

of the W(100) surface resonance, we wish to point out that in fact other characteristics of the (100) clean spectrum (the 0.8-eV peak and the general spectrum shape) vanish and return in precisely the same manner. The effect of overlayer symmetry on the surface density of states appears to be more significant than previously assumed. The Kar-Soven hypothesis implies that this could occur but the extent to which the band structure mixing and consequent SDOS scrambling apparently proceeds is surprising.

To summarize briefly, we find that the atomic ordering and crystal structure of gold and copper overlayers on tungsten is the primary factor determining the SDOS. Both metals can effectively mimic tungsten even with two adsorbed monolayers. With integral monolayers of gold the measured energy spectra are essentially undistinguishable from those for clean tungsten. The proposed condition is simply that the overlayer atoms assume a (1×1) pseudomorphic order. Considerable practical complication and interpretive richness is present, however, since the kinetic mechanisms of ordering are very sensitive to experimental conditions. Changes of substrate temperature and crystal orientation, among others, are sufficient to cause effects such as the switch from a (1×1) island adsorbate growth to a dispersed low-density structure. Although ordering behavior is the main consideration, electronic effects such as the ability of copper to form a surface state, thus enhancing one part of the spectrum, must also be considered.

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Light Scattering as a Probe of Dynamical Critical Properties of Antiferromagnets

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It is shown that well-known coupling of electric fields to pairs of spin operators leads to the possibility of studying certain response functions of interest in critical phenomena by means of inelastic-light-scattering experiments.

Light-scattering experiments have been widely used to study dynamical critical phenomena in liquids.¹ In magnetic materials, however, inelastic-neutron-scattering experiments have been more often employed,² partly because light does not always couple in a simple way to the magnetization (or staggered magnetization) of a magnet (or antiferromagnet). It would be useful in improving understanding of the dynamics of critical phenomena in antiferromagnets to be able to more readily use light-scattering

techniques.

Here it is pointed out that for certain classes of well-studied antiferromagnets, a well-characterized coupling between the light and a quantity coupled to the energy density and (below T_N) to other hydrodynamic variables exists. This coupling should permit several new things to be learned about dynamic critical phenomena in these systems. I will review the situation for cubic antiferromagnets such as RbMnF_3 . The coupling in question, which has been shown to account in detail for results of Raman-scattering experiments at high energy transfers in RbMnF_3 , is³

$$\mathcal{H}' = B \sum_{\vec{\delta}, \vec{r}} (\mathcal{E}_{\vec{r}} \cdot \vec{\delta})(\mathcal{E}_{\vec{r}+\vec{\delta}} \cdot \vec{\delta}) S_{\vec{r}} \cdot S_{\vec{r}+\vec{\delta}}. \quad (1)$$

Here $\vec{\delta}$ is summed over vectors to the nearest neighbor of the spin at \vec{r} , and $\vec{\mathcal{E}}_{\vec{r}}$ is the optical electric field at the point \vec{r} . The light-scattering extinction coefficient $h_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\omega, \vec{k})$ is related to this by⁴

$$h_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\omega, \vec{k}) = \left(\frac{\omega_n}{c}\right)^4 \int \frac{dt}{2\pi} e^{-i\omega t} \langle H_{\hat{\epsilon}_n, \hat{\epsilon}_0}(-\vec{k}, t) H_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\vec{k}, t) \rangle, \quad (2)$$

where

$$H_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\vec{k}, t) = B \sum_{\vec{\delta}, \vec{r}} e^{i\vec{k} \cdot \vec{r}} (\hat{\epsilon}_n \cdot \vec{\delta})(\hat{\epsilon}_0 \cdot \vec{\delta}) \vec{S}_{\vec{r}}(t) \cdot \vec{S}_{\vec{r}+\vec{\delta}}(t). \quad (3)$$

