j, scales as j^{-2} for $d \leq 4$, independent of the dimensionality [Eqs. (6) or (15)]. Indeed, such a dependence agrees with Eq. (20) for W_N which is amply supported by numerical calculations.[6] Direct computer results for φ_j are unfortunately unavailable. A related but nonidentical quantity is the probability for a chain of n steps to form a loop, which has been reported[8] to scale with a power slightly larger than n^{-2}.

In conclusion, the main shortcomings of the present theory seem to be (1) the *ad hoc* assumption that the loop elimination procedure treats the problem of self-avoiding chains adequately, despite the redundancy due to the eliminated loops; (2) the intuitive (and risky!) reasoning which leads to the derivation of Eq. (9); and (3) the lack of a systematic procedure for improving the calculation and for assessing its error. The second and third objections can be met by carrying out the elimination with the help of a computer.[9] The main advantage of the theory seems to lie in providing a fairly accurate technique for the evaluation of the critical behavior of chains; the technique is related to RG concepts but is independent of its standard methods.

I wish to thank the State University of New York for a generous grant of the scholarship which supported this study.

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[5] This corresponds to lengths $2j+1$ *without* the condition that subset j is in a loop as well. Yet the condition is not important since, on the average, out of the $2j+1$ links about j are anyhow in loops, as

$$(2j+1)\int_j^{2j} j'\varphi_{j'}\,dj' = 4\kappa(2-d/2)^{-1}j \sim j$$

[Eqs. (6), (8), and (13)].

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One- to Three-Dimensional Crossover in the Lattice Dynamics of $Hg_{3-\delta}AsF_6$: Low-Temperature Specific Heat

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(Received 16 April 1979)

The temperature dependence (0.35 K to 6 K) of the low-temperature specific heat of the linear chain mercury compound, $Hg_{3-\delta}AsF_6$ is reported. The one- to three-dimensional crossover in the low-temperature lattice specific heat due to the phase-ordered incommensurate Hg chains is observed. The results are analyzed with use of Tarasov's phenomenological theory for the specific heat of the weakly interacting one-dimensional chains. The specific-heat results yield a value for the phason mode energy, $\Delta/k_B = 1.75$ K.

The incommensurate linear chain structure of $Hg_{3-\delta}AsF_6$ leads to independent chain one-dimensional (1D) lattice dynamics,[1] highly anisotropic electronic properties,[1] and anisotropic superconductivity.[1] The three-dimensional (3D) host $(AsF_6)^-$ lattice constrains the incommensurate Hg chains to form an ordered array. However, the interactions between Hg chains and between a given chain and the host lattice are sufficiently weak to allow the emergence of 1D lattice dynamics, as indicated by the experimental observation of 1D phonons[2] from randomly phased linear chains[3,4] with the structure factor of a 1D liquid.[5-7] As the temperature is lowered, the weak interchain coupling becomes increasingly significant. At 120 K, the crystal undergoes a phase transition with 3D *phase* ordering of the two nonintersecting arrays of Hg chains.[1,2] In this low-temperature ordered state, there exist restoring forces to relative phase motion between chains (phasons) resulting in transverse dispersion and an energy gap, Δ, at the point $(3-\delta, 0, 0)$ in reciprocal space. Using inelastic neutron scattering, Heilmann *et al.*[8] have measured Δ vs T; they find that $\Delta/k_B \simeq 1.5$ K at low temperatures and goes to zero at the transition. As a result of this small energy gap, deviations from the 1D lattice-dynamical contributions to thermodynamic properties are expected only at low temperatures.

In this Letter we report the results of a study of the temperature dependence of the specific heat of $Hg_{3-\delta}AsF_6$ in the low-temperature range between 0.35 K and 6 K. The results cross over from 1D behavior ($C \propto T$) aobve 2 K to 3D behavior ($C \propto T^3$) below 1 K. A comparison of the experimental data with a phenomenological theory for the specific heat of a coupled chain system is presented, and the results are discussed in terms of the 1D phonon excitations of the Hg chains and the phason energy gap Δ.

The specific heat was measured by a computerized adiabatic calorimeter. The measuring system is designed to work in discrete steps or in a continuous mode and provides the computed results on line during the measurements. The samples were synthesized following the method of Miro *et al.*[9] based on the earlier work of Cutforth *et al.*[3,10] Single crystals as large as 2.5 $\times 2.5 \times 0.2$ cm^3 were chopped into small crystallites and loaded, in a dry box, into a specially designed thin-wall copper can. During the loading, the dry box contained a partial pressure of He^4 gas to allow thermal contact and a short thermal relaxation time. About 13 g of the small crystals were loaded; the can was subsequently sealed and placed in the calorimeter to prevent exposure to air. The addenda were less than 10% of the total specific heat. The sample temperature was determined by two calibrated Ge thermometers. Overall accuracy of the apparatus was checked by measuring Cu (99.999%) and comparing the results to the accepted values. The accuracy of our results is estimated to be about 3% at 0.3 K and to improve continuously to 0.5% in the temperature range above 1.5 K.

