er was taken to be

dT/dx = (1/v)dT/dt.

Measuring the shift of the boundary at 100 V we obtained $\Delta T/E^2 \approx 5 \times 10^{-6} (\pm 25 \%)$ with dc and about half that value with ac⁶ (in cgs and centigrade). The effect is of the order of magnitude predicted on the basis of (4).

More exact measurements are in preparation. If external electric fields are incorporated into the microscopic theory⁷ of the nematic-isotropic phase change, an interesting critical phenomenon may be expected.⁸ Large electric fields produce a preferential alignment of the molecules on the isotropic side of the phase transition. Above a critical temperature the isotropic and nematic phases should become indistinguishable. In other words, there should be a critical point at a certain E, P, T where P is the polarization. (E and P take the place of pressure and volume in liquid-gas transitions.) It may be noted that some problems in the application of (3) could arise from heterophase fluctuations.⁹ These pretransitional phenomena are another consequence of the weak dependence of Δg on ΔT , as taken for the "pure" phases. The data given for q in the literature do not separate any pretransitional effects because of experimental difficulties. However, it is generally assumed that the phase transitions are of first order, with a nonvanishing latent heat and, as a rule, a nonvanishing $\epsilon_2 - \epsilon_1$.

I am greatly indebted to G. H. Heilmeier, J. A.

Castellano, A. Sussman, and M. T. McCaffrey for equipment and materials assistance.

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³Mention is made in J. G. Kirkwood, "Chemical Thermodynamics, Notes on the Lectures Delivered at the California Institute of Technology 1950-51," written by I. Oppenheim, M. Karplus, and A. Rich (unpublished).

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 5 J. J. Wysocki, J. Adams, and W. Haas, Phys. Rev. Letters 20, 1024 (1968).

⁶The observation of a well-defined shift at 1 kHz suggests that the phases change slowly compared to this frequency.

⁷W. Maier and A. Saupe, Z. Naturforsch. <u>14a</u>, 822 (1959), and 15a, 287 (1960).

⁸A theory of field-induced phase transitions in terms of the model of Ref. 6, including a critical point, was recently proposed by J. Hanus, Phys. Rev. <u>178</u>, 420 (1969).

⁹J. Frenkel, <u>Kinetic Theory of Liquids</u> (Dover, New York, 1955); V. N. Tsvetkov and E. I. Ryumtsev, Kristallografiya <u>13</u>, 290 (1968) [Soviet Phys. Crystallogr. <u>13</u>, 225 (1968)].

INDIRECT SPIN INTERACTIONS IN SOLID ³He

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We show that the low-temperature specific-heat anomaly in bcc solid 3 He can be explained in terms of an indirect interaction among pairs of spins brought about by virtual absorption and emission of phonons in the exchange process.

Several experiments¹⁻⁴ have revealed that the specific heat of the bcc phase of solid ³He does not conform to Debye T^3 behavior at low temperatures. Recently through precision strain-gauge measurements in very pure ³He, Henriksen et al.⁴ have removed any doubts that this anomalous behavior could be due to impurities or "apparatus" effects.

In this Letter, we explain the specific-heat

anomaly as arising from a phonon-mediated longrange spin interaction in solid ³He, which provides a contribution to the specific heat varying as T^{-2} . In bcc solid ³He, we obtain quantitative agreement with experimental results without adjusting any parameter. For hcp solid ³He, we predict that the specific-heat anomaly will occur at temperatures lower than have been investigated experimentally, but which are easily accessi-

¹H. Arnold, Mol. Cryst. <u>2</u>, 63 (1966), and further references cited therein. A list of some of these results is given by A. Saupe, Angew. Chem. Intern. Ed. Engl. <u>7</u>, 97 (1968).

ble.

By phonon-mediated spin interaction, we mean an interaction among pairs of particles due to the virtual emission and absorption of phonons in the exchange process. To explain this statement, we briefly review the relevant theory of exchange⁵⁻⁷ in solid ³He. The exchange process in this system is described by a Heisenbergtype Hamiltonian

$$H_{x} = -\sum_{i,j} \mathcal{G}_{ij} \vec{\mathbf{I}}_{i} \cdot \vec{\mathbf{I}}_{j}, \qquad (1)$$

where \mathbf{I}_i is the nuclear spin operator for the particle *i*, and \mathbf{g}_{ij} is an operator, the "exchange operator," which has diagonal as well as off-diagonal matrix elements in phonon coordinates. The exchange frequency J_{ij} of a pair of particles is given in terms of the diagonal elements of \mathbf{g}_{ij} by

$$J_{ij} = \operatorname{Tr}(\rho g_{ij}), \tag{2}$$

where ρ is the phonon density matrix. The offdiagonal elements of ϑ_{ij} lead to the scattering, emission, or absorption of phonons in the exchange process; they are in evidence, for example, in spin-lattice relaxation in solid ³He at low temperatures. We can formally express the operator \mathfrak{s}_{ij} in powers of deviation $\overline{\mathfrak{u}}_{ij}$ of the pair i, j from the mean distance R_{ij} :

$$g_{ij} = J_{ij} + g_{ij}' \mathbf{\bar{u}}_{ij} + \frac{1}{2} g_{ij}'' \mathbf{\bar{u}}_{ij}^2 + \cdots$$
(3)

