SPECTRAL WIDTH OF THE CRITICAL OPALESCENCE DUE TO CONCENTRATION FLUCTUATIONS

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At the conference on "Phenomena in the Neighborhood of Critical Points," arranged by Melville Green and held in Washington, D. C., 5-8 April 1965, S. S. Alpert of Columbia University reported about the extraordinary sharpness of the spectral line characterizing the light scattered by a binary mixture in the vicinity of its critical point if excited by laser light. He found that the width of that line depended materially on the angle of scattering and on the temperature distance from the critical point. The line sharpens up with decreasing scattering angle and with decreasing temperature distance.

In this case the linewidth is theoretically mainly determined by the diffusion coefficient of the two liquids in each other, and the effect, as described by Alpert, indicated that this coefficient tends to become zero at the critical point.

This interesting behavior induced me to make a discussion remark with the intention of explaining the effect. I was asked to put this remark in writing. I am doing this in the following, leaving out all obviously possible elaboration.

If the angle I of scattering is characterized by the function

$$s = 2\sin\tfrac{1}{2}I, \tag{1}$$

the light observed at this angle, in accordance with Brillouin's calculation,[1] is considered as reflected from a standing concentration wave with a wavelength Λ which is connected with s and the wavelength λ of the incident light by Bragg's relation

$$1/\Lambda = s/\lambda. \tag{2}$$

This wave is one of the Fourier components of the fluctuation pattern.

If we would have set up a concentration wave, say in the x direction, of that form at moment $t = 0$, and we apply the diffusion equation, it follows immediately that at time t this wave will be represented by an expression (defining a relaxation time θ) of the form

$$Ae^{-t/\theta}\sin(2\pi x/\Lambda), \tag{3}$$

with

$$1/\theta = (4\pi^2/\Lambda^2)D, \tag{3'}$$

and in which D is the diffusion coefficient.

Since Bragg's relation (2) holds, and since $1/2\pi\theta$ is the spectral width in cycles per second of the Fourier transform of (3), there follows a first rule:

(a) the scattered line broadens proportional to s^2 with increasing scattering angle.

The next point to consider is the dependence of the diffusion coefficient on the temperature. There exists a well-known relation due to Einstein which connects diffusion with the Brownian motion and expresses D in the form

$$D = kT/\rho, \tag{4}$$

in which k is Boltzman's constant, T the absolute temperature, and ρ the friction coefficient of the diffusing particle which is being considered (the reciprocal of its mobility) under an outside influence of driving force. This relation really is the limiting form for dilute solutions of a more general relation, namely

$$D = (1/\rho)\partial P/\partial n, \tag{4'}$$

in which kT is replaced by the rate of change of the osmotic pressure with the number n of particles per cc. What is mainly of importance for the evaluation of the diffusion constant, therefore, is the "driving force," expressed by the concentration gradient of the osmotic pressure.

Now if we consider a diagram of isotherms for the osmotic pressure as a function of the concentration and for different temperatures near the critical point, we are considering an isotherm which approaches a form with an inflection point and a horizontal tangent. At the critical point itself the concentration gradient of P is zero, so we conclude that also D should tend to zero near the critical point, since we cannot expect the friction coefficient ρ to change materially.

Supposing that the experiment is done at a temperature T above the critical temperature T_C and at the critical concentration, we should now consider how the concentration gradient of P changes with changing temperature distance $T-T_C$. All classical theories leading to an expression for the free energy of mixing, like, for instance, the expression preferred by Hilde-

brand, lead invariably to the conclusion that this gradient is proportional to $T-T_c$. So from the point of view of the theory in its classical form, we come to the second rule:

(b) The scattered line should broaden proportional to the temperature distance $T-T_c$.

It seems that Alpert's experiments are consistent with these two rules.

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[1]L. Brillouin, Ann. Physique 17, 103 (1921).

POSSIBILITY OF PHONON-INDUCED SUPERCONDUCTIVITY

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In recent investigations[1-3] it was shown that superconductivity is by no means restricted to metals. The first necessary condition for superconductivity is the attractive interaction between electrons. This interaction is attractive if the interaction through virtual phonons is larger than the screened Coulomb repulsion. Cohen[2] and others have pointed out that a large dielectric constant will increase the screening and reduce the electronic repulsion. On the other hand, increase of the effectiveness of the phonon interaction increases the attraction between the electrons. This interaction is the result of the creation of a virtual phonon in the phonon vacuum, since at the temperatures involved one can for all practical purposes assume that there are no phonons available to begin with. The phonon is subsequently absorbed by another electron. The mechanism of this process was pointed out by Fröhlich[4] and is, due to the discovery of the isotope effect, firmly established. In the general theory of superconductivity, only the fact that it gives rise to a negative energy is used. If one considers the unitary transformation introduced by Fröhlich in detail, one finds that the resulting effective interaction is the product of a strength factor and several matrix elements divided by a denominator which becomes negative in certain regions of the electron and phonon spectra. The strength factor is a "constant of the material," and the interval of the spectra cannot be influenced either. However, the aforementioned matrix elements are subject to the condition that no phonons are present, which at such low temperatures is definitely the case, provided no exterior influence is used to stimulate their presence. If one could induce a number of phonons, this process would be more effective since the matrix element of phonon creation is proportional to $(n+1)^{1/2}$.

It follows from the Fröhlich Hamiltonian[4] that the high-frequency phonons are more effective than the low-frequency ones. Since all man-made phonons are low-frequency phonons in the sense that their frequency is only a very small fraction of the Debye frequency, the ultrasonically produced phonons will aid little to change the effective interaction between the electrons.

However, there is one exception. It has been shown a few years ago that it is possible to produce very high-frequency phonons in the junction of a diode.[5-8] These phonons result from electrons that reach the other side of a junction in a different band than the one they started out in, and simultaneously change their crystal momentum, because the minima in k space of the bands were not at the same position.[9]
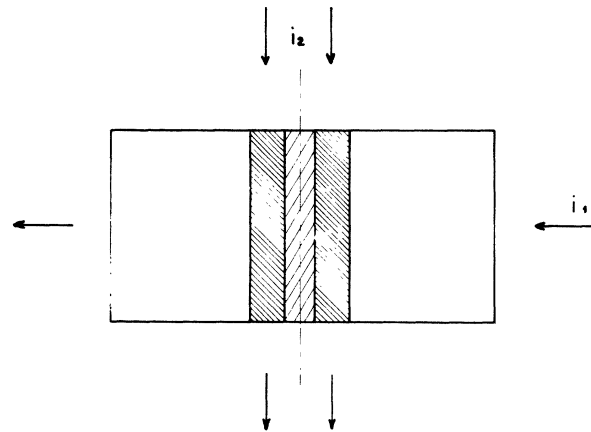

FIG. 1. Sketch of the sample and the arrangement of currents. The middle part represents the junction with its adjacent layers. i_1 = current to produce phonons; i_2 = supercurrent.