two factors of S_3.[11] For a frequency shift $\omega \simeq 2\Delta_3$ and $\beta|\omega - 2\Delta_3| < 1$ the spectrum is proportional to $\exp[\beta\gamma(\omega - 2\Delta_3)]$, with $\gamma = \mu_3/(m_3^* - \mu_3)$, while for $\beta(\omega - 2\Delta_3) > 1$ the spectrum varies as $(\omega - 2\Delta_3)^{-1/2}$. Again the spectrum is thermally broadened compared with the two-roton Raman spectrum. The ratio of the intensities of the two-He^3-roton and two-roton Raman spectra is approximately $(n_3/n_4)^2$, where n_3 and n_4 are the He^3 and He^4 densities, respectively.

Raman scattering in which a He^3 roton near k_3 and a He^4 roton near k_4 (where the density of states in each case is largest) are created is forbidden by momentum conservation when $k_4 > k_3$. Thus Raman scattering at a frequency shift $\omega \sim \Delta_3 + \Delta_4$ would not be expected to show any special feature.

We wish to thank Professor G. Benedek for hospitality at the Massachusetts Institute of Technology where this work was carried out.

*Work supported in part by the National Science Foundation.

[1]C. M. Surko and R. E. Slusher, Phys. Rev. Lett. 30, 1111 (1973).
[2]R. L. Woerner, D. A. Rockwell, and T. J. Greytak, Phys. Rev. Lett. 30, 1114 (1973).
[3]V. I. Sobolev and B. N. Esel'son, Zh. Eksp. Teor. Fiz. 60, 240 (1971) [Sov. Phys. JETP 33, 132 (1971)]. Values for ρ_n in mixtures have also been obtained by D. A. Rockwell from light-scattering measurements (to be published). The results are in reasonable agreement with those given in this reference.
[4]L. P. Pitaevski, in Proceedings of the U.S.–Soviet Symposium on Condensed Matter, Berkeley, California, May 1973 (to be published).
[5]R. P. Feynman, Phys. Rev. 94, 262 (1954).
[6]R. P. Feynman and M. Cohen, Phys. Rev. 102, 1189 (1956).
[7]L. Goldstein and J. Reekie, Phys. Rev. 98, 857 (1955).
[8]W. E. Massey, C. W. Woo, and H. T. Tan, Phys. Rev. A 1, 519 (1970).
[9]We are grateful to R. L. Woerner for these calculations.
[10]This was suggested by Dr. R. Meservey.
[11]M. J. Stephen, Phys. Rev. 187, 279 (1969).

Critical Scattering in a Field and Below T_c

H. B. Tarko and Michael E. Fisher
Baker Laboratory, Cornell University, Ithaca, New York 14850
(Received 5 July 1973)

Series expansions for spin-spin correlations of simple-cubic, bcc, and square lattice Ising ferromagnets for general field and temperature have been analyzed. To within the attainable precision (of ±1 to ±5%) the exponents ν' and ν^c are consistent with scaling predictions. Deviations of the scattering from Ornstein-Zernike forms are significantly larger quantitatively than above T_c; the second-moment correlation lengths verify $\xi_1^+(T)/\xi_1^-(T) = 1.96 \pm 0.03$ as $T \to T_c^\pm$.

The behavior of the spin-spin correlation functions, and thence of the critical scattering, in Ising models has been studied in considerable detail as the critical point is approached along the critical "isochore" (or $H=0$) above T_c.[1-3] We report here the results of the first calculations by series expansion techniques which include the complete field dependence, so enabling one to study the scattering in zero field *below* T_c (i.e., along the phase boundary) and *at* the critical temperature as a function of field H. To within the comparatively low precision attainable (±1 to ±5%), the estimated exponent values confirm scaling predictions (but they throw little new light on "hyperscaling" relations such as $d\nu' = 2 - \alpha'$, etc.). More significantly, the calculations reveal large deviations in the form and scale of the critical scattering from the Ornstein-Zernike perdictions. These have been elucidated quantitatively and should be susceptible to experimental test (as have similar predictions above T_c).[4,5]