The coefficients in this expansion are renormalized, in the spirit for example of the self-consistent harmonic theory, such that all contributions of \mathfrak{s}_{ij} diagonal in phonon coordinates are contained in the first term, all contributions differing in initial and final phonons by one are contained in the second term, etc. The quantities $\mathfrak{s}_{ij'}$, $\mathfrak{s}_{ij''}$ are complicated entities which describe the rates of change of \mathfrak{s}_{ij} with $\tilde{\mathfrak{u}}_{ij}$ brought about by the effect of $\tilde{\mathfrak{u}}_{ij}$ on the coordinates and momentum of the pair (i, j) and of the particles surrounding this pair.⁸

Equation (3) can be expressed in terms of phonon creation and annihilation operators $a_{\vec{k}\lambda}^{\dagger}$, $a_{\vec{k}\lambda}$ (\vec{k} , λ label the momentum and the polarization):

$$\mathbf{\tilde{u}}_{ij} = \left(\frac{1}{2mN}\right)^{1/2} \sum_{\vec{k}\lambda} \epsilon_{\vec{k}\lambda} \omega_{\vec{k}\lambda}^{-1/2} \left\{ a_{\vec{k}\lambda} (e^{i\vec{k}\cdot\vec{R}_j} - e^{i\vec{k}\cdot\vec{R}_j}) + a_{\vec{k}\lambda}^{\dagger} (e^{-i\vec{k}\cdot\vec{R}_j} - e^{-i\vec{k}\cdot\vec{R}_j}) \right\},$$
(4)

where $\epsilon_{\vec{k}\lambda}$ is a polarization vector and we have taken $\hbar = 1$. The virtually emitted phonons in the exchange of the pair (i, j) can be absorbed by some other pair (or the same pair) in the exchange of this pair. Such a process gives an effective coupling among the pairs. We consider the two simplest processes in which one and two phonons are emitted, respectively.

We use second-order perturbation theory to calculate the energy of interaction among pairs (i, j) and (m, n) due to the above processes. We find that the interaction due to the one-phonon process can be expressed as an effective spin Hamiltonian

$$H_{ij,mn}^{(1)} = 8(\mathfrak{s}_{ij}')(\mathfrak{s}_{mn}')(\vec{\mathbf{I}}_{i}\cdot\vec{\mathbf{I}}_{j})(\vec{\mathbf{I}}_{m}\cdot\vec{\mathbf{I}}_{n})(\frac{1}{2}mN)\sum_{\vec{k},\lambda} |\epsilon_{\vec{k}\lambda}|^{2}\omega_{\vec{k}\lambda}^{-2}\sin\left(\frac{\vec{k}\cdot\vec{R}_{ij}}{2}\right)\sin\left(\frac{\vec{k}\cdot\vec{R}_{nm}}{2}\right)\cos(\vec{k}\cdot\vec{R}), \tag{5}$$

where \vec{R} is the vector joining the midpoint of the vector \vec{R}_{ij} to that of \vec{R}_{mn} . Similarly, the two-phonon process is described by the Hamiltonian

$$H_{ij,mn}^{(2)} = 32(\mathfrak{g}_{ij}^{"}\mathfrak{g}_{mn}^{"})(\mathbf{\tilde{I}}_{i}\cdot\mathbf{\tilde{I}}_{j})(\mathbf{\tilde{I}}_{m}\cdot\mathbf{\tilde{I}}_{n})(\frac{1}{2}mN)^{2}\sum_{\vec{k}\lambda}\sum_{\vec{k}'\lambda'}|\epsilon_{\vec{k}\lambda}|^{2}|\epsilon_{\vec{k}'\lambda'}|^{2}(\omega_{\vec{k}\lambda}\omega_{\vec{k}'\lambda'})^{-1}(\omega_{\vec{k}\lambda}+\omega_{\vec{k}'\lambda'})^{-1}$$

$$\times \sin\left(\frac{\mathbf{\tilde{k}}\cdot\mathbf{\tilde{R}}_{ji}}{2}\right)\sin\left(\frac{\mathbf{\tilde{k}}\cdot\mathbf{\tilde{R}}_{mm}}{2}\right)\sin\left(\frac{\mathbf{\tilde{k}}\cdot\mathbf{\tilde{R}}_{jj}}{2}\right)\sin\left(\frac{\mathbf{\tilde{k}}\cdot\mathbf{\tilde{R}}_{jm}}{2}\right)\cos\left((\mathbf{\tilde{k}}+\mathbf{\tilde{k}'})\cdot\mathbf{\tilde{R}}\right].$$
(6)

