Critical Surface Scattering of X Rays and Neutrons at Grazing Angles

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(Received 5 July 1983)

The authors propose to probe the effects of a surface on critical behavior by x-ray and neutron scattering under conditions of total reflection. It is shown that the temperature and angular dependence of the scattered intensity at grazing angles allows one to determine the three critical surface exponents β_1, γ_{11}, and $\eta_{\|}$.

PACS numbers: 61.10.Dp, 64.60.Cn, 68.20.+t

In the past few years, the theory of critical surface phenomena has advanced considerably and yielded a number of significant results.[1] For instance, universal scaling laws relating surface with bulk critical exponents have been derived and numerical values of the surface exponents have been computed to $O(\epsilon^2)$ in the ϵ expansion. On the experimental side, however, pertinent data are scarce.[2] This fact has prevented any serious test of the theoretical predictions. One reason for the dearth of empirical data might be that with standard methods of surface analysis, such as low-energy electron diffraction (LEED) and ion scattering, it appears to be difficult to extract precise information on critical behavior because of strong multiple scattering. Thus, these methods lack the conceptual simplicity of conventional x-ray and neutron techniques, which have been so successful in the investigation of bulk critical phenomena but are, unfortunately, not specifically surface sensitive.

Various authors[3-7] have recently noticed, however, that x-ray and neutron scattering can be rendered into a new and promising tool for surface structure studies by employing conditions of total reflection. Although severe intensity problems have to be faced, such measurements are feasible.[3]

In this Letter we take up this intriguing idea to explore the extent to which total reflection can be applied for investigating critical surface phenomena. Felcher[4] has already pointed out that the magnetization profile near the surface of a ferromagnet may be probed by totally reflected neutrons. We shall show that grazing-angle scattering of x-rays and neutrons provides information not only on the profile and the exponent[8] β_1 of the local order parameter (OP) but also on OP correlations in the vicinity of the surface, and hence provides two further exponents, γ_{11} and $\eta_{\|}$, which can hardly be obtained by other means.

The physics behind surface scattering at grazing angles is the following: When x rays or neutrons with wave vector $\vec{K}_i$ impinge on the plane surface of a solid, total reflection occurs if the angle of incidence α_i (cf. Fig. 1) has a value less than $\alpha_c(K_i)$. The latter is given by $\sin\alpha_c = (1-n^2)^{1/2}$ in terms of the index of refraction $n(K_i)$. For x-ray frequencies not too close to an absorption edge and normally also for neutrons, one has $\delta \equiv 1 - n^2 > 0$. In both cases, multiple scattering in condensed matter is weak and δ is typically of the order of 10^{-5}. If $\alpha_i < \alpha_c$, then the amplitude of the transmitted wave inside the sample decays exponentially towards the interior. Inhomogeneities in the electronic or nuclear density of the sample scatter the evanescent wave which in turn gives rise to outgoing waves in addition to the reflected beam. Since this grazing-angle scattering is confined to a layer of microscopic depth, it provides information about structural properties of the surface.

As an example we consider a binary alloy located in the half space $z \geq 0$ which undergoes a continous order-disorder transition. Following the approach described in Refs. 5–7, the elastic scattering cross section is obtained in the form

$$d\sigma/d\Omega = |M|^2 \Gamma(\vec{k}, \kappa). \tag{1}$$

Here, Γ denotes the Fourier transform,

$$\Gamma = \sum_{m,n} \langle S_m S_n \rangle \exp[i\vec{k}\cdot(\vec{r}_m - \vec{r}_n) + i(\kappa z_m - \kappa^* z_n)], \tag{2}$$

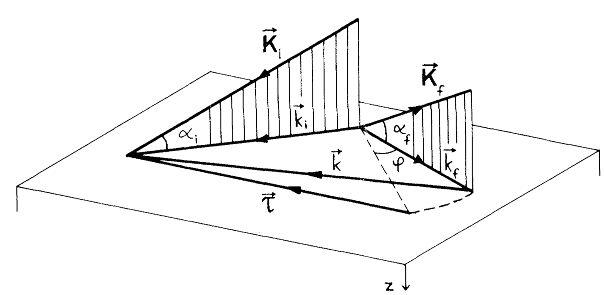

FIG. 1. Scattering geometry. $|\vec{K}_i| = |\vec{K}_f|$. The Bragg condition is $\varphi = 0$. The reflected wave is not shown.

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of the correlation function of occupation numbers S_m with values $+1$ (-1) if atom A (B) is on the lattice site $(\vec{r}_m, z_m \geq 0)$. Further, $\vec{K} = \vec{K}_i - \vec{K}_f$ (cf. Fig. 1) and[9]

$$\kappa = K[\sin^2\alpha_i - \delta]^{1/2} + K[\sin^2\alpha_f - \delta]^{1/2}, \tag{3}$$

where $K = |\vec{K}_i| = |\vec{K}_f|$. Finally, M denotes a product of transmission coefficients and atomic form factors (scattering lengths) including Debye-Waller terms. The explicit expression for M is not given here since it is not essential in the present context.[10] If both $\alpha_i, \alpha_f \gg \alpha_c$, we may neglect δ in Eq. (3). Then $\kappa = K_i^z - K_f^z$ and Eq. (2) reduces to a proper Fourier transform familiar from bulk scattering. On the other hand, if either α_i or α_f or both are less than α_c, then κ is complex with $\mathrm{Im}\,\kappa > 0$. In this case the sum over lattice sites in Eq. (2) is effectively restricted to a surface layer of thickness $(\mathrm{Im}\,\kappa)^{-1}$. For the rest of this Letter, we consider exclusively the latter case.