Series expansions were generated in powers of the variables

$$u = x^2 = \exp(-4J/k_BT) \text{ and } \quad y = \exp(-2mH/k_BT), \tag{1}$$

for the correlation functions

$$\Gamma(\vec{r}, H, T) = \langle S_{\vec{0}} S_{\vec{r}} \rangle - \langle S_{\vec{0}} \rangle \langle S_{\vec{r}} \rangle \tag{2}$$

of nearest-neighbor Ising models using the semi-invariant techniques as applied by Jasnow and

TABLE I. Coefficients $m_{2,n}^c$ in expansion $\mu_l(H,T_c) = \sum m_{l,n}^c y^n$. [The values used for T_c were those of Sykes *et al.* (Ref. 15).]

n	sc $m_{2,n}^c$	bcc $m_{2,n}^c$	sq $m_{2,n}^c$
2	0.167 497	0.182 201	0.066 945
3	0.320 924	0.327 507	0.125 332
4	0.459 546	0.450 116	0.187 572
5	0.583 309	0.559 239	0.243 820
6	0.700 214	0.661 408	0.310 193
7	0.809 035	0.756 714	0.430 258
8	0.913 371		

TABLE II. Coefficients $m_{2,n+k}^-$ in the expansion $\mu_2(0,T) = \sum m_{2,n+k}^- u^{n+k}$.

n	sc $m_{2,n+5}^-$	bcc $m_{2,n+7}^-$	sq $m_{2,n+3}^-$
0	24	32	16
1	− 24	− 32	272
2	528	0	3248
3	− 960	960	32 768
4	8496	− 2048	299 072
5	− 21 312	1792	
6	125 904	19 136	
7	− 380 016	− 66 688	
8	1 813 416	106 240	
9	− 6 046 440	252 832	
10	25 675 200	− 1 566 016	
11		3 649 248	
12		566 592	

Wortis.[6,7] From these data, series were constructed for the moments[8]

$$\mu_l(H,T) = \sum_{\vec{r}} (r/a)^l \Gamma(\vec{r}, H, T), \tag{3}$$

where a denotes the nearest-neighbor lattice spacing, for the second-moment correlation length $\xi_1(H,T)$ defined by

$$\xi_1^2/a^2 = \mu_2(H,T)/2d\mu_0(H,T), \tag{4}$$

and for other functions involving the correlations. Note that $\mu_0 = \hat{\chi}_0 \propto \chi_T$ is proportional to the zero-angle scattering or thermodynamic susceptibility, which has previously been extensively studied.[9,10] The various single-variable series (for $T = T_c$ or $H = 0$, $T < T_c$) were analyzed by standard ratio and Padé approximate techniques[1,9] to estimate critical-point behavior in terms of

$$t = (T/T_c) - 1 \text{ and } h = mH/k_B T_c. \tag{5}$$

On the *critical isotherm*, $T = T_c$, seven terms in powers of y were obtained for the simple-cubic (sc) ($d = 3$) and square (sq) ($d = 2$) lattices, but only six for the bcc lattice.[11] The series for μ_2 are reproduced in Tables I and II; note that the series for μ_0 are already in the literature.[9] An interfering, nonphysical singularity near $y = -1$ was observed for all three lattices and Euler transforms of the form $w = (1+c)y/(1+cy)$ were helpful in the analysis. The correlation length could be described by

$$\xi_1(H, T_c) \approx (f_1^c a/h^{\nu^c})\{1 - e_1^c h^{\zeta} + \cdots\} \tag{6}$$

as $H \to 0^+$, and corresponding forms held for the moments μ_0, μ_2, and μ_4. The estimates for the exponents ν^c and amplitudes f_1^c are shown in Table III. The exponent values may be compared with the scaling prediction[9] $2\nu^c = 2\nu/\beta\delta = 2\nu/(\beta+\gamma)$ which yields $2\nu^c = \frac{16}{15} = 1.066\cdots$ for $d = 2$, and, us-

TABLE III. Summary of series estimates and exact results, and comparison with mean-field theory (MFT). The values used for $\tilde{D}_\infty^+$, ν, and η are those in Ref. 1 (for δ see Ref. 10). The square-lattice values for $2\nu'$ and f^+/f^- are exact; so are the MFT results.