In (5) and (6), if (m, n) = (i, j) or m = j, we merely get a term of the usual Heisenberg form. This leads to a renormalization of the exchange frequency J_{ij} . Such terms are not of importance to us in the present context, since J_{ij} is known from susceptibility and other measurements and is too small to account for the specific-heat anomaly.

We now expand the angular factors in (5) and (6) in terms of spherical harmonics about the direction \mathbf{R} . We assume that *i* and *j* are nearest neighbors and so are *m* and *n*. To simplify the calculation we use the isotropic Debye approximation for the phonon spectrum. Keeping the first nonzero spherical harmonic, we have after some calculation that

$$H_{ij,mn}^{(1)} \cong (6/m) (\mathfrak{g}'/\Theta_0)^2 (\bar{\mathbf{I}}_i \cdot \bar{\mathbf{I}}_j) (\bar{\mathbf{I}}_m \cdot \bar{\mathbf{I}}_n) (x_0^2/x^3) [\sin x - x \cos x] \mathfrak{F}_1(\hat{\mathbf{R}}_{ij}, \hat{\mathbf{R}}_{mn}), \tag{7}$$

where Θ_0 is the T = 0 Debye temperature, $x_0 = k_m R_0$, where R_0 is the nearest-neighbor distance, and k_m is the Debye wave vector, $x = k_m R$, $\beta' = \beta_{1i}' = \beta_{mn}'$, and

$$\mathfrak{F}_{1}(\hat{R}_{ij},\hat{R}_{mn}) = \sum_{m} P_{1}^{m}(\hat{R}_{ij}) P_{1}^{m}(\hat{R}_{mn}) \cos(\varphi_{ij} - \varphi_{mn}).$$
(8)

In (8), $P_1^{\ m}(\theta)$ are the associated Legendre functions and φ_{ij} is the azimuthal angle associated with R_{ij} .

Under similar approximations, we have for the two-phonon Hamiltonian

$$H_{ij,mn}^{(2)} \cong (9\mathfrak{I}''/8m\Theta_0^{3/2})^2 (\tilde{\mathbf{I}}_i \cdot \tilde{\mathbf{I}}_j) (\tilde{\mathbf{I}}_m \cdot \tilde{\mathbf{I}}_n) x_0 (x_0/x)^3 [\ln(2x)\sin(x) - (20/3)\sin(2x)] \mathfrak{F}_2(\hat{R}_{ij}, \hat{R}_{mn}), \tag{9}$$

where

$$\mathfrak{F}_{2}(\hat{R}_{ij},\hat{R}_{mn}) = \sum_{m,m'} P_{1}^{m}(\hat{R}_{ij}) P_{1}^{m}(\hat{R}_{mn}) P_{1}^{m'}(\hat{R}_{ij}) P_{1}^{m'}(\hat{R}_{mn}) \cos m(\varphi_{ij} - \varphi_{mn}) \cos m'(\varphi_{ij} - \varphi_{mn}).$$
(10)

We have neglected the higher spherical harmonics, since they give a faster-decaying interaction. Also, in (9), we have kept only the leading term in x^{-1} .

At temperatures high compared with the alignment temperature, the contribution of the indirect spin interaction to the specific heat per mole C_{is} is given by

$$C_{is} \cong \langle H_{is}^2 \rangle / T^2, \tag{11}$$

where

$$H_{is} = \frac{1}{2} \sum_{ij,mn} (H_{ij,mn}^{(1)} + H_{ij,mn}^{(2)} + \cdots).$$

To draw any quantitative conclusions about C_{is} , we need the coefficients (\mathcal{G}') and (\mathcal{G}'') . We have no way of estimating \mathfrak{I}' ; however, we may use \mathfrak{I}'' as deduced from spin-lattice relaxation measurements at low temperatures. The Raman process by which relaxation proceeds at low temperatures is proportional to $(\mathfrak{g}'')^2$ and Richards, Hatton, and Giffard⁹ have estimated that for the bcc phase $g''/2\pi = 380 \pm 80$ MHz Å⁻², approximately independent of density. Using this value of \mathfrak{I}'' and the values of Θ_0 for T = 0 extrapolated from experiment, we have calculated the contribution of $H_{ij,mn}^{(2)}$ to C_{is} . We have used only the nearest value for R and have spherically averaged over the angles \hat{R}_{ii} and \hat{R}_{mn} . The results are shown in Fig. 1 for three molar volumes in terms of an effective Debye temperature Θ given in terms of Θ_0 by

$$234(T/\Theta)^3 = 234(T/\Theta_0)^3 + C_{is}.$$
 (12)