We chose the surface to be a (110) plane of a bcc lattice and denote by $\vec{\tau}$ the reciprocal vector $(2\pi/a, 0, 0)$ of the ordered superlattice lying in the surface with a being the lattice constant. The local order parameter (OP), ϕ_n, is then introduced by $S_n = \phi_n \exp(-i\vec{\tau}\cdot\vec{r}_n) + \psi_n$. The mean value $\langle\phi_n\rangle \equiv \phi(z_n)$ yields the OP profile. The quantity ψ_n describes deviations from stochiometry caused by a surface chemical potential which arises because local binding energies in the surface will in general differ from their bulk values. In the critical regime the nonordering field ψ_n is irrelevant[11] and will therefore be neglected.

Information on the behavior of Γ in the critical region $|T - T_c|/T_c \equiv |t| \ll 1$, $|\vec{K} - \vec{\tau}| \equiv p \ll a^{-1}$ is obtained from recent renormalization-group work on continuum Ginzburg-Landau models for semi-infinite systems.[1] The results reveal that the OP correlation functions vary spatially, even in the vicinity of the surface, on the scale of the bulk correlation length $\xi \sim |t|^{-\nu}$.

We shall not go into computational details but simply quote the final result for Γ in Eq. (2), valid at the so-called ordinary transition where the bulk drives the surface ordering. As in the case of bulk scattering there is a superlattice Bragg peak $(\bar{\Gamma})$ below T_c, reflecting the temperature dependence of the local OP, and a diffuse scattering $(\tilde{\Gamma})$ in the vicinity of the position of this peak which is caused by critical OP fluctuations.

The Bragg intensity for $|t| \ll 1$ is given by

$$\bar{\Gamma} = (2\pi/a)^2 N_\parallel \delta(\vec{K} - \vec{\tau})|\bar{F}(\kappa\xi)/\kappa a|^2 |t|^{2\beta}, \tag{4}$$

where $N_\parallel$ denotes the number of illuminated atoms in the surface. The scaling function displays the two relevant length scales. From a short-distance expansion[12] one finds $\bar{F}(\zeta) \sim \zeta^{(\beta_1 - \beta)/\nu}$ as $\zeta \to \infty$. For fixed κ and $t \to -0$ this leads

$$\bar{\Gamma} = (2\pi/a)^2 N_\parallel \delta(\vec{K} - \vec{\tau}) D_1(|\kappa|a)^{-2\mu}|t|^{2\beta_1}, \tag{5}$$

where $\mu \equiv 1 + (\beta_1 - \beta)/\nu$. In Eq. (5) and subsequently, D_α denotes a numerical coefficient $O(1)$. For a scalar OP, $\beta_1 \approx 0.82$ from the ϵ expansion[1] up to $O(\epsilon^2)$.

The diffuse intensity also takes a scaling form,

$$\tilde{\Gamma} = N_\parallel(|\kappa|a)^{-3+\eta}\tilde{F}(p/|\kappa|, p\xi, v), \tag{6}$$

with $v \equiv \mathrm{Im}\,\kappa/|\kappa|$. More specific results are obtained in the following two limits: For $t \equiv 0$ and small p, $\tilde{\Gamma}$ approaches

$$\tilde{\Gamma}_p = N_\parallel A(\kappa)[1 - D_2 g(v)(p/|\kappa|)^{\eta_\parallel - 1}]; \tag{7}$$

whereas for $p \equiv 0$ and small $t > 0$, $\tilde{\Gamma}$ tends to

$$\tilde{\Gamma}_t = N_\parallel A(\kappa)[1 - D_3(|\kappa|a)^{1-\eta_\parallel} g(v) t^{-\gamma_{11}}]. \tag{8}$$

In Eqs. (7) and (8), $A(\kappa) = D_4(|\kappa|a)^{-3+\eta}/g(v)$ and $g(v) = v + O(\epsilon)$. The surface exponents in Eqs. (5), (7), and (8) are related via scaling[1,12]: $2\beta_1 = \nu(1 + \eta_\parallel)$, $\gamma_{11} = \nu(1 - \eta_\parallel)$. For a scalar OP, $\eta_\parallel \approx 1.48$ and $\gamma_{11} \approx -0.34$.

