temperature dependence can be ignored. This region does not correspond to the region in which our attenuation measurements fit a power law $\alpha=A/|T_{\lambda}-T|^n$. In fact, if C_p is approximated by a power law $|T_{\lambda}-T|^{-m}$ in the temperature region for which the critical behavior of the attenuation was determined, then $m\simeq 0.25$ for $0.01~{\rm K} < T-T_{\lambda} < 0.1~{\rm K}$. It thus seems improper to compare the exponents obtained from our measurements with those cited in the literature.

Superfluid region (T < 2.0 K). – In the superfluid region, the attenuation is described in a theory by Khalatnikov and Chernikova.¹³ Dissipative terms include a contribution associated with the relaxation times for the several processes involved in establishing equilibrium in the gas of elementary excitations. At higher temperatures these relaxation times are short compared with the acoustic period (hydrodynamic regime) and long at lower temperatures (collisionless regime). A peak in attenuation separates the two regimes. The measurements are seen to be in good agreement with the attenuation calculated14 from this theory. In particular there is clear evidence of a maximum in attenuation at 1.5 K. We do not find any evidence that the theory may require modifications at high frequencies as indicated by measurements of Woolf, Platzman, and Cohen and Heinicke, Winterling, and Dransfeld.

This work was initiated with Professor R. W. Leonard, now deceased, who conceived the interferometer system in its present form.

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- ¹J. S. Imai and R. W. Leonard, Bull. Am. Phys. Soc. <u>13</u>, 505 (1968); J. S. Imai and I. Rudnick, J. Acoust. Soc. Am. 45, 317(A) (1969).
- ²M. A. Woolf, P. M. Platzman, and M. G. Cohen, Phys. Rev. Letters 17, 294 (1966).
- ³W. Heinicke, G. Winterling, and K. Dransfeld, Phys. Rev. Letters 22, 170 (1969).
 - ⁴C. E. Chase, Phys. Fluids <u>1</u>, 193 (1958).
- ⁵M. Barmatz and I. Rudnick, Phys. Rev. <u>170</u>, 224 (1968).
- ⁶C. E. Chase, Proc. Roy. Soc. (London), Ser. A <u>220</u>, 116 (1953).
- ⁷J. R. Pellam and C. F. Squire, Phys. Rev. $\underline{72}$, 1245 (1947); J. A. Newell and J. Wilks, Phil. Mag. $\underline{4}$, 745 (1959).
- ⁸L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk. SSSR 96, 469 (1954).
- ⁹A sealed system, isolated from the open bath by a vacuum jacket, with a controlled heat input rate, is currently being prepared for higher resolution measurements.
- 10 L. P. Kadanoff, Comm. Solid State Phys. $\underline{1}$, 5 (1968).
- ¹¹J. Swift and L. P. Kadanoff, Ann. Phys. (N.Y.) <u>50</u>, 312 (1968).
- ¹²R. A. Ferrell, N. Menyhárd, H. Schmidt, F. Schwabl, and P. Szépfalusy, Ann. Phys. (N.Y.) <u>47</u>, 565 (1968);
 P. Szépfalusy, Phys. Letters <u>27A</u>, 128 (1968);
 T. Tsuzuki, to be published.
- ¹³I. M. Khalatnikov and D. M. Chernikova, Zh. Eksperim. i Teor. Fiz. <u>49</u>, 1957 (1965), and <u>50</u>, 411 (1966) [translations: Soviet Phys.-JETP <u>22</u>, 1336 (1966), and <u>23</u>, 274 (1966)].
- ¹⁴We are indebted to Dr. W. M. Whitney for providing us with the computed curve shown in Fig. 2.

FERROELASTICITY OF NIOBIUM DUE TO HYDROGEN AS A LATTICE GAS

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We have measured the elastic response of niobium in the region of the critical point of hydrogen in niobium. The elastic susceptibility exceeds commonly observed values by two or three orders of magnitude and follows a Curie-Weiss relation over the temperature range investigated. The diffusion coefficient of hydrogen shows "critical slowing down" behavior but no anomaly in the transport coefficient.