	$2\nu^c$	f_1^c	$2\nu'$	f_1^-	f_1^+/f_1^-	f^+/f^-	$\tilde{D}_\infty^-$	$\tilde{D}_\infty^+$
sq	1.06	0.233	2	0.176	3.23	2	1.96	0.414
	± 0.02	± 0.004		± 0.005	± 0.08		± 0.09	
sc	0.84	0.257	1.28	0.244	1.96		1.31	0.898
	± 0.03	± 0.008	± 0.04	± 0.001	± 0.03		± 0.04	
bcc	0.84	0.242	1.25	0.227			1.27	0.906
	± 0.03	± 0.010	± 0.10	± 0.005			± 0.06	
MFT $d = 2$	2/3	0.346 68	1	0.353 55	$\sqrt{2}$	$\sqrt{2}$	1	1
MFT $d = 3$	2/3	0.283 06	1	0.288 68	$\sqrt{2}$	$\sqrt{2}$	1	1

ing accepted values,[1,9,10] $2\nu^c \simeq 0.823 \pm 0.008$ for $d=3$. The agreement is good considering the relatively low precision; within appreciably larger uncertainties the second and fourth moments also yield agreement when values for $\gamma^c = (\delta - 1)/\delta = \gamma/\beta\delta$ are used. The amplitude estimates may be compared with the mean-field and Bethe-approximation results[1,9] shown in Table III. (For these approximations one has $2\nu^c = \frac{2}{3}$ which is clearly erroneous, as expected.)

The singular correction exponent ζ in (6) was estimated by studying the coefficients of the series for $(\xi_1)^{1/\nu^c}$. For the sc lattice the result is $\zeta = 0.77^{+0.05}_{-0.10}$ and the same estimate follows from the μ_2 series. The bcc lattice data confirm the same value but within uncertainties of $^{+0.15}_{-0.20}$. No significant conclusions could be drawn for the sq lattice. The amplitudes of the singular correction are $e_1{}^c = 0.56^{+0.20}_{-0.17}$ (sc) and 0.41 ± 0.20 (bcc); note that although these values are similar they are not expected to be "universal." The quoted uncertainties assume the scaling prediction for ν^c is exact. The same singular corrections have been noticed before in the magnetization by Gaunt and Sykes[10] (who argue for the relation[10b] $\zeta \simeq 1 - 1/\delta$).

On the *phase boundary*, $H=0$, $T \leqslant T_c$, eleven terms in powers of u were obtained for the sc lattice, thirteen for the bcc, and five for the square lattice.[11] The series, especially for the bcc lattice, behave poorly so that extrapolation is not very certain. However, in view of the estimate[1,2] $2\nu = 1.282 \pm 0.005$ it is evident from Table III that the results are consistent with the scaling prediction $\nu' = \nu$. In two dimensions this is, of course, an exact result.[9] To within the limited precision, the equality $\gamma' = \gamma \simeq 1.250$ is preferred by the μ_2 series, to the suggestion of a breakdown of scaling with $\gamma' \simeq 1.31$.[9]

Assuming[1] that $\nu' = \nu = \frac{9}{14}$, the correlation-length amplitudes in

$$\xi_1(0, T) \simeq f_1{}^- a/|t|^{\nu'}, \quad t \to 0^-, \tag{7}$$

can be reliably estimated (see Table III). The ratio of $f_1{}^-$ to the corresponding amplitude $f_1{}^+$ for $T > T_c$ should be universal, depending, for Ising systems, only on d. The evidence for the sc and bcc lattices supports this to a precision of 2% or better.[11]

On the other hand the $f_1{}^\pm$ for ξ_1 must be distinguished carefully from the amplitudes $f^\pm$ for the *true range of correlation,* which is defined in terms of the exponential decay of $\Gamma(\vec{r})$, or from the nearest singularity to the real $\vec{k}$ axis in the scattering function

$$\hat{\chi}(\vec{k}, H, T) = \hat{\Gamma}(\vec{k}, H, T) = \sum_{\vec{r}} e^{i\vec{k}\cdot\vec{r}}\Gamma(\vec{r}, H, T). \tag{8}$$

Above T_c it was found[1] that $f^+/f_1{}^+ = 1.000\,05$ for $d=2$ and 1.0003 for $d=3$, so that $\xi_1(T)$ is very closely equal to $\xi(T)$. Except within Ornstein-Zernike theory,[9] however, this is not the case below T_c. Thus, it is known rigorously[1,9] that $f^+/f^- = 2$ in two dimensions; it follows from Table III that $f^-/f_1{}^- \simeq 1.62$ for the square lattice. It has been argued[12] that one might expect $f^+/f^- \simeq 1.5$ for the true range when $d=3$. If this is accepted then $f^-/f_1{}^- \simeq 1.31$, but we have not been able to check this at all precisely, as will become clear.