Three independent experimental runs of the specific heat were carried out from 0.35 K to 6 K over a three month period. The results were in agreement indicating that the sealed can arrangement was adequate to prevent sample deterioration. Typical data are given in Fig. 1 and plotted as C/T vs T^2. The major features of the specific heat are the unusually large linear term in $C(T)$ and the dramatic change in the functional form of the temperature dependence below 1.4 K.

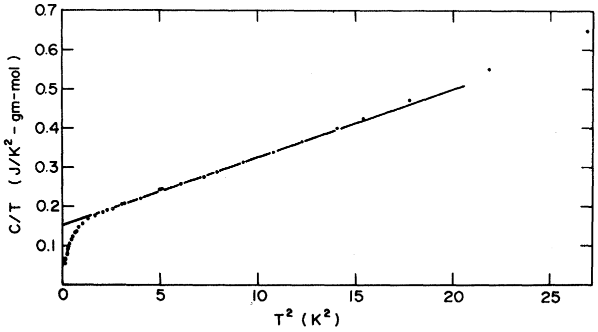

FIG. 1. C/T vs T^2 for $Hg_{3-\delta}AsF_6$.

In an attempt to evaluate the electronic contribution to the specific heat in the normal and superconducting states,[11] another two experimental runs were carried out with the sample in a constant external magnetic field of 500 G. The specific heat results were indistinguishable from those for $H=0$; maximum deviation was less than 2%, indicating that the electronic contribution, $C_{el}(T)$, is small. The electronic density of states $D(E_F)$ was estimated previously from the ^{199}Hg Knight shift[12] and from magnetic susceptibility data[13]; $D(E_F) \simeq 0.08$ states/eV/Hg atom, consistent with the nearly-free-electron behavior indicated by the optical studies.[14] With use of this value, $C_{el}(T)$ is found to be less than 2% and undetectable in the present measurements. The temperature dependence of the diamagnetic susceptibility $\chi(T)$ of $Hg_{3-\delta}AsF_6$ has been measured near the two superconducting transition temperatures (0.43 K and 4.1 K by Spal *et al.*[11] They find $\chi(T)$ continuous through these transitions implying that $C_{el}(T)$ should also be continuous, with no sharp anomalies.

We conclude that the low-temperature specific heat is predominantly of lattice origin and that the unusual T dependence results from phonon excitations of the coupled Hg chain system. The neutron scattering studies[2,8] indicate that the excitation spectrum can be separated into two contributions: the phonons of the coupled incommensurate Hg chains and the 3D phonons of the remainder of the lattice. Within the 1D Debye model, the specific heat due to the longitudinal phonon contribution of the Hg chains is $C = \frac{1}{3}\pi^2 N k_B T/\theta_1$ where θ_1 is the Debye temperature for the 1D chain phonons. Extrapolating the high-temperature data (see solid line in Fig. 1), we find from

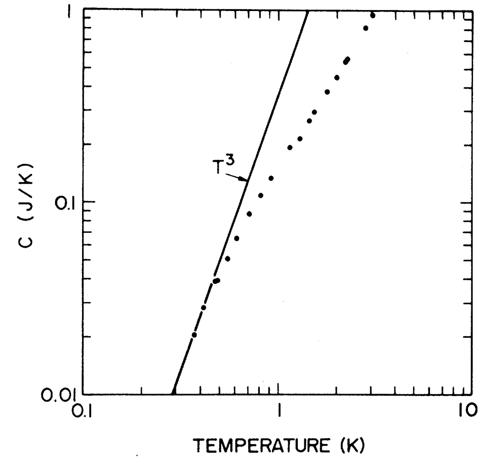

FIG. 2. Log-log plot of C vs T. The limiting low-temperature behavior is T^3.

the intercept $\theta_1 = 540$ K corresponding to a sound velocity $v_s \simeq 6\times10^5$ cm/sec ($v_s = \theta_1 a k_B/\pi\hbar$). The sound velocity has been determined directly from the slope of the phonon spectrum; $v_s = 4.4\times10^5$ cm/sec.[2,6,8] at 70 K. The Debye temperature associated with the 3D phonons of the host lattice, θ_{3D} can be determined in the standard manner from the slope of the C/T vs T^2 plot (Fig. 1); $\theta_{3D} = 70$ K. The magnitudes of the linear term and the T^3 term for $T > 2$ K, and the increase in slope above 3.5 K, are in agreement with the results of Wei *et al.*[13]

In order to find the limiting functional form of the specific heat for $T \to 0$, a log-log plot of C vs T is given in Fig. 2. The data indicate T^3 behavior at the lowest temperatures changing monotonically to T at the higher temperatures. The crossover from 1D to 3D behavior is the result of the phason energy gap, Δ, as described above.

