quencies, a correction must be introduced to obtain a spectrum proportional to the number of nuclei at a given frequency. We have determined that, for our method of measurement, the ratio of the echo amplitude and the frequency is the appropriate quantity to be used in the analysis of spectra. Our conclusion is based on results obtained for the relative intensities of the two separated Fe resonances in Fe_3Si [T. J. Burch, thesis, Fordham University, 1968 (unpublished)] and the relative intensities of the two Ru-isotope resonances in Ni-rich Ni:Ru alloys (J. J. Murphy, unpublished). We have made no frequency correction to the data reported here since the error introduced is only a few percent over the frequency range in question and would not affect our conclusions.

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TEMPERATURE DEPENDENCE OF THE LINEWIDTH IN CRITICAL SPIN FLUCTUATION

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(Received 29 December 1969)

Starting from the kinetic equations obeyed by the time-dependent spin-correlation functions, we have calculated the homogeneous function which appears in the dynamical scaling expression for the linewidth of critical fluctuations in ferromagnets and antiferromagnets. In agreement with recent experimental findings, this function shows a minimum for $\kappa/q \equiv$ inverse correlation length/wave number $\neq 0$.

A series of recent experiments[1-4] on magnetic substances has provided a remarkable confirmation of the dynamical scaling assumptions (DSA) of Halperin and Hohenberg.[5,6] Moreover, DSA have also received strong theoretical support from the work of Kadanoff and Swift,[7] Kawasaki,[8] and Mori.[9]

Nevertheless the only formulation leading to a fully microscopic understanding of DSA is based on the kinetic equations obtained independently by De Leener and one of the authors (P.R.)[10,11] (Ref. 11 is hereafter referred to as RDL IV) and by Kawasaki.[12,13] Unfortunately, these equations have only been justified in the Weiss limit, where the number of neighbors is taken large (see Ref. 10).

Although the Weiss condition is a severe limitation (it is known at equilibrium to lead to erroneous critical indices), the simplest dimensional predictions of this kinetic theory are well verified.

For example, let us consider the spectral function for the spin autocorrelation function, $\Gamma_q(\omega)$ (q is wave number, ω is frequency), and let us denote by $\omega_0(q)$ and $\omega_0{}^\tau(q)$, respectively, the linewidths of this function at T_c for ferromagnets ($q \simeq 0$) and antiferromagnets ($q \simeq \tau$, where τ is the vector characterizing the staggered magnetization); one finds

$$\omega_0(q) \propto q^{5/2}, \quad \omega_0{}^\tau(q) \propto (q-\tau)^{3/2} \equiv q^{*3/2}. \tag{1}$$

These results are in remarkable agreement with experiments.

It is thus very tempting to explore further the consequences of this kinetic theory which, in principle, allows us to go beyond DSA. For instance, DSA predicts that, at a temperature $T \neq T_c$ (characterized by a correlation length κ^{-1}), the following results replace Eqs. (1):

$$\omega_\kappa(q) = \omega_0(q) f(\kappa/q),$$
$$\omega_\kappa{}^\tau(q) = \omega_0{}^\tau(q) f^\tau(\kappa/q^*), \tag{2}$$

where f and f^τ are homogeneous functions of κ/q; they are unknown except for their asymptotic behavior:

$$f(x) \to 1, \quad f^\tau(x) \to 1, \text{ when } x \to 0;$$
$$f(x) \propto x^{1/2}, \quad f^\tau(x) \propto x^{3/2}, \text{ when } x \to \infty. \tag{3}$$

On the contrary, kinetic theory allows us to compute f and f^τ explicitly for all values of x. We have performed such a calculation which we now summarize briefly.

The starting point is the kinetic equation obeyed by the time-dependent spin-correlation function $\tilde{\Gamma}_q(t)$ [normalized in such a way that $\tilde{\Gamma}_q(t=0)=1$]: It reads [see RDL IV, Eq. (I.5)]

$$\partial_t \tilde{\Gamma}_q(t) = \int_0^t \tilde{G}_q(\tau | \tilde{\Gamma}_{q'}) \tilde{\Gamma}_q(t-\tau) dt, \tag{4}$$

where the non-Markoffian kernel $\tilde{G}_q$ is a functional of $\tilde{\Gamma}_{q'}$ and can be expanded according to rules given in RDL IV:

$$\tilde{G}_q(\tau | \tilde{\Gamma}_{q'}) = \tilde{G}_q{}^{(2)}(\tau | \tilde{\Gamma}_{q'}) + \tilde{G}_q{}^{(4)}(\tau | \tilde{\Gamma}_{q'}) + \cdots. \tag{5}$$

