

Unusual specific heat of a linear-chain mercury compound*†

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The temperature dependence of the low-temperature specific heat and the magnetic susceptibility for the linear-chain mercury compound $\text{Hg}_{2.36}\text{AsF}_6$ are reported. The measured specific heat from 1.8 to 5 K exhibits an unusually large linear term contribution γT , where $\gamma = 46 \text{ mJ}/(\text{K}^2 \text{ g-atom Hg})$, while the density of states from the temperature-independent spin susceptibility is relatively small. The data are discussed in terms of several contributions to the linear term γ which include phonon excitations of separate hard one-dimensional and soft three-dimensional lattices and excitations arising from disorder within the mercury chains.

INTRODUCTION

Recently, Gillespie, Cutforth, Datars, and co-workers¹⁻³ have reported a new fractional-oxidation-state metal-chain compound $\text{Hg}_{2.36}\text{AsF}_6$ which exhibits a strong temperature-dependent metallic conductivity⁴⁻⁶ from 300 to 2 K and a resistivity ratio $\rho(300 \text{ K})/\rho(4.2 \text{ K})$ of 10^5 . $\text{Hg}_{2.36}\text{AsF}_6$ forms as golden tetragonal crystals in which the closed-shell AsF_6 anions provide two mutually orthogonal nonintersecting linear channels filled by the Hg atoms.² Interest in this compound arises in the context of the numerous studies of the electronic and structural properties of one-dimensional (1D) conductors⁷ which crystallize as parallel linear chains and of the intermetallic A_3B compounds with the A -15 or β -tungsten structure⁸ where the A transition-metal atoms form three mutually orthogonal linear chains. A significant difference between these solids is the channel structure of the Hg linear-chain compound. From the original x-ray measurements of Brown *et al.*,² the Hg-Hg intrachain lattice spacing is known to be incommensurate with respect to the main tetragonal lattice spacing of the AsF_6 anions, and the individual Hg atom sites are disordered in relation to those in nearby Hg chains.

In this study, we report an anomalous temperature-dependent behavior of the low-temperature specific heat for the compound. The measured specific heat from 1.8 to 5 K follows the form $C = \gamma T + \beta T^3$, exhibiting an unusually large linear term $\gamma = 46 \text{ mJ}/(\text{K}^2 \text{ g-atom Hg})$. Magnetic-susceptibility measurements from 300 to 4 K show temperature-independent behavior over the entire temperature range. The data are discussed in terms of several contributions to the linear term γ which include phonon excitations of separate

hard 1D and soft three-dimensional (3D) lattices and excitations arising from disorder within the mercury chains.

EXPERIMENT

The samples were synthesized following the method of Gillespie *et al.*^{1,3} and Miro *et al.*⁹ Since the compound is extremely sensitive to air, synthesis and handling were carried out either under vacuum ($\leq 10^{-6}$ Torr) or dry Ar (99.999% purity) atmospheres. Single crystals as large as $2.5 \times 2.5 \times 0.2 \text{ cm}$ have been grown. The measurements reported here used both single-crystal and polycrystalline samples. Elemental analysis of three samples agrees with that reported by Cutforth³ and gives a compound stoichiometry of Hg_3AsF_6 (calculated, wt%Hg: 76.11; wt%As: 9.47; wt%F: 14.42; found, wt%Hg: 75.99; wt%As: 9.61; wt%F: 14.44, with standard deviations of 0.09-wt%Hg; 0.05-wt%As; and 0.15-wt%F).

The specific heat was measured using an adiabatic calorimeter described earlier.¹⁰ To ensure sample integrity, a specially designed can with an indium or gold O-ring seal was utilized. Before sample loading, the can was degassed and stored in a dry box filled with high-purity Ar (99.999%) for two weeks. Approximately 2 g of sample was loaded in the can, and the can top piece was securely tightened against the sample to maintain good thermal contact. After the measurements, the sample was visibly unchanged. The data were checked with three samples and a total of 15 runs. The addenda were approximately 10%, and the apparatus was checked using Cu (99.999%) metal in which the Debye temperature agreed with the accepted value within 0.5%.

For the susceptibility measurements, polycrystalline samples were sealed in quartz tubes and

carefully examined under an optical microscope before and after each experimental run. The magnetic susceptibility was determined at approximately 10 kG using a Faraday method described earlier.¹¹ Honda plot of χ vs $1/H$ revealed ferromagnetic impurities of less than 2 ppm.