It has been pointed out that interstitially dissolved hydrogen in metals like Nb, Ta, V, Pd, etc., can, to a first-order approximation, be considered as an example for the theoretically well-explored lattice gas. The characteristic feature common to the phase diagrams for hydrogen in these metals is a miscibility gap whose

boundary can be interpreted as the coexistence curve for the lattice gas and lattice liquid. The van der Waals isotherms of the lattice gas can be deduced from solubility measurements. These isotherms have topologically the same appearance as the van der Waals isotherm of a free real gas, including a critical temperature below

which separation into two phases occurs. The metal lattices provide the structured space in which the lattice gas can undergo phase transitions similar to a free gas.

However, in contrast to the originally theoretical lattice gas model² the space for the hydrogen lattice gas is not completely inert: E.g., the lattice is expanded by the lattice gas. For Nb the following relation holds³: $\Delta a/a = 7 \times 10^{-4}/\text{at.\%}$ H. This interaction of the lattice gas with its lattice couples the critical phenomena of the lattice gas to the host lattice. It will be shown that the steep rise of the lattice-gas compressibility on approach to the critical point causes a phenomenon which can be called "ferroelasticity." The energy of interaction of the interstitial hydrogen with a strain field $\epsilon_{ij} = s_{ijkl} \sigma_{kl}$ can be written as^{4,5}

$$U = -P_{ij}s_{ijkl}\sigma_{kl}; (1)$$

 P_{ij} is the elastic dipole-moment tensor. In the following we are not interested in paraelasticity caused by the orientation of elastic dipoles^{4,6} but in paraelasticity caused by the migration of hydrogen in an inhomogenous elastic field.⁷ In the presence of a lattice gas the response of an elastic solid to a stress which causes a gradient in volume dilatation consists of two parts, an instantaneous strain and a time-dependent strain. The latter is caused by a concentration gradient in the lattice gas, which builds up under the action of the gradient in dilatation. Therefore

$$\epsilon_{ij}(r,t) = s_{ijkl} \left\{ \sigma_{kl}(r) + \left[\rho(r,t) - \rho_0 \right] P_{kl} \right\}, \tag{2}$$

(ρ = lattice gas density). The static elastic susceptibility can be defined (ignoring the tensor character from now on) as

$$\chi = \frac{\partial \left[(\rho - \rho_0) P \right]}{\partial \sigma} \bigg|_{t \to \infty, \ \sigma \to 0} \tag{3}$$

The spatial distribution of the lattice gas in an elastic field is determined by the equation

$$\mu(\rho(r), T) - Ps\sigma(r) = \text{const}, \tag{4}$$

(μ = chemical potential of the lattice gas). Expanding μ in density changes we find

$$\frac{\partial \mu}{\partial \rho} (\rho - \rho_0) = Ps\sigma. \tag{5}$$

The constant on the right-hand side in Eq. (4) is equal to $\mu(\rho_0)$ for the experimental situation which will be considered below. Inserting Eq. (5) into Eq. (3) yields for the elastic susceptibility

$$\chi = P_S^2 / (\partial \mu / \partial \rho). \tag{6}$$

 $\partial \mu/\partial \rho$ is connected with the isothermal latticegas compressibility κ by the relation

$$\left. \frac{\partial \mu}{\partial \rho} \right|_{T} = \frac{1}{\rho^{2} \kappa} \,. \tag{7}$$

For a noninteracting lattice gas, $\partial \mu/\partial \rho$ is equal to kT/ρ_0 . Therefore, Eq. (6) yields a paraelastic susceptibility which is proportional to the density ρ_0 , the square of the dipole moment, and the reciprocal temperature, in complete analogy to the paramagnetic susceptibility. Since $\partial \mu/\partial \rho = 0$ on approach to the critical point of the lattice gas, the elastic susceptibility should go to infinity for $T-T_C$, again in analogy to the magnetic case.

We have measured the elastic susceptibility of Nb loaded with 26 at. % H which is in the region of the critical concentration. The specimen was a coiled spring to which a torque was applied. The elastic field across such a specimen corresponds to the bending of a bar. The time-dependent strain therefore is caused by the diffusion of lattice gas from the compression side to the dilatation side of the specimen. The critical temperature was expected at approximately 150°C. Figure 1 shows examples at three different temperatures for the elastic response to application and removal of such a small stress ($\sigma = 2 \times 10^{-7}E$), for which a linear response has been found. The strain is completely reversible. The elastic susceptibility increases strongly with falling temperature and at 166°C reaches 425%, which is two to three orders of magnitude larger than commonly observed for paraelasticity. In Fig. 2 the reciprocal susceptibility is plotted against temperature, showing, within experimental errors, a Curie-Weiss behavior for the temperature range investigated.