Here $\hat{\epsilon}_n$ and $\hat{\epsilon}_0$ are unit vectors in the direction of the electric field vectors of the scattered and incident light, respectively; ω_n is the frequency of the scattered light; and ω and \vec{k} are the frequency and wave-vector transfer. To find the form of the correlation function when \vec{k} and ω are small, write⁵

$$H_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\vec{k}, t) = \sum_{\alpha} A_{\alpha}(\vec{k}, t) \langle A_{\alpha}(-\vec{k}) H_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\vec{k}) \rangle / \langle A_{\alpha}(-\vec{k}) A_{\alpha}(\vec{k}) \rangle + H_{\hat{\epsilon}_n, \hat{\epsilon}_0}'(\vec{k}, t), \quad (4)$$

where the A_{α} are the slowly varying variables (locally conserved quantities and order-parameter fluctuations, but $H_{\hat{\epsilon}_n, \hat{\epsilon}_0}'(\vec{k}, t)$ is supposed to be rapidly varying in time). For $T > T_N$ for a cubic antiferromagnet the variables $A_{\alpha}(\vec{k}, t)$ are⁶ the three components $\vec{m}(\vec{k}, t)$ of the magnetization and the energy density $E(\vec{k}, t)$. A simple symmetry argument for $T > T_N$ shows that only $E(\vec{k}, t)$ gives a nonzero contribution to (5). One finds

$$H_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\vec{k}, t) = E(\vec{k}, t) \frac{\langle E_{-\vec{k}} H_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\vec{k}) \rangle}{\langle E_{-\vec{k}} E_{\vec{k}} \rangle} + H_{\hat{\epsilon}_n, \hat{\epsilon}_0}'(\vec{k}, t), \quad T > T_N. \quad (5)$$

The coefficient is

$$\frac{\langle E_{-\vec{k}} H_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\vec{k}) \rangle}{\langle E_{-\vec{k}} E_{\vec{k}} \rangle} = \frac{JNB \sum_{\vec{r}} e^{i\vec{k} \cdot \vec{r}} \langle (\sum_{\vec{\delta}} \vec{S}_{\vec{r}} \cdot \vec{S}_{\vec{r}+\vec{\delta}}) (\sum_{\vec{\delta}} \vec{\delta} (\hat{\epsilon}_n \cdot \vec{\delta})(\hat{\epsilon}_0 \cdot \vec{\delta}) \vec{S}_{\vec{r}} \cdot \vec{S}_{\vec{r}+\vec{\delta}}) \rangle}{\langle E_{-\vec{k}} E_{\vec{k}} \rangle}. \quad (6)$$

For $|\vec{k}| \ll |\vec{\delta}|$ I interchange the sum on \vec{r} and $\vec{\delta}'$ and argue on physical grounds that the sum on \vec{r} should be essentially independent of the direction of $\vec{\delta}'$. Then the coefficient becomes $(B/zJ) \sum_{\vec{\delta}} (\hat{\epsilon}_n \cdot \vec{\delta}') \times (\hat{\epsilon}_0 \cdot \vec{\delta}')$, where z is the number of nearest neighbors. Thus for small \vec{k} combining (6) and (4) gives for the extinction coefficient

$$h_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\omega, \vec{k}) = \left(\frac{\omega_n}{c}\right)^4 \frac{B^2}{z^2 J^2} \left| \sum_{\vec{\delta}} (\hat{\epsilon}_n \cdot \vec{\delta})(\hat{\epsilon}_0 \cdot \vec{\delta}) \right|^2 \langle E_{\vec{k}} E_{-\vec{k}} \rangle(\omega), \quad T > T_N.$$

For RbMnF_3 the spin lattice is simple cubic, giving

$$h_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\omega, \vec{k}) \simeq \left(\frac{\omega_n}{c}\right)^4 \frac{B^2}{9J^2} (\hat{\epsilon}_n \cdot \hat{\epsilon}_0)^2 \langle E_{\vec{k}} E_{-\vec{k}} \rangle(\omega), \quad T > T_N. \quad (7)$$

With insertion of the hydrodynamic form⁶ for $\langle E_{\vec{k}} E_{-\vec{k}} \rangle(\omega)$,

$$h_{\hat{\epsilon}_n, \hat{\epsilon}_0}(\omega) = \left(\frac{\omega_n}{c}\right)^4 \frac{a^4 B^2}{9J^2} (\hat{\epsilon}_n \cdot \hat{\epsilon}_0)^2 \frac{2ck_B T^2 D_T k^2}{\omega^2 + (D_T k^2)^2}. \quad (8)$$

Here c is the (magnetic) specific heat at zero magnetic field and $D_T = K/c$ when K is the (magnetic contribution to) the thermal conductivity. When $\omega \sim D_T k^2 \ll \omega_n, \omega_0$, one obtains $k \simeq k_0 \sin \theta / 2$, where θ is the scattering angle of the light and ω_0 and \vec{k}_0 characterize the incident light.