RESULTS

The magnetic susceptibility of the compound given in Fig. 1 is temperature independent between 300 and 210 K where the susceptibility decreases in magnitude and then resumes its temperature-independent behavior down to 15 K. At 15 K there is a small Curie-like upturn characteristic of a residual number of localized impurities, where $\chi_{\text{measured}} = \chi_{\text{intrinsic}} + C'/T$. A plot of χ vs T^{-1} gives a Curie constant C' of 1.8×10^{-4} emu K/mole, corresponding to 0.04-wt% ($S = \frac{1}{2}$) or 0.004-wt% ($S = \frac{5}{2}$) impurities. The intrinsic low-temperature susceptibility $\chi_{\text{intrinsic}}$ is -1.94×10^{-4} emu/mole. Taking into account the diamagnetic core contribution $\chi_D = -2.10 \times 10^{-4}$ emu/mole estimated from Pascal's constants results in a spin susceptibility $\chi_s = \chi_{\text{intrinsic}} - \chi_D$ of 0.16×10^{-4} emu/mole Hg_3AsF_6 . χ_s is independent of temperature from 300 to 4 K (Fig. 1). Initial ¹⁹⁹Hg Knight-shift results¹² at selected temperatures confirm the magnitude and temperature-independent behavior of the spin susceptibility from 300 to 2.2 K.

Three experimental runs of the specific heat were carried out from 1.8 to 5 K, and the resulting data given in Fig. 2 were analyzed by least-squares procedures in several ways. The results for several functional forms for representing the temperature dependence of the measured

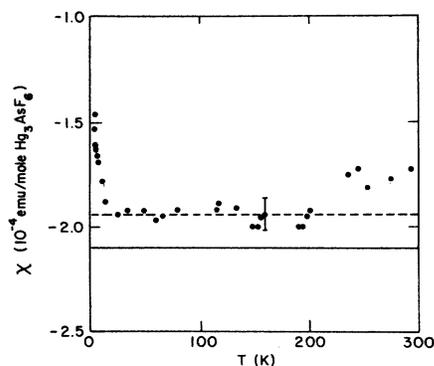


FIG. 1. Temperature dependence of the measured magnetic susceptibility χ of Hg_3AsF_6 where the solid and dashed lines correspond to χ_D and $\chi_{\text{intrinsic}}$ at low temperatures ($T < 200$ K), respectively. (See text for notation and discussion.)

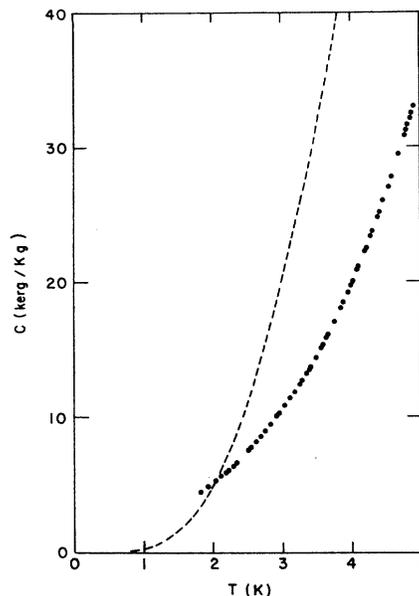


FIG. 2. Temperature dependence of the specific heat C of Hg_3AsF_6 . The dashed curve corresponds to the normal-state specific heat of mercury metal (Ref. 13).

specific heat are listed in Table I along with values for the variance s^2 of each trial representation f . The latter quantity is defined as

$$s^2 = \frac{1}{n-p} \sum_{i=1}^n [y_i - f(x_i; \theta_1, \dots, \theta_p)]^2$$

for n data points (x_i, y_i) , $i = 1, \dots, n$, where p is the number of parameters θ_j , $j = 1, \dots, p$ and used as a natural criterion for judging the goodness of fit for each representation.

Over the entire temperature range 1.8–5 K, the simple form (Table I) $C = \gamma T + \beta T^3$ with $\gamma = 1.59 \pm 0.01$ kerg/ K^2 g [41.9 ± 0.4 mJ/ K^2 g-atom Hg] and $\beta = 0.210 \pm 0.001$ kerg/ K^4 g ($\Theta_D = 78$ K), adequately represents the data with a variance of 1.89×10^{-2} , whereas the expression using a local Einstein mode and the usual Debye term has a large variance. The simple form with a variable temperature exponent α in the first term resulted in a smaller variance, but the exponent α assumed an unusual value of 0.6. The variance of the simple form can also be reduced by including a constant term.