We have also plotted there the experimental results of Sample and Swenson; the results of Pandorf and Edwards agree very well with these. The experiment by Henriksen <u>et al</u>. gives values for $\gamma^{1/3}\Theta$, where γ is the Grüneisen parameter, which is also in general temperature dependent. In Fig. 1, we have not displayed the experimental scatter. The error bars on the theoretical curves reflect the error quoted in \mathscr{I}'' . Thus with no adjustable parameters, the two-phonon indirect spin interactions account for the magnitude, temperature dependence, and density dependence of the specific-heat anomaly quite well.

For hcp ³He, Richards, Hatton, and Giffard⁹

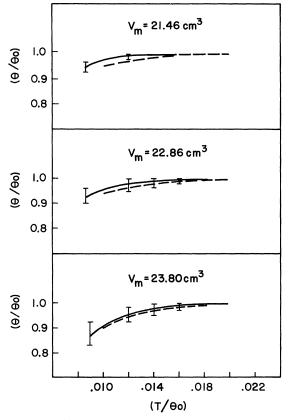


FIG. 1. The normalized effective Debye temperature (Θ / Θ_0) versus the normalized temperature (T / Θ_0) for three different molar volumes. The dashed lines are the experimental results of Ref. 2; the experimental scatter is not shown. The solid lines are the predictions of the theory; the error bars reflect the uncertainty in g'' quoted in Ref. 9.

estimate $(g''/2\pi) = 130 \pm 40$ MHz Å⁻². From this, we predict that the anomaly in specific heat in hcp ³He should be observable below about *T* $\approx 0.005\Theta_0$ at molar volumes of about 19 cm³.

It should be noted that a Hamiltonian of the form (6) does not contribute to the zero-field susceptibility at high T. The bcc phase of solid ³He exhibits an anomaly in the NMR measurements^{10,11} also. The spectral function for the transverse relaxation is quite distinctly not a Gaussian, as is expected approximately for an exchange-narrowed line. On a preliminary examination, we find that indirect spin interactions may be responsible for this anomaly. We intend to explore this matter further as well as other consequences of indirect spin interactions including their effect on thermal conductivity.

I wish gratefully to acknowledge discussions with Professor H. Suhl, Dr. W. F. Brinkman, Dr. N. R. Werthamer, and Dr. C. Herring.

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OBSERVATION OF COLLISIONLESS ELECTROSTATIC SHOCKS*

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Large-amplitude ion-acoustic waves $(e\varphi/kT_e \lesssim 0.3)$ are excited in the University of California, Los Angeles double-plasma device by the interpenetration of two plasmas with high electron-to-ion temperature ratios $(6 < T_e/T_I < 20)$. A compressional wave with a ramp shape is found to steepen in a fashion consistent with the classical overtaking predicted by the usual Riemann invariants. This steepening continues until dispersive short scale $(k \approx \frac{1}{2}k_D)$ oscillations develop at the front. Ions streaming in front of the shock are also observed.

Moiseev and Sagdeev¹ and Montgomery² have shown that, in the limit $T_e/T_i \gg 1$, the development of a finite-amplitude ion-acoustic wave is given by a Riemann solution which results in a steepening of the ion waves into a shock-like front. Andersen et al.³ have reported observation of steepening of ion-acoustic waves in a Qdevice. Their shock thickness was determined by the ion-ion collision distance and was more than 1000 Debye lengths λ_D .

Here we wish to report the observation of a magnetic-field-free collisionless shock formation with a thickness of about $5\lambda_D$. These shocks are excited by either a step or a ramp voltage applied between two plasmas (the driver and the target). Steepening is observed (of course) only for the ramp initial condition.

The two plasmas are produced in the University of California, Los Angeles double-plasma device⁴ by electron bombardment of argon at about 5×10^{-4} Torr in two identical chambers, placed end to end, which are insulated from each other and separated by a negatively biased grid, held at a fixed potential. The grid isolates the electrons in one plasma from those of the other. The chamber dimensions are length = diam = 30 cm = $1000\lambda_D$. Ion-ion collisions are unimportant since typical densities are 10^9 cm⁻³ with ion temperature about 0.2 eV ($\lambda_{ff} > 10^3\lambda_D$). The ion-neutral collision effects can also be ignored. The mean free path for charge transfer is greater than $300\lambda_D$.

Our wave excitation mechanism is different from the well-known grid excitation.⁵ Although

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