The explicit form of $\tilde{G}_q{}^{(2)}$ is given in RDL IV, Eq. (3.1). In a ferromagnet close to T_c, it re-

duces to Eq. (3.7) of the same reference, which we repeat here for convenience:

$$\tilde{G}_q^{(2)}(\tau|\tilde{\Gamma}_{q'}) = -\gamma^2(q^2+\kappa^2)\int d\vec{q}_1 \frac{[(\vec{q}+\vec{q}_1)^2-q_1^2]}{(\kappa^2+q_1^2)}\tilde{\Gamma}_{|\vec{q}+\vec{q}_1|}(\tau)\tilde{\Gamma}_{q_1}(\tau), \quad T\to T_c, \quad q\to 0. \tag{6}$$

Here γ is a constant, irrelevant for our present purpose.

In order to get a semiquantitative idea of the linewidth $\omega_\kappa(q)$ associated with $\tilde{\Gamma}_q$, we first assume that $\omega_\kappa^{-1}(q)$ can be measured by the zero-frequency Fourier component of $\tilde{\Gamma}_q(t)$ [14]:

$$\omega_\kappa(q) = [\int_0^\infty \tilde{\Gamma}_q(t)dt]^{-1} = \int_0^\infty \tilde{G}_q(\tau|\tilde{\Gamma}_{q'})dt \simeq \int_0^\infty \tilde{G}_q^{(2)}(\tau|\tilde{\Gamma}_{q'})dt. \tag{7}$$

Moreover, in the right-hand side of (7), we insert $\tilde{\Gamma}_{q'}$, as calculated from the Markoffian approximation to (4), namely

$$\partial_t \tilde{\Gamma}_q(t) = [\int_0^\infty \tilde{G}_q^{(2)}(\tau|\tilde{\Gamma}_{q'})dt]\tilde{\Gamma}_q(t). \tag{8}$$

Although our previous investigations have shown that this simplification does not lead to the correct shape of the spectral function, we can repeat the argument given in RDL IV to suggest that this "zeroth-order" approximation leads to semiquantitatively correct results. Inserting (6)-(8) into (2), we get immediately, with $f(x) = \bar{f}(x)/\bar{f}(0)$,

$$\bar{f}(x) = 2\pi(1+x^2)\int_0^\infty dy \int_{-1}^{+1} d\alpha\, y^2(1+2\alpha y)(x^2+y^2)^{-1} \times [(1+y^2+2\alpha y)^{5/4}\bar{f}(x/(1+y^2+2ay)^{1/2}) + y^{5/2}\bar{f}(x/y)]^{-1}. \tag{9}$$

We have solved Eq. (9) numerically by iteration; the result is shown in Fig. 1(a).

The same calculation has been repeated for antiferromagnets. The only difference is that we now have to consider simultaneously the critical behavior close to $q=0$ and to $q=\tau$. This point is discussed in detail in Ref. 13 and will not be considered again here. We obtain then, instead of (9), a set of coupled integral equations $\bar{f}^{q=0}(x)$ and $\bar{f}^{\tau}(x)$. The solution of this system is shown in Fig. 1(b).

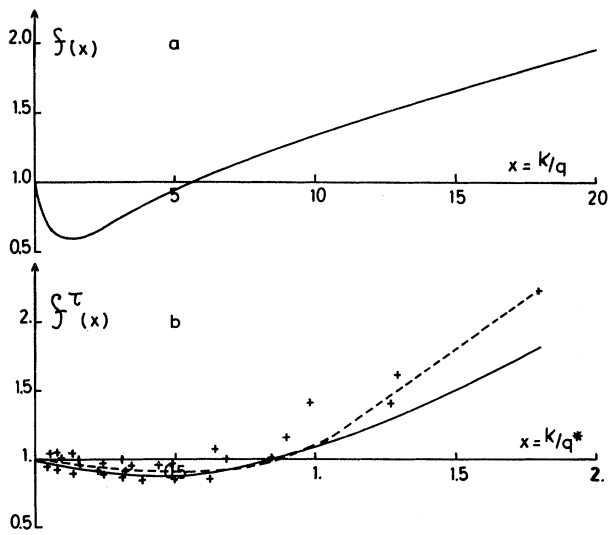

FIG. 1. Temperature dependence of the linewidth. (a) The solution $f(x)$ of Eq. (9) for ferromagnets. (b) The function $f^\tau(x)$ for antiferromagnets: theory (plain curve), experimental results for $RbMnF_3$ (crosses), best fit of these experimental data (Ref. 4) (dashed line). Notice the change of scale from (a) to (b).