Besides the susceptibility, the diffusion coefficient D can be determined from the relaxation

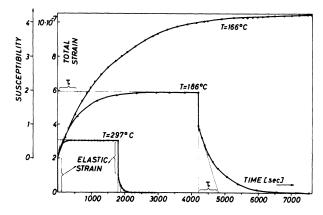


FIG. 1. Elastic response of Nb with 26% H.

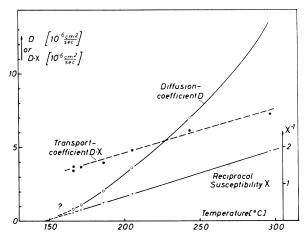


FIG. 2. Reciprocal susceptibility, diffusion coefficient D, and transport coefficient $\Lambda = D\chi$ close to the critical point of hydrogen in niobium.

time τ of the response function using the relation $13.2D\tau = d^2$, which is valid for a cylindrical specimen with diameter $d.^{7,8}$ In the long-wavelength limit the diffusion coefficient is determined by the relation

$$D = B \rho_0 \partial \mu / \partial \rho \tag{8}$$

(B = mobility). Equation (8) is a special case of the generalized Einstein relation⁹

$$D = \Lambda(T)/\chi(T). \tag{9}$$

The transport coefficient $\Lambda(T)$ reflects the temperature dependence of the individual jumps.

Since the relaxation process in Fig. 1 follows a simple exponential function, the slope at t = 0 is proportional to $\Lambda(T)$. Figure 1 shows that $\Lambda(T)$ changes only by a factor of 2 between 297 and 166°C, whereas $\tau(T)$, and thus D(T), changes by almost a factor of 20. Both D(T) and $\Lambda(T)$ are plotted in Fig. 2. The temperature dependence of D is only slightly influenced by the temperature dependence of the jump probability but is predominantly determined by the temperature dependence of the reciprocal susceptibility. This slowing down of diffusion in the range of a critical point as caused by the disappearance of the driving force, grad $\mu(\rho) = (\partial \mu/\partial \rho)$ grad ρ , has been called "critical slowing down," especially in connection with spin-diffusion on approach of the Curie temperature. 10

The analogies between the properties of an anisotropic ferromagnet and a lattice gas have been emphasized on the basis that the phase transition in both systems can be described by the Ising model^{2,11}: Magnetization corresponds to a devia-

tion of the density from the critical density whereas the magnetic field corresponds to a change in chemical potential. According to Eq. (4), which for $\rho = \rho_C$ can be written as $\mu - \mu_C = Ps\sigma$, the chemical potential of the lattice gas can be changed by an elastic field. The elastic equations (1)-(3) can easily be translated into magnetic equations by the substitutions

$$m \rightarrow P$$
, $B \rightarrow \epsilon$, $H \rightarrow \sigma \sim (\mu - \mu_c)$,
$$M \rightarrow P(\rho - \rho_c).$$

A sample with increased hydrogen concentration on one side and decreased hydrogen concentration on the other side, as induced by the elastic field applied in our experiment, corresponds to a magnetic system with magnetization in opposite direction on both sides. Positive and negative spontaneous magnetization below the critical point corresponds, for the elastic case, to the separation of hydrogen into high- and low-density regions, thereby causing positive and negative strains.

In summary the following can be said: The experiments presented in this paper show that the coupling of the properties of the lattice gas to the lattice gives rise to paraelastic properties of the lattice, which phenomenologically strongly resemble the paramagnetic behavior of a ferromagnet close to the Curie point. The transformation of lattice-gas properties into elastic properties [Eq. (2)] makes the well-known analogies between ferromagnetism and lattice gas even more apparent.

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¹G. Alefeld, to be published.

²T. D. Lee and C. N. Yang, Phys. Rev. <u>87</u>, 410 1952).

³W. M. Albrecht, W. D. Goode, and M. W. Mallet, J. Electrochem. Soc. 106, 981 (1959).