We note that the form of the diffuse surface scattering differs significantly from the behavior found in the bulk case: Eq. (7) as well as Eq. (8) displays a *cusp singularity* instead of the familiar divergence. The reason is that, at the ordinary transition, the OP fluctuations in the surface layer decay faster than in the bulk.[13]

In order to ensure $\mathrm{Im}\,\kappa > 0$, only one of the angles α_i, α_f needs to be less than α_c. The other one could be chosen arbitrarily within the limits set by the condition $|\vec{K} - \vec{\tau}|a \ll 1$. However, the shape of the cusp anomalies depends sensitively via κ on the scattering geometry. The choice $\alpha_c < \alpha_i \ll 1$ and $\alpha_f < \alpha_c$ is favorable for producing a clearly visible variation of the cusp behavior. Furthermore, with this choice we may set $p = K|\varphi|$ (cf. Fig. 1), giving $p/|\kappa| = (R_i^2 - R_f^2)^{-1/2}|\varphi/\alpha_c|$ with $R_{i,f} = \alpha_{i,f}/\alpha_c$. The advantage of scanning the diffuse intensity in the φ direction at fixed $R_{i,f}$ is that κ remains constant.

The asymptotic expressions for Γ in Eqs. (5), (7), and (8) are valid in some range of t and p (or φ) which is limited by the size of corrections from higher-order terms in $1/(\xi|\kappa|)$ and $p/|\kappa|$ and by the experimental temperature and angular resolution. The critical range could be inferred from the scaling functions $\bar{F}$ and $\tilde{F}$, which are not known in detail, however. To obtain at least a crude estimate we used the mean-field approximation for $\bar{F}$ and $\tilde{F}$ with material parameters from[14] CuZn ($a = 2.95$ Å). If we choose $\alpha_i = 2.5\alpha_c$, $\alpha_f = \alpha_c/2$, and a wavelength $\lambda_i = 5.75$ Å, then $\alpha_c = 26$ mrad (7.4 mrad) for x rays (neutrons). Assuming resolutions $\Delta t = \pm 5 \times 10^{-4}$ and $\Delta\varphi = \pm 0.5$ mrad, we obtain that corrections to the asymptotic behavior are at most 10% if $5 \times 10^{-4} \lesssim t \lesssim 10^{-2}$ (10^{-3}) and 1 mrad $\lesssim \varphi \lesssim 30$ (10) mrad for x rays (neutrons). Furthermore, the contribution of thermal diffuse scattering was found to be negligible. Compton scattering yields a background comparable in size to the critical diffuse intensity.

We believe that the above estimate is realistic also beyond the mean-field approximation. It indicates that the critical range is accessible and sufficiently extended to render x-ray measurements of β_1, γ_{11}, and $\eta_\parallel$ feasible, especially if highly collimated synchrotron radiation is used.

We have also studied critical magnetic scattering of neutrons. In the vicinity of (superlattice) Bragg positions the cross section of (anti-) ferromagnets shows the same temperature and cusplike angular dependence as discussed here.[15] Finally, we mention that grazing-angle scattering should provide a suitable tool for investigating the roughening transition on crystal surfaces.

We are grateful to H. Peisl for discussions on experimental prospects of this work and for his encouraging optimism. We also thank G. Vineyard for correspondence.

[1]For reviews, see H. W. Diehl, J. Appl. Phys. 53, 7914 (1982); K. Binder, to be published.

[2]We are aware of only one recent experiment [S. F. Alvarado, M. Campagna, and H. Hopster, Phys. Rev. Lett. 48, 51 (1982)], where the surface magnetization in Ni has been measured via scattering of spin-polarized electrons.

[3]W. C. Marra, P. Eisenberger, and A. Y. Cho, J. Appl. Phys. 50, 6927 (1979).

[4]G. Felcher, Phys. Rev. B 24, 1595 (1981).

[5]G. Vineyard, Phys. Rev. B 26, 4146 (1982).

[6]P. Mazur and D. L. Mills, Phys. Rev. B 26, 5175 (1982).

[7]S. Dietrich, doctoral thesis, Universität München, 1982 (unpublished).

[8]For the definition of critical surface exponents, see Ref. 1.

[9]In contrast to Ref. 5 we have taken into account the refraction at the surface of the outgoing scattered wave by employing the Green's function appropriate for the half space.

[10]A detailed version of our work will be published elsewhere.

[11]In the case of binary alloys exhibiting phase separation, the surface chemical potential couples to the order parameter and thus suppresses critical surface fluctuations.

[12]H. W. Diehl and S. Dietrich, Z. Phys. B 42, 65 (1981).

[13]At the "special transition," where a genuine surface ordering coincides at a multicritical point with the bulk ordering, we find $\tilde{\Gamma}_p \sim (p/|\kappa|)^{\eta_\parallel^{sp}-1}$ and $\tilde{\Gamma}_t \sim |t|^{\gamma_\parallel^{sp}}$ with $\eta_\parallel^{sp} \approx -0.3$, $\gamma_\parallel^{sp} \approx 0.81$.

[14]In the case of x-ray scattering, a substance like Fe_3Al is preferable because of its higher scattering power.

[15]In the case of ferromagnets one might contemplate using "small angle" scattering with $\vec{k} \to 0$. However, in this special direction a divergent term $\sim k^{-1+\eta}$ occurs in the diffuse intensity at $t = 0$ which conceals the cusp anomaly. This term is due to critical bulk fluctuations and contributes even for the case of total reflection because of the long range of the magnetic dipolar force between neutrons and electrons.