The remarkable feature of the curves giving $f(x)$ and $f^\tau(x)$ is a minimum for $x\neq 0$. This nontrivial result is confirmed by the experiments of Nathans, Menzinger, and Pickart[1] on $RbMnF_3$ and by the more precise findings of Lau et al.[4] on the same substance.

As is seen in Fig. 1(b), these latter experiments semiquantitatively agree with the present theory, except for large x. In this region, however, resolution effects (which were not corrected in this particular case) may be large because the corresponding q^* value is small ($q^* \simeq 0.025$ Å^{-1}) and it is hard to decide whether the discrepancy indicates a failure of the theory or an experimental difficulty.[15]

We should also point out the deeper and more extended minimum in the ferromagnetic case. It would be interesting to have an experimental confirmation of this prediction, although it is difficult to work with a Heisenberg ferromagnet and we do not know if the results of the present theory can be extended to metals.

Finally, let us stress that the calculation presented here involves no adjustable parameter. Nevertheless, the agreement between theory and experiment depends on the fact that we have chosen κ as an independent variable. If we had taken instead the variable $(T-T_c)$, we would have found the well-known difficulty that, in the Weiss limit, $\kappa \propto (T-T_c)^\nu$ with $\nu = \frac{1}{2}$ while, in realistic system, one has $\nu \simeq \frac{2}{3}$. This is a further indication in favor of the argument presented in RDL IV, ac-

cording to which the Weiss limit might well play an important role only in the determination of the equilibrium properties of spin systems, and not in their dynamical behavior.

We thank Dr. H. Y. Lau et al. for sending us their work prior to publication.

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[14]From the sum rule $\int_0^\infty \Gamma_q(\omega)d\omega = \pi/2$ for the spectral function $\Gamma_q(\omega)$, we expect of course that $\Gamma_q(0) = \int_0^\infty \tilde{\Gamma}_q(t) \times dt$ gives an estimate of the linewidth, although, strictly speaking, this latter is of course shape dependent.

[15]After this note was submitted for publication, D. Huber and D. Krieger reported a similar calculation in Phys. Rev. Letters 24, 111 (1970), where a plot is given of $\omega_K(q)/\omega_K(0)$ against $(q/\kappa)^2$. Their method is however developed mainly for $q/\kappa \ll 1$ (because of a cutoff at $k_m \lesssim 5\kappa$). Moreover, for comparison with the experiments of Lau et al., they need the experimental value of $\omega_K(0)$ which is possibly subject to important resolution effects. Our solution, given in Fig. 1 (and obtained with no cutoff) is probably best in the nonhydrodynamical region $q/\kappa \gg 1$, where most experimental results were reported (see Fig. 1) and exhibits the observable nontrivial minimum at $q/\kappa \approx 0.5$ which cannot be seen in the above-mentioned work; otherwise the two results agree semiquantitatively. We thank P. C. Hohenberg for pointing out this work to us.

COVALENT BONDING AND THE NEUTRON MAGNETIC FORM FACTOR OF THE Mn^{2+} ION*

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(Received 23 December 1969)

Fully variational unrestricted Hartree-Fock calculations for the $(MnF_6)^{4-}$ cluster are reported. Charge and spin densities are analyzed and shown to result in a neutron magnetic form factor which is contracted relative to the free-ion value in agreement with experiment but contrary to predictions of simple covalent-bonding theory.

Covalency or electron-transfer effects have been identified by NMR and neutron magnetic scattering experiments as playing an important, indeed vital, role in understanding the observed magnetic and optical properties of transition-metal compounds. An unresolved question is the apparent failure of covalent theory to explain the measured neutron magnetic scattering from Mn^{2+} ions in magnetic salts. These experiments show relatively little loss of intensity at low scattering angles[1] and a form factor which lies well below the free Mn^{2+} ion value [or an expanded spin density relative to the free-ion Hartree-Fock (H-F) result]. By contrast, Ni^{2+} shows a large reduction in absolute intensity in the forward direction and a neutron magnetic form factor which lies above the free-ion value[2] (or a contracted spin density). Hubbard and Marshall[3] have shown, using a simple linear combination of atomic orbitals (LCAO) model, that bonding effects will raise the form factor above the free-ion value and result in a loss of intensity at low scattering angles, consistent with the Ni^{2+} results. Since core polarization[4] and unquenched orbital angular momentum[5] contributions also raise the measured form factor, the observation that the spin density in