With the simple form, the data can be best represented over two temperature intervals of the experimental range (Table I). From 1.8 to 3.5 K, γ is 1.76 ± 0.01 kerg/ K^2 g (46.3 ± 0.2 mJ/ K^2 g-atom Hg) and β is 0.192 ± 0.001 kerg/ K^4 g ($\Theta_D = 80$ K), and from 3.3 to 5 K, γ is 1.45 ± 0.01 kerg/ K^2 g (38.1 ± 0.3 mJ/ K^2 g-atom Hg) and β is 0.217 ± 0.001 kerg/ K^4 g ($\Theta_D = 77$ K). This form is shown as the

TABLE I. Parameters of least-squares analyses (C is in units of kerg/Kg).

Temperature range (K)	Functional form f	Parameters	Variance s^2
1.8-5	$\gamma T + \beta T^3$	$\gamma = 1.59 \pm 0.01$ $\beta = 0.210 \pm 0.001$	1.89×10^{-2}
1.8-5	$\gamma T^\alpha + \beta T^3$	$\gamma = 2.17 \pm 0.04$ $\alpha = 0.600 \pm 0.022$ $\beta = 0.230 \pm 0.001$	2.86×10^{-3}
1.8-5	$\frac{A}{T^2} \left(\frac{e^{B/T}}{(e^{B/T} - 1)^2} \right) + \beta T^3$	$A = 0.0697 \pm 0.0492$ $B = 0.143 \pm 0.047$ $\beta = 0.225 \pm 0.029$	2.82
1.8-3.5	$\gamma T + \beta T^3$	$\gamma = 1.76 \pm 0.01$ $\beta = 0.192 \pm 0.001$	6.17×10^{-4}
3.3-5	$\gamma T + \beta T^3$	$\gamma = 1.45 \pm 0.01$ $\beta = 0.217 \pm 0.001$	2.77×10^{-3}

solid lines in Fig. 3 where the data are plotted as C/T vs T^2 .

DISCUSSION

The major features of the specific-heat data are the unusually large value γ , and the value of the Debye temperature Θ_D of approximately 80 K. The linear term γ is substantially greater than the value of mercury metal¹³ ($\gamma = 1.8$ mJ/K² g-atom Hg) whose specific heat is shown for comparison as the dashed curve in Fig. 2. The value for Θ_D of mercury metal is 72 K.¹³ The large linear term γ may be composed of several possible contributions, and these are separately considered below according to currently available models.

Low-temperature specific heats of the form $C = \gamma T + \beta T^3$ for several metallic compounds containing linear chains of metal atoms have been known for some time to exhibit anomalously large linear terms γ . These include the well-studied intermetallic A_3B compounds¹⁴ and several metallic transition-metal oxides¹⁵ with values of γ of 34 mJ/(K² g-atom V) for V_3Ga and 32 mJ/(K² g-atom V) for V_2O_3 . These large values have been generally described as basically electronic in origin; for example, as a result of sharp structure in the electronic density of states at the Fermi level,¹⁶ strong electron-phonon coupling,¹⁷ electron-paramagnon coupling,¹⁸ or electron-electron Coulomb correlations.¹⁹ For Hg_3AsF_6 , the spin susceptibility and its temperature dependence provides no evidence for a large density of states near the Fermi level, ferromagnetic electron-paramagnon interactions, or enhancement effects from electron-electron Coulomb repulsions. As shown in Fig. 1, the spin susceptibility $\chi_s = (0.16 \pm 0.02) \times 10^{-4}$ emu/(mole Hg_3AsF_6) is temperature independent over the range $T < 200$ K characteristic of a

Pauli susceptibility of a degenerate electron gas. The spin susceptibility $\chi_s = 2\mu_B^2 D(E_F)$ corresponds to a density of states for a noninteracting gas of 0.25 states/(eV spin molecule).