According to scaling theory the shape of the critical scattering can be described on each of the critical loci considered above[13,8] by

$$\hat{\chi}(\vec{k}, H, T) = \hat{\chi}_0(H, T)\hat{D}(\xi_1{}^2k^2), \tag{9}$$

where $\hat{D}(x^2) = \hat{D}^+$, $\hat{D}^c$, or $\hat{D}^-$ depends on the locus. For small x (i.e., $k \to 0$), one should always have

$$1/\hat{D}(x^2) = 1 + x^2 - \Sigma_4 x^4 + \Sigma_6 x^6 - \cdots, \tag{10}$$

while[1,9] as $x \to \infty$ on the zero-field ($\pm$) loci (i.e., $t \to 0^\pm$), one expects

$$\hat{D}(x^2) = (\tilde{D}_\infty/x^{2-\eta})\{1 + B_1 x^{-(1-\alpha)/\nu} + B_2 x^{-1/\nu} + \cdots\}, \quad (t \gtrless 0). \tag{11}$$

Ornstein-Zernike (OZ) theory[1,9] corresponds to $\Sigma_4 = \Sigma_6 = \cdots = 0$ in (10) and $\eta = 0$, $B_1 = 0$, and $\nu = \frac{1}{2}$ in (11). *Above* T_c a rather accurate approximant was shown to be[1,8]

$$\hat{D}^+(x^2) = (1 + \varphi_c{}^2 x^2)^{\eta/2}/(1 + \psi_c x^2), \tag{12}$$

where $\psi_c = 1 + \frac{1}{2}\eta\varphi_c{}^2$ and $\varphi_c \simeq 0.0294$ for $d=2$, and $\varphi_c \simeq 0.14$ to 0.16 for $d=3$. As is evident from the plot in Fig. 1 the fractional deviations from OZ theory are, here, numerically quite small over a wide range of x. In particular $\Sigma_4{}^+$, which may be estimated from μ_4, takes the values 1.1×10^{-4} ($d=2$) and $(6.5 \pm 0.8) \times 10^{-4}$ ($d=3$).

Below T_c, however, the deviations from the OZ form must be much larger. This follows directly from the continuity of the correlation functions through T_c and the values of the ratios $f_1{}^+/f_1{}^-$ and C^+/C^- (for the susceptibility amplitudes[9]) which together determine $\tilde{D}_\infty{}^-$ (see Table III). The essentially common values of $\tilde{D}_\infty{}^-$ for the bcc and sc lattices again confirm the universality of the scaling function. For the sc lattice we estimate $\Sigma_4{}^- = (1.2 \pm 0.6) \times 10^{-2}$. The bcc data also indicate

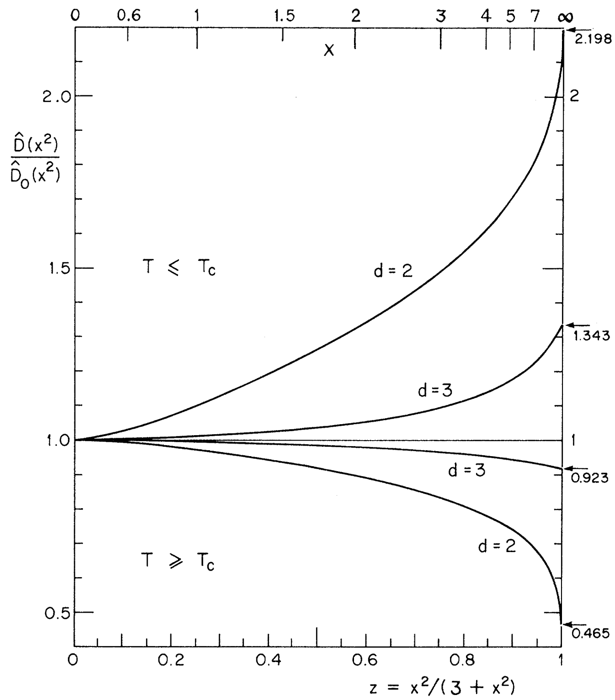

FIG. 1. Approximants for the scaling function $\hat{D}(x^2)$ reduced by the "zero order approximant" (Ref. 1) $\hat{D}_0(x^2) = (1+\psi x^2)^{-1+\eta/2}$ with $\psi^{-1} = 1 - \frac{1}{2}\eta$, versus the variable $z = x^2/(3+x^2)$ (chosen for convenience).

a similar value but with a much larger uncertainty.