⁴E. Kröner, <u>Kontinuumstheorie der Versetzungen</u> und Eigenspannungen (Springer-Verlag, Berlin, 1958).

⁵J. D. Eshelby, Solid State Phys. <u>3</u>, 79 (1956).

 $^{^{6}}$ W. Känzig, J. Phys. Chem. Solids <u>23</u>, 479 (1962).

⁷G. Schaumann, J. Völkl, and G. Alefeld, Phys. Rev. Letters <u>21</u>, 891 (1968).

⁸C. Z. Zener, <u>Elasticity and Anelasticity of Metals</u> (University of Chicago Press, Chicago, Ill., 1948).

⁹B. I. Halperin and P. C. Hohenberg, "Scaling Laws

for Dynamic Critical Phenomena" (to be published). ¹⁰L. Van Hove, Phys. Rev. <u>93</u>, 1374 (1954).

 $^{11}\mathrm{M.~E.~Fisher,~Rept.~Progr.~Phys.~}\underline{30},~731$ (1967), pt. II.

DIRECT OBSERVATION OF STRESS-INDUCED SHIFTS IN CONTACT POTENTIALS*

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The effect of stress on contact potential has been measured semiquantitatively in Al, Cu, Au, steel, and brass using a high-sensitivity version of the Kelvin method. The observed shifts are in all samples positive (i.e., the electric field outside the sample is more positive when pressure is applied) and the magnitude is a few microvolts per kg/cm² applied stress. Both sign and magnitude agree with the theories of Dessler, Michel, Rorschach, and Trammell, and of Herring, provided one assumes that gravitationally produced stress is equivalent to hydraulically produced stress.

Considerable interest has developed in the last few years in the existence of electric fields associated with metals in a gravitational field. Most of this interest stems from the magnificent series of experiments performed by Fairbank and Witteborn designed to investigate the gravitational force acting upon electrons and, eventually, upon positrons. The most striking result of these experiments is the observation that free electrons located inside a conductive tube appear not to feel gravity.

This result has lead to a number of theoretical papers. Schiff and Barnhill² showed how the gravitational potential acting upon the mobile electrons in the surrounding metals produces a downward shift in the electron distribution precisely large enough to yield a downward electric field which produces an upward force on electrons just sufficient to cancel the gravitational force. In this model conventional positrons will be accelerated downward with a force of 2g. Later Dessler et al.3 showed that if one takes into account gravitational compression of the lattice as well as of the electron gas, the predicted potential is of opposite sign (i.e., positive potential at the bottom of the column) and a factor of roughly 10⁴ larger. The precise magnitude involves the relative compressibilities of the lattice and of the electron gas. Herring4 has reached a similar conclusion based upon investigation of stress-induced shifts in work function. Particular models have been investigated by Peshkin⁵ and by Barnhill.6

Experiments of Witteborn and Pallesen⁷ in apparent disagreement with the theory of Dessler et al. have been criticized by Tannhauser⁸ and by Michel.⁹ Evidence supporting Dessler et al. and

Herring was found by Beams, ¹⁰ who substituted a centrifugal potential for the gravitational potential and was able to observe an effect of the predicted magnitude and sign. In this experiment the potential at the outer rim of a centrifuge was compared with that at the center.

The theories of the gravitationally induced emf in metals all appear to assume local thermodynamic equilibrium within the metal. If this is the case, then the potential outside of a particular element of metallic surface depends only upon local conditions in the metal. In this case the origin of local stress in the metal is not in itself important. No difference would be expected upon substituting an externally applied compression for the gravitationally produced stress.

The present experiment accepts this viewpoint and utilizes a hydraulic press to supply compressions equivalent to hundreds of meters of material in a gravitational field. The parameter I have chosen to measure is the pressure-induced shift in contact potential. The main complication in relating an externally measured contact potential to interior properties of the metal arises in the complexity of the surface layers, with their equivalent dipole sheets.³,⁴,¹¹ The strength of the method is that a noncontacting measurement of the electric field outside of a metal surface would appear to sense a property very similar to that which influences the electrons in the Witteborn-Fairbank experiment.

Noncontacting measurements of the small shifts expected are feasible using the Kelvin technique for measuring contact potentials. 11,12 The apparatus is shown in Fig. 1.13 A brass reference electrode is vibrated at a distance of about a millimeter from the sample face, thereby producing