Electron-phonon coupling can result in an enhanced electronic specific heat from mass renormalization while the spin susceptibility remains unaffected in the lowest approximation. However, for Hg_3AsF_6 , the predicted enhancement is too small to account for the experimental value of γ . The effect of the coupling on the electronic contribution is given by $\gamma_e = \frac{2}{3}\pi^2 k_B^2 D(E_F)(1 + \lambda)$, where λ is the electron-phonon coupling constant and $D(E_F)$ the density of states at the Fermi surface. Using the value of $D(E_F)$ from the spin susceptibility for Hg_3AsF_6 and λ of 1.6 for mercury metal would only amount to $\gamma_e = 1$ mJ/(K² g-atom Hg) compared to the experimentally determined value $\gamma = 46$ mJ/(K² g-atom Hg). In the case of the 1D strong-coupling limit, electron-phonon inter-

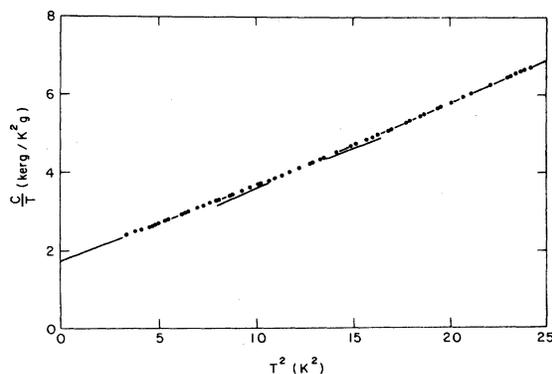


FIG. 3. Plot of C/T vs T^2 for Hg_3AsF_6 . The solid lines represent the form $C/T = \gamma + \beta T^2$ for two temperature intervals. (See text for discussion.)

actions markedly alter the electronic density of states and strongly renormalize the phonon frequencies; however, the spin susceptibility becomes highly temperature dependent.²⁰

Excitations of a uniform lattice alone can result in a linear temperature dependence of the measured specific heat when the phonon density of states is constant in energy as in the case of isolated 1D linear chains of atoms. In Hg_3AsF_6 , this case would require the situation of sets of 1D linear chains of mercury atoms within the 3D tetragonal lattice of AsF_6 anions being uncoupled and the 1D phonon excitations localized to individual chains. Within the 1D Debye continuum model, the specific heat due to the longitudinal-phonon contribution of the mercury linear chains is $C = \frac{1}{3}Nk_B\pi^2(T/\Theta_1)$, corresponding to a one-dimensional Debye temperature Θ_1 of 596 K. This would imply a sound velocity along the chains of 6.6×10^5 cm/sec which is four times larger than the sound velocity in mercury metal. Thus, the Debye continuum model for Hg_3AsF_6 would consist of a hard ($\Theta_1 = 596$ K) 1D lattice of mercury metal chains and a soft 3D ($\Theta_D = 80$ K) lattice of mostly AsF_6 anions. The model would then predict two distinct phonon dispersions with widely differing slopes associated with the respective 1D and 3D lattices.

Interchain coupling, or interactions of individual chains with the remainder of the lattice, result in exclusively a T^3 lattice contribution at low temperatures that changes to T^2 or T at higher temperatures as is frequently observed in polymeric materials and other anisotropic materials.^{21,22} In contrast, both T and T^3 dependences are simultaneously present at low temperatures for Hg_3AsF_6 . This behavior is distinctly different from 1D conductors such as tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ),¹⁰ or the conducting polymer (SN)_x,²³ where no unusual low-temperature T -dependent term has been observed solely due to the lattice specific heat of isolated 1D linear chains.

It is well known that a constant density of states can also arise from excitations associated with disordered regions of a solid lattice. There are many reported examples of low-temperature specific heats with an anomalous linear term of the order 5–50 erg/gK², particularly among glasses and other disordered solids.²⁴ In the case of Hg_3AsF_6 , the empirical formula determined from the elemental analyses is in agreement with analyses initially reported by Cutforth *et al.*^{2,3} X-ray² and neutron³ scattering measurements yield an empirical formula of $\text{Hg}_{2.86}\text{AsF}_6$, and each measurement shows diffuse scattering due to primarily the incommensurability of the Hg sites

with respect to the AsF_6 lattice. These results for the empirical formula are consistent with each other with an actual stoichiometry of $\text{Hg}_{2.86}\text{AsF}_6 \cdot \text{Hg}_{0.14}$ where approximately 5 mole% of the mercury is present as disordered zero-valent mercury atoms, or by $\text{Hg}_{2.86}(\text{AsF}_6)_{0.95}$ corresponding to approximately 5-mole% AsF_6 vacancies. Additional evidence comes from direct visual observation. Upon sample contraction by cooling to liquid nitrogen temperatures, minute beads of mercury metal form on the crystal faces, which upon warming to room temperature, re-enter the crystal lattice. Thus, in this case, the diffuse scattering exhibited in the x-ray and neutron measurements would actually contain a second contribution. In addition to the major 1D scattering, there would be a weaker one due to the random location of the free mercury atoms within each channel, which should persist down to low temperatures.