One can obtain a very rough estimate of the magnitude of this scattering as follows. Using an esti-

mate for B from the excited-state exchange model⁷ of the light-spin coupling parameter B , we obtain from Eq. (8) the expression

$$\int h d\omega \approx k_n^4 (8c^2 a_B^2 J'/E_0^2) (k_B T)^2 / 9J^2,$$

where the integral is over the Lorentzian peak. Here I have assumed $c \approx k_B$. J' is the excited-state exchange, a_B the Bohr radius, and E_0 the energy of the first excited Mn^{2+} p state. For $J \approx J'$, $E_0 \approx 1$ Ry, $T \approx 100^\circ K$, and $k_n \approx 0.2 \times 10^{-5} \text{ cm}^{-1}$ I obtain $\int h d\omega \approx 7 \times 10^{-10} \text{ cm}^{-1}$. While this is a very crude estimate, it indicates that the intensity is probably observable. (Brillouin scattering in liquid helium is observed⁸ with intensity $\int h d\omega \approx 10^{-11} \text{ cm}^{-1}$.)

This result suggests a useful experiment: An outstanding question⁹ in the theory of dynamical critical phenomena in antiferromagnets is whether the magnetic energy is effectively conserved in real crystals. Alternatively, it is possible that the magnetic energy is freely exchanged with the lattice. If magnetic energy is conserved then (7) predicts a Lorentzian line shape in the inelastic line shape just above T_N at small ω and \vec{k} . If not, any "central peak" in the scattering T_N will be much broader, corresponding to rapid relaxation of the energy to the lattice and the width will be essentially k independent. In $RbMnF_3$ this experiment may be quite feasible because one-spin scattering¹⁰ is very small as a consequence of the fact that spin-orbit effects are small for the S -state Mn^{2+} ions.

Below T_N , the analysis leading to (5) is unchanged. The conserved and slow variables in an isotropic antiferromagnet are now⁶ the energy density, magnetization $\vec{m}(r, t)$, and the two components $n^y(\vec{r}, t)$ and $n^z(\vec{r}, t)$ of the staggered magnetization which are perpendicular to the direction of the static staggered magnetization (called x). The only terms in the sum in (5) which contribute to the second-order scattering are now those proportional to $E(\vec{k}, t)$ and $m_x(\vec{k}, t)$. An essentially identical analysis gives

$$h \hat{\epsilon}_n \cdot \hat{\epsilon}_0(\omega) = \left(\frac{\omega_n}{c}\right)^4 \left\{ \left(\frac{B}{3J}\right)^2 \langle E_{\vec{k}} E_{-\vec{k}} \rangle(\omega) + \frac{B^2}{9} \langle m_{\vec{k}^x} m_{-\vec{k}^x} \rangle(\omega) \right\} (\hat{\epsilon}_n \cdot \hat{\epsilon}_0)^2 \quad (9)$$

or, using the hydrodynamic results (and for the single cubic case)

$$h \hat{\epsilon}_n \cdot \hat{\epsilon}_0(\omega) = \left(\frac{\omega_n}{c}\right)^4 \left\{ \left(\frac{B}{3J}\right)^2 \frac{2ck_B T^2 D_T k^2}{\omega^2 + (D_T k^2)^2} + \frac{B^2}{9} \frac{2\chi_{\parallel} k_B T D_{\parallel} k^2}{\omega^2 + (D_{\parallel} k^2)^2} \right\} (\hat{\epsilon}_n \cdot \hat{\epsilon}_0)^2, \quad T < T_N.$$

Here D_{\parallel} is the diffusion constant for the component at the magnetization parallel to the sublattice magnetization and χ_{\parallel} is the parallel susceptibility (not staggered) in units of $(g\mu_B)^2$.