Unfortunately the values of $\tilde{D}_\infty^-$ preclude the construction of a satisfactory approximant of the simple form (12). For the square lattice we have found that the expression

$$\hat{D}^-(x^2) \simeq [1 - p + p(1+\psi x^2)^{1/2}]^{-(2-\eta)} \tag{13}$$

with $p = 0.406$ and $\psi = (1.678)^2$ provides a reasonable approximant. The square root branch point represents the rigorously known asymptotic decay of correlation in the square lattice Ising model below T_c.[9,14] The behavior of (13) for large x ($z \lesssim 1$ in Fig. 1) cannot be completely accurate since, like (12), it does not reproduce the form of the correction factor in (11) which, in turn, represents the energylike singularity, $|t|^{1-\alpha}$, which should occur[1,9] in $\hat{\Gamma} = \hat{\chi}(\vec{k}, T)$ at constant $\vec{k}$. However, numerical study suggests that this will be significant only for very large x.

In three dimensions there is more freedom in the choice of an approximant. It seems reasonable to expect[14] the OZ decay law still to apply *away* from T_c. Accordingly an approximant with a dominant simple pole, of the form

$$\hat{D}^-(x^2) \simeq \frac{(1+\varphi'^2 x^2)^{\theta+\eta/2}}{(1+\psi' x^2)(1+\varphi''^2 x^2)^{\theta}}, \tag{14}$$

with $\psi' = 1 + \frac{1}{2}\eta\varphi'^2 + \theta(\varphi'^2 - \varphi''^2)$, was tried and found satisfactory for parameter values $\theta = 0.118$, $\varphi' = 0.5150$, and $\varphi'' = 0.1245$. The position of the pole in (14), at $x^2 \simeq -0.9645$, fixes the amplitude ratios as $f^-/f_1^- = 1.018$ and $f^+/f^- = 1.92$. However, these estimates are very sensitive to the assumed form of the approximant and cannot be considered reliable. Note again that the singular correction factor in (11) is not reproduced by (14).

Scaling function approximants $\hat{D}^c(x^2)$ may also be developed for the critical isotherm but, as they are of less practical application, they are not reported here.

In conclusion we see that significant deviations from Ornstein-Zernike theory arise in the scattering below T_c. Despite the numerical uncertainties, the curves in Fig. 1 should give a quantitatively quite accurate representation of the true behavior.

We thank Professor K. G. Wilson for computing assistance and Dr. D. S. Ritchie for correspondence. The support of the National Science Foundation, in part through the Materials Science Center at Cornell University, is gratefully acknowledged.

[1]M. E. Fisher and R. J. Burford, Phys. Rev. 156, 583 (1967); see also Table XXI of D. S. Ritchie and M. E. Fisher, Phys. Rev. B 5, 2668 (1972), and corrections in Footnote 30.

[2]M. A. Moore, D. Jasnow, and M. Wortis, Phys. Rev. Lett. 22, 940 (1969).

[3]M. Ferer and M. Wortis, Phys. Rev. B 6, 3426 (1972).

[4]J. Als-Nielsen and O. Dietrich, Phys. Rev. 153, 706, 711, 717 (1967); J. Als-Nielsen, Phys. Rev. 185, 664 (1969); L. Guttman and H. C. Schnyders, Phys. Rev. Lett. 22, 520 (1969).

[5]D. Bally, M. Popovici, M. Totia, B. Grabçev, and A. M. Lungu, Phys. Lett. 26A, 396 (1968); J. Als-Nielsen, Phys. Rev. Lett. 25, 730 (1970); M. Popovici, Phys. Lett. 34A, 319 (1971).

[6]D. Jasnow and M. Wortis, Phys. Rev. 176, 739 (1972); D. Jasnow, Ph.D. thesis, University of Illinois, 1969 (unpublished).