Current models which may describe the thermal excitations of such a lattice and in the first approximation leave the susceptibility largely unchanged include (i) localized tunneling states between different spatial configurations²⁵; (ii) atoms trapped in cavities²⁶; and (iii) pinned defects or dislocations.²⁷ In the tunneling model of Anderson, Halperin, Varma,²⁵ and Phillips,²⁵ certain atoms occupy two equilibrium positions and the two-level system has a uniform distribution of excitation energies giving a linear temperature dependence of the specific heat, $C = (\frac{1}{6}\pi^2)k_B^2 T n(0)$, where $n(0)$ is the constant density of states. For Hg_3AsF_6 with approximately 5% of free mercury atoms forming the level pairs, $n(0)$ is 7.7×10^{18} states/g K [39 states/(eV Hg site)] and ΔE , the energy-level splitting, 1.3×10^{-3} eV. With a jump rate Γ_0 of 10^{12} sec⁻¹ and an average separation distance Δx between occupied sites of approximately 4 Å (where mercury atom radius is 1.6 Å), the energy barrier V is estimated as 2.3×10^{-4} eV. This value is unusually low (compared to bond energies of several eV), consistent with the fact that some of the mercury atoms present in the samples can move in the lattice with relative ease. Such two-level models correspondingly would predict anomalous low-temperature behavior in the thermal conductivity and ultrasonic attenuation due to the phonon relaxation pathways characteristic of two-level systems.²⁸

In the related model of atoms trapped in cavities proposed early by Rosenstock,²⁶ the equivalent uniform distributions of randomly sized boxes leads to the specific-heat expression $C = 4.6k_B T n$, where using the experimental value for γ , n is 2.7×10^{18} trapped atoms per gram, per unit temperature interval K. For the experiment-

al interval of 3 K, this corresponds to 8×10^{18} (trapped atoms)/g, or approximately 0.4% of the Hg atoms present.

Defects such as chain vacancies and chain kinks²⁹ can affect the distribution of frequencies and modes of vibration of the lattice. Granato²⁷ analyzed the pinned-dislocation contribution to the low-temperature specific heat and found the expression $C = (\frac{1}{3} p \pi^2) (\Lambda d^2 / Z) (N k_B / \Theta_D) T$, where $p = v_0 / c$ [v_0 is the velocity of sound in the perfect lattice and c is given by $c = (G/\rho)^{1/2}$ with G the shear modulus and ρ the density], Λ is the dislocation density, d is the lattice constant along the mercury chains, Z is the number of atoms per unit, and N is the number of atoms per mole. Thus for Hg_3AsF_6 , we calculated a dislocation density Λ of $6 \times 10^{15} \text{ cm}^{-2}$, using $v_0 = 9.5 \times 10^4 \text{ cm/sec}$ from our specific-heat results, and the value $G = 3.6 \times 10^{11} \text{ dyn/cm}^2$ for graphite. This Λ should be compared with the values corresponding to the saturation condition in which adjacent dislocation cores are contiguous, which implies $\Lambda = (2r_c^2 \sqrt{3})^{-1}$, where r_c is the core radius.³⁰ Thus saturation occurs for $\Lambda = 2 \times 10^{14} \text{ cm}^{-2}$. Therefore the observed γ can not be completely accounted for by the contribution of dislocations alone.

Finally, at the crossover in the temperature dependence of the specific heat (Fig. 3 and Table I), no large anomalies were observable within experimental limits of approximately 1%. Since the electronic contribution is relatively small

[0.4 mJ/(K² g-atom Hg)], the change in temperature dependence likely arises from phonon or lattice excitations. For example, from the relatively small barrier height calculated by the tunneling model, the changeover may be associated with movements of the mercury atoms within the channels.

In summary, the anomalous temperature-dependent behavior of the low-temperature specific heat of Hg_3AsF_6 can be represented by the usual form $C = \gamma T + \beta T^3$ with an unusually large linear term γ . Included is a relatively small conduction electron contribution consistent with the measured spin susceptibility. The major contributions to the linear term γ as predicted by the usual 1D Debye model and current disorder and dislocation models are phonon excitations of separate hard 1D and soft 3D lattices and excitations due to randomly located mercury atoms within the channel structure. Each model gives additional predictions for expected behavior, and the thermal properties of this complex solid can be further analyzed upon completion of