the ratio of $\alpha^2F(\omega)$ of these two phases from tunneling is 6.4. On the other hand, the ratio of $F(\omega)$ from our data is 4.3. Thus, the electron-phonon interaction must be also enhanced in the amorphous phase, by a factor of 1.5 at 2 meV. The frequency dependence of α^2 can be inferred from the fact that $F(\omega)$ is dominated by propagating phonons, i.e., $F(\omega) \propto \omega^2$. Given the linear dependence of α^2F from tunneling, this would imply $\alpha^2 \propto \omega^{-1}$ in the amorphous phase, in accordance with existing theories.[4,15]

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Observation of Phasons in Metallic Rubidium

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The heat-capacity anomaly caused by phasons—the collective excitations of an incommensurate charge-density wave—is identified in rubidium metal at 0.8 °K. Data analysis leads to a value $\Theta_\varphi = 4.5$ °K for the phason cutoff frequency. The velocity ratio of a purely longitudinal to a purely transverse phason is found to be ~11.

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Heat-capacity data of Lien and Phillips[1] reveal a low-temperature anomaly having the expected size, shape, and location for the phase excitations[2] of a charge-density wave[3] (CDW). Analysis of their data permits the first determination of the phason spectrum in a metal having a CDW ground state.

Alkali metals have many anomalous properties that require a broken translational symmetry.[4] Most studies have been of potassium, but the optical anomaly[5] and the high-field magnetoresistance[6] have been reported also in rubidium. Phasons are collective excitations that arise from the broken symmetry, and they have a frequency spectrum that goes to zero. They can influence a number of physical properties,[7] but an anomaly in the low-temperature heat capacity[8] is perhaps their most fundamental effect. The first observation of such an anomaly was in $LaGe_2$ by Sawada and Satoh.[9]

A conduction-electron CDW requires a sinusoidal lattice displacement to maintain charge neutrality.[3] Accordingly, the lattice displacement of a phase-modulated CDW is

$$\vec{U} = \vec{A}\cos[\vec{Q}\cdot\vec{r} + \beta\sin(\vec{q}\cdot\vec{r} - \omega t)]. \quad (1)$$

The phason amplitude, wave vector, and frequency are β, $\vec{q}$, and ω. It has been shown[3] that a phason is a coherent linear combination of two phonon modes having wave vectors $\vec{q}+\vec{Q}$ and $\vec{q}-\vec{Q}$. Since the CDW wave vector $\vec{Q}$ lies outside the Brillouin zone, the phonon mode which screens the CDW has wave vector $\vec{Q}' \equiv \vec{G}_{110} - \vec{Q}$, where $\vec{G}_{110}$ is the (110) reciprocal-lattice vector of the bcc lattice. It is the soft transverse phonon at $\vec{Q}'$ which screens the CDW.[10] Its frequency, $\omega_\varphi \equiv k_B\Theta_\varphi/\hbar$, defines the phason cutoff frequency and characteristic temperature. For rubidium, with $Q = 1.35(2\pi/a)$ and tilted 3.2° from a [110] direction,[10] $\Theta_\varphi = 4.2$ °K.

When two phonon modes are coupled together, a 2×2 dynamical matrix results. The eigenvalue equation is

$$\begin{vmatrix} \omega_\varphi^2 - \omega^2 & \omega_\varphi^2 F(\vec{q}) \\ \omega_\varphi^2 F(\vec{q}) & \omega_\varphi^2 - \omega^2 \end{vmatrix} = 0. \quad (2)$$

The lowest root of this equation is the phason frequency $\omega(\vec{q})$. The highest root is an amplitude mode[11]—a collective oscillation of the amplitude A of Eq. (1). The off-diagonal coupling arises from new terms in the electronic dielectric matrix caused by the CDW.[12] It is easy to show from Eq. (2) that

$$F(\vec{q}) \approx 1 - (c_{\vec{q}}\, q/\omega_\varphi)^2 + \cdots, \quad (3)$$

for small q, in order that the phason dispersion relation have the required linearity and zero frequency[2] at $\vec{q}=0$. $c_{\vec{q}}$ is the phason velocity in the $\vec{q}$ direction and is expected to be highly anisotropic.[2] A purely longitudinal phason, $\vec{q}$ parallel to $\vec{Q}$, has a much higher velocity than a purely transverse one, $\vec{q}$ perpendicular to $\vec{Q}$. Since $F(\vec{q})$ is unknown for large $\vec{q}$, we choose two arbitrary functions satisfying Eq. (3) for illustration.

$$F_1 = \exp[-(q/q^*)^2], \qquad F_2 = [1 + \tfrac{1}{2}(q/q^*)^2]^{-2}, \quad (4)$$

where $q^* \equiv \omega_\varphi/c_{\vec{q}}$. Eigenvalues of the dynamical matrix for the case F_1 are shown in the inset of Fig. 1. Phason and amplitude modes merge quickly into the phonon spectrum. The number of phason modes N_φ is characterized by the ellipsoidal volume of $\vec{q}$ space defined by $|\vec{q}| = q^*$.