[7]We are indebted to Professor K. G. Wilson for the use of his version of the expansion program as a first basis for the present calculations.

[8]The notation of Ref. 1, Sects. 2–3, is followed as far as practicable.

[9]See, e.g., M. E. Fisher, Rep. Progr. Phys. 30, 615 (1967), and references contained therein.

[10a]D. S. Gaunt and M. F. Sykes, J. Phys. C: Proc. Phys. Soc., London 5, 1429 (1972).

[10b]G. A. Baker and D. S. Gaunt, Phys. Rev. 155, 545 (1967).

[11]In an independent calculation for the fcc lattice Dr. D. S. Ritchie (private communication) has obtained 6 terms on the critical isotherm and 21 terms for $H=0$, $T \leq T_c$. He reports $f_1^+/f_1^- \simeq 1.93$, but using a smaller estimate of ν' than here.

[12]M. E. Fisher, in *Fluctuations in Superconductors*, edited by W. S. Goree and F. Chilton (Stanford Research Institute, Stanford, Calif., 1968), pp. 356–380, Footnote 15.

[13]Note that this form of scaling is not expected to hold for *general* H and T.

[14]See also M. E. Fisher and W. J. Camp, Phys. Rev. Lett. 26, 565 (1971).

[15]M. F. Sykes, D. S. Gaunt, P. D. Roberts, and J. A. Wyles, J. Phys. A: Proc. Phys. Soc., London 5, 640 (1972).

Raman Scattering from Microcrystals of MgO

R. G. Schlecht and H. K. Böckelmann
Department of Physics, Southern Illinois University, Carbondale, Illinois 62901
(Received 19 July 1973)

We have observed the Raman scattering spectrum from finite crystals of MgO. Lines have been observed at 595, 719, and 1096 cm^{-1}. Very good agreement is obtained between the observed lines and the lattice dynamic theory of finite crystals. However, no agreement is obtained with the macroscopic theory.

The nature of vibrations of finite crystals has received a great deal of both theoretical and experimental interest recently. In this Letter we wish to report what we believe to be the first direct observation of such vibrations by Raman spectroscopy. We have observed the modes of vibration in cubic microcrystals of MgO.

Theoretical investigations of such modes have followed two directions: (1) a macroscopic approach, and (2) a lattice dynamic approach. Although most of the theoretical work has been carried out on a slab geometry, we will only consider work done on a spherical geometry as this geometry is more representative of our experimental conditions. Fröhlich[1] first investigated the modes of vibration of an isolated sphere using the macroscopic approach. He assumed the radius of the sphere to be small with respect to the wavelength of the polarization wave. For an ionic crystal of cubic symmetry only one vibrational mode was found to occur lying between the transverse optic frequency ω_T and the longitudinal optic frequency ω_L of the bulk crystal. Fuchs and Kliewer[2] and Ruppin and Englman[3] have extended Fröhlich's result to other geometries and have refined Fröhlich's calculations for the sphere. Fuchs and Kliewer[2] have solved the wave equation for the sphere, and Ruppin and Englman[3] have included both retardation effects and the effects of a dielectric media surrounding the sphere. Two series of modes then result. One series lies in the gap between ω_T and ω_L and a second series lies below ω_T. Genzel and Martin[4] and more recently Barker[5] have attempted to include the effect of neighboring particles on the effective dielectric function of the macroscopic theory and have included this effect on the vibrational modes.

Maradudin and Weiss[6] have approached the problem of finite crystals from the lattice dynamic viewpoint, and have employed the Kellermann model of cubic ionic crystals.[7] They have found two vibrational modes for cubic crystals which lie between ω_T and ω_L. These modes become degenerate for spherical crystals when $k=0$, where $\vec{k}$ is the wave vector of the mode. As k increases, one mode tends towards ω_L and the other tends towards ω_T. Lucas[8] has modified the results of Maradudin and Weiss for spherical particles to include retardation effects with the result that the degeneracy at $k=0$ is lifted. One mode is the same as obtained by Maradudin and Weiss and lies in the gap between ω_T and ω_L for k large. The other mode has frequency greater than ω_L and tends to the line $\omega = kc$. The dispersion curves are given by Lucas. It is seen that the macroscopic theory and the lattice dynamic theory give very different results for the vibrational modes of a sphere.

Experimental results on the modes of finite crystals of MgO have been reported by several