(a) agree with Eq. (3) up to the Néel point and for all the other samples agreement is perfect for $T\lesssim 0.7T_N$. To whatever extent there is disagreement closer to T_N we cannot say whether this represents a failure of Eq. (3) or an uncertainty where to locate $\omega(T)$ in a very broad experimental line.

Finally, we want to emphasize that in view of the near perfect agreement for $T\lesssim 0.7\ T_N$ the spectral data are the reliable measure of the magnetic contribution to the heat-capacity data. This relation can be used to separate the lattice and magnetic contributions to the measured heat capacity in any magnetic solid for which spectral data are available.