Tarasov[15] has developed a phenomenological theory of the specific heat in highly anisotropic quasi-one-dimensional materials. The theory assumes that the phonon density of states is three dimensional [i.e., $g(\omega) \propto \omega^2$] for $\hbar\omega < k_B\theta_3$ and one dimensional [$g(\omega)$ constant] for higher frequencies as sketched in the inset of Fig. 3. In detail, the Tarasov theory predicts, for the coupled chain structure,

$$C/3Nk_B = D_1(\theta_1/T) - (\theta_3/\theta_1)[D_1(\theta_3/T) - D_3(\theta_3/T)],$$

where

$$D_m\left(\frac{\theta_n}{T}\right) = m\left(\frac{T}{\theta_n}\right)^m \int_0^{\theta_n/T} \frac{x^{m+1}e^x}{(e^x-1)^2}\,dx.$$

In Figure 3, we show the resulting fit of this expression to the experimental data of $Hg_{3-\delta}AsF_6$. The total specific heat is determined by three characteristic Debye temperatures: θ_1 and θ_3 associated with the incommensurate Hg chain structure, and θ_{3D} which characteristizes the specific-heat contribution due to the 3D lattice (including the AsF_6 ions). The Debye temperatures θ_1 and θ_{3D} are known from the high-temperature linear portion of the C/T vs T^2 plot (Fig. 1), and θ_3 is taken as the only free parameter. We find that the optimum value of θ_3 is 1.75 K as indicated by the solid curve in Fig. 3. The dashed and dot-dashed curves represent $\theta_3 = 1.25$ and 2.25 K, respectively, and are well outside the limits of error. The inferred value for the zone-boundary energy gap, $\theta_3 = 1.75$ K, is in good agreement with the value obtained directly from neutron scattering,[8] $\Delta/k_B = 1.5$ K.

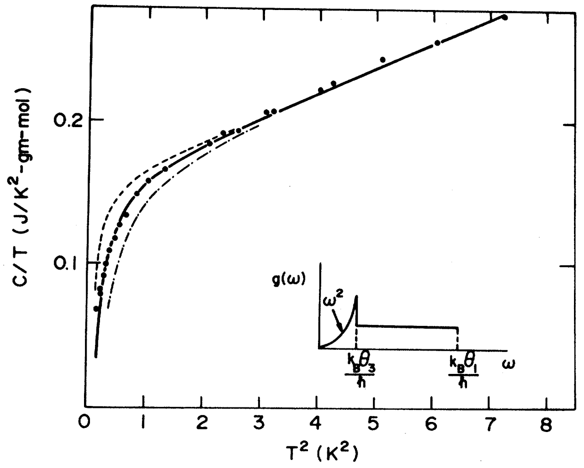

FIG. 3. C/T vs T^2 for $Hg_{3-\delta}AsF_6$. The solid curve is a best fit of the Tarasov theory with $\theta_3 = 1.75$ K (see text). The dashed and dot-dashed curves represent $\theta_3 = 1.25$ and 2.25 K, respectively. The inset shows the density of excitations in the Tarasov model.

The agreement between the experimental results and the analysis based on the phonon spectrum provides proof that the unusual specific heat of $Hg_{3-\delta}AsF_6$ results directly from the excitations of the coupled incommensurate linear chains. The suggestion by Wei *et al.*[13] that the large linear term might result from imperfections, disorder, and dislocations in the lattice is thus ruled out. This is consistent with the remarkable crystal perfection implied by the resolution-limited widths of the Bragg peaks and the Hg-chain satellites below 120 K[1,2,4,6] and with the absence of a central peak as the phason mode softens near 120 K.[8]

As discussed above, neutron scattering measurements have demonstrated that the low-temperature phase ($T < 120$ K) is characterized by a long-range phase ordering of the incommensurate Hg chains.[1,6] This ordering is established by the chain-chain interaction; each of the two orthogonal sets of Hg chains form body-centered monoclinic sublattices sharing common reciprocal-lattice points. Actually, two inequivalent domains are formed, and the point of observation of the energy gap, $\vec{q} = 2.79a^*$, is close to a zone boundary for both of the domains. The observed zone-boundary mode can thus be thought of as an out-of-phase vibration of neighboring parallel chains with displacements along the chain direction—a phason mode. As suggested by Heilmann *et al.*,[8] but not studied experimentally, smooth dispersion of the spectrum is expected perpendicular to the chain direction in reciprocal space with $\omega(\vec{q})$ going to zero on the satellite points. The limiting T^3 behavior of the specific heat (Fig. 2) verifies the expected smooth dispersion.

In summary, we have observed the 1d to 3d crossover in the low-temperature lattice specific heat of the phase-ordered incommensurate Hg chains in $Hg_{3-\delta}AsF_6$. The crossover results from weak interchain coupling giving rise to interchain phason modes. The specific-heat results yield a value for the phason mode energy of $\Delta/k_B = 1.75$ K in agreement with neutron measurements, and the T^3 limiting behavior verifies the expected smooth phason dispersion.

We are grateful to J. W. Kaufer and C. R. Fincher for their help in building the interface electronics and their assistance with the software. We thank R. Spal for help and adivce on sample handling. This work has been supported by the National Science Foundation Materials Research Laboratory program under Grant No. DMR-76-80994.

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