In the critical region, one does not expect the response function of the slow variables to have the hydrodynamic form. Predictions have been obtained for the longitudinal-magnetization correlation function using mode-mode coupling and ϵ -expansion calculations.¹¹ [$\langle E_{\vec{k}} E_{-\vec{k}} \rangle(\omega)$ has not been calculated in this way.] The present analysis then suggests that, even without calculations of $\langle E_{\vec{k}} E_{-\vec{k}} \rangle(\omega)$ one may extract $\langle m_{\vec{k}^x} m_{-\vec{k}^x} \rangle(\omega)$ from data above and below T_N if (as is found in hydrodynamics) $\langle E_{\vec{k}} E_{-\vec{k}} \rangle$ is symmetric as a function of T about T_N . Similar results can easily be obtained for other magnetic systems for which the hydrodynamics is known, such as planar magnets. The available experimental systems seem, however, to be less than ideal.

Note that for fluids, early suggestions¹² that depolarized second-order light scattering be used to study four-point dynamical correlation functions were shown by Oxtoby and Gelbart¹³ to be incorrect. Gelbart showed that the depolarized com-

ponent of the light scattering arises from double scattering of real photons (a volume-dependent effect) near the critical point. (The predicted effect was observed by Reith and Swinney.¹⁴) There is, however, an essential difference between the fluid case and magnetic one considered here: In the fluid the coupling corresponding to \mathcal{H}' of Eq. (1) in the magnetic case is of form

$$\mathcal{H}'' = \int d^3 r' \int d^3 r \rho(\vec{r}) \vec{E}(\vec{r}) \cdot \vec{T}(\vec{r}, \vec{r}') \cdot \vec{E}(\vec{r}') \rho(\vec{r}').$$

Here $\vec{T}(\vec{r}, \vec{r}')$ is the electric dipole-dipole interaction and is of much longer range (proportional to $1/|\vec{r} - \vec{r}'|^3$) than the nearest-neighbor interaction (probably arising from higher-order exchange⁷) which appears in (1). It is this difference in the range of the interactions appearing in the two problems which results in qualitatively different behavior of the second-order scattering near the critical point in the two cases.

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CO on Cu(100)—Explanation of the Three-Peak Structure in the X-Ray-Photoemission-Spectroscopy Core Spectrum

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The x-ray-photoemission-spectroscopy core-level spectrum for CO chemisorbed on Cu(100) is calculated with the transfer of screening charge to the adsorbate taken into account. Using a realistic substrate density of states, we obtain the observed three-peak structure and give a simple interpretation of the results.

X-ray photoemission from core levels of adsorbed molecules has been used extensively to obtain information about the state of the adsorbate. In particular, a multipeak structure in the energy distribution of the emitted electrons has usually been attributed to the presence of different adsorption states, e.g., partial dissociation of the adsorbed molecules. Recent experiments^{1,2} suggest, however, that a multipeak structure can also occur for one single adsorption state. We give in this paper the first discussion of the relationship between the shape of the x-ray photoemission spectroscopy (XPS) spectrum and the substrate density of states (DOS). We find that the shape of the *valence* DOS can influence dramatically the form of the XPS *core* spectrum. The formalism is applied to CO chemisorbed on Cu(100). In this case the sharp decrease in the DOS at the top of the *d* band splits the leading

peak of the core spectrum, while the rapid DOS change at the bottom of the *d* band gives rise to negligible structure.

CO on Cu has recently been studied using ultraviolet photoelectron spectroscopy (UPS),²⁻⁵ XPS,^{1,2,5} low-energy electron diffraction spectroscopy,⁶ ir spectroscopy,⁷ and electron-energy-loss⁸ spectroscopy. The assignment of the UPS spectrum has been controversial and the presence of different adsorption states has been proposed. Recent experiments¹⁻³ suggest strongly, however, that only one state exists and the three-peak structure observed in the XPS core spectrum^{1,2} must then be due to shakeup peaks. As only weak satellites are observed for CO in the gas phase,⁹ the strong satellites in the chemisorbed phase are caused by extra molecular effects, and, in particular, the screening of the core hole by the substrate valence electron. In