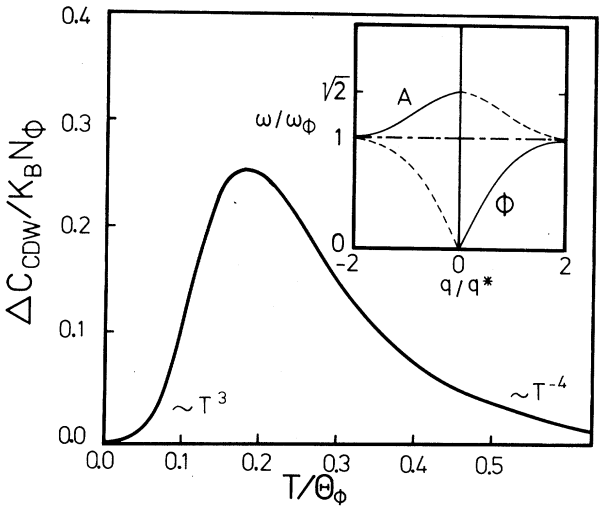

FIG. 1. Heat-capacity anomaly caused by an incommensurate CDW. The inset shows the vibrational spectrum near $\vec{Q}'$. φ is the phason branch and A the amplitude-mode branch. The horizontal line, at $\omega = \omega_\varphi$, is the phason cutoff frequency—the phonon frequency at $\vec{Q}'$ with no CDW.

The heat-capacity anomaly caused by the CDW structure is

$$\Delta C_{CDW} = \sum_{\vec{q}} (C_{\text{phason}} + C_{\text{amp. mode}} - 2C_{\text{phonon}}). \quad (5)$$

Each term is, of course, the heat capacity of an harmonic oscillator. The result for the case F_1 is shown in Fig. 1. The peak in ΔC_{CDW} occurs at $T = 0.18\Theta_\varphi$ for both F_1 and F_2. For the case F_2 the peak is higher by a factor of 1.67. In all cases $\Delta C_{CDW} \sim T^3$ for low T and $\sim T^{-4}$ for high T.

The low-temperature heat capacity of a normal metal is

$$C_0 \cong \gamma T + AT^3 + BT^5 + \cdots. \quad (6)$$

The T^5 term is caused by dispersion of the acoustic waves. The coefficient B is determined by a plot of $(C - \gamma T)/T^3$ vs T^2, which should be a straight line. The best fit of Lien and Phillips is shown by the dashed line in Fig. 2(a) and depends mainly on higher-temperature points not shown. The expanded plot shown here emphasizes the downward singularity of the data points near $T = 0$. This is caused by too large a value for the Sommerfeld constant γ. A slightly smaller value leads to an upward singularity shown in Fig. 2(c). An intermediate value, $\gamma = 2.37$ mJ/mole °K, eliminates the singularity, as shown in Fig. 2(b).

A new plot of Lien and Phillips' data is shown

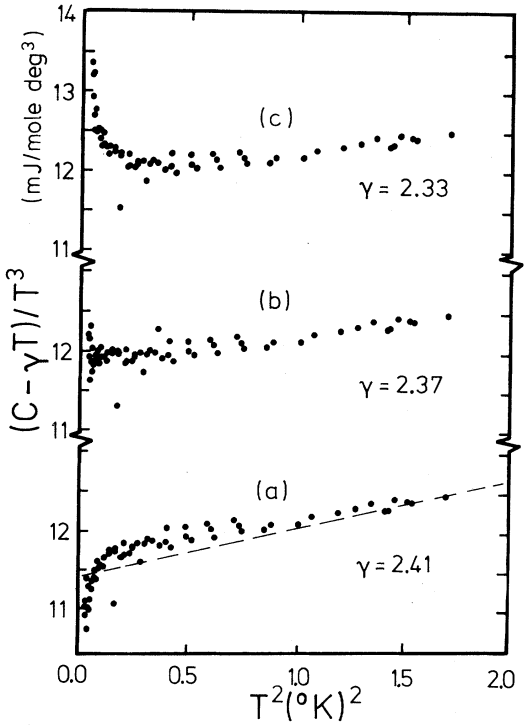

FIG. 2. Plots of Lien and Phillips' data on Rb for three values of the Sommerfeld constant γ (in mJ/mole units). The dashed line in (a) is Lien and Phillips' best straight-line fit, from Eq. (6), which depends mostly on higher-T points not shown.

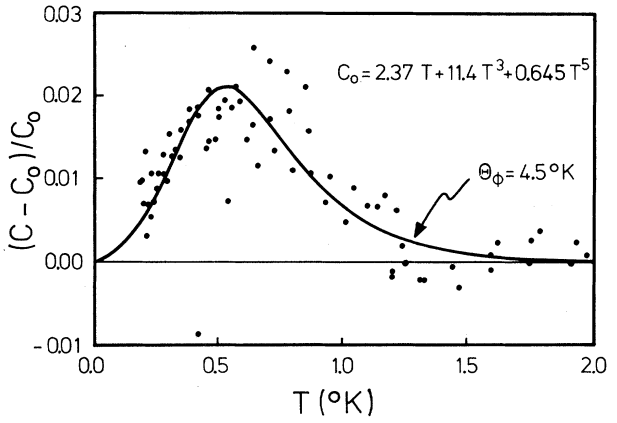

FIG. 3. Deviations of Lien and Phillips' data from the heat capacity C_0 of a normal metal (no CDW). C_0 incorporates the revised value of γ from Fig. 2(b). The curve is the theoretical phason anomaly, calculated from Eq. (5).

in Fig. 3, where C_0 incorporates the revised value of γ.[13] The deviations of the data from C_0 show a significant anomaly near 0.8 °K. (This peak appears shifted to lower T in Fig. 3 because percentage deviations are plotted.) The smooth curve through the data is the theoretical anomaly computed from Eq. (5). The best fit was obtained with $\Theta_\varphi = 4.5$ °K, for both choices in Eq. (4). The excellent agreement with the theoretical value quoted above is noteworthy. The height of the anomaly is 5 standard deviations, computed from point scatter about the theoretical curve.

Mathematical scaling of Eq. (5) readily shows that the size of ΔC_{CDW} is proportional to $c_t^{-2} c_l^{-1}$, where c_t is the velocity of a purely transverse phason and c_l is that of a longitudinal phason. The observed anomaly implies that this product has a value 1.6×10^{-16} or 1.0×10^{-16}, if F_1 or F_2 is used in Eq. (4).

The nearly spherical Fermi surfaces in alkali metals allow one to compute transverse phason velocities.[14] The theoretical value for potassium was found to be 1.4×10^5 cm/sec. For rubidium it is 0.9×10^5 cm/sec. We believe these velocities to be reliable because they depend only on observed elastic moduli. Transverse phase modulation corresponds to a small periodic rotation of $\vec{Q}$ from its optimum direction,[2] which does not alter the many-electron effects[3] responsible for a CDW instability.

If the theoretical c_t is combined with the values given above for the velocity product, we obtain $c_l = (8-12)\times 10^5$ cm/sec. The longitudinal- to transverse-velocity ratio is, accordingly,

$$c_l/c_t \sim 11. \tag{7}$$

This result is the first indication of the anticipated phason anisotropy from experimental evidence.

The anomaly shown in Fig. 3 cannot be made to disappear by adjusting the coefficients A and B of Eq. (6). We emphasize that the electronic term γ should be determined first by elimination of a low-T singularity, as we have shown in Fig. 2. Of course, it is always possible to ascribe an anomaly to experimental uncertainties (e.g., the temperature scale).[15] We hope that the analysis given here will stimulate further work to eliminate such problems. In particular high-precision calorimetry on potassium, where the effects of CDW structure are so numerous, provides an important challenge.

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Metallic-Nonmetallic Phase Coexistence above the Consolute Point of Sodium-Ammonia Solution

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The heat capacity under saturated vapors, C_σ, of three different concentrations of Na-NH_3 solution ($X = 0.045$, 0.046, 0.063 molar part of Na) has been measured in the temperature range 200–300 K. All three $C_\sigma(T)$ curves show anomalies consistent with the existence of a new two-phase region above the well-known liquid-liquid critical point ($X_c = 0.0415$, $T_c = 232$ K). Its location is compatible with the metal-nonmetal transition line; so it is believed that in equilibrium these are metallic and insulating phases with different concentrations of electrons.

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Although thermodynamics of metal-ammonia solutions have been studied intensively,[1] heat-capacity data have never been obtained because of experimental difficulties. Interest to heat-capacity data is connected with the investigation of singularity of thermodynamic potential in the vicinity of the critical (consolute) point of these solutions in presence of metal-insulator transition which is typical for them.[2]

We succeeded in measuring the heat capacity of three sodium-ammonia solutions ($X = 0.0450$; 0.0462, and 0.0631, all ± 0.0006 of molar part of metal) in the temperature range from 200 to 300 K with an adiabatic calorimeter. Our data gave us evidence of a new two-phase region above the well-known critical point just in the interval where metal-insulator transition takes place. This new fact has to be very stimulating especially for the interpretation of data and looking for new details in the extensive investigation of variety of ionic systems[3] and expanding metals exhibiting the analogous metal-insulator transition.[4]

Our calorimeter and its technique have been described before.[5] The solutions, prepared as usual by multiple vacuum distillation of sodium and ammonia and analyzed by conventional procedures, were filled in small pyrex glass containers which were placed in the calorimeter with proper coils and thermocouples. The glass containers could resist an inner pressure of up to ~10 bars, corresponding to the normal ammonia vapor pressure at room temperature. Their heat capacity was only 20% of that of the solution; it therefore does not affect the accuracy of our data. The error of the heat capacity obtained with the calorimeter does not exceed 0.2%. Additional scattering of data is observed only when the system is not in equilibrium. It happens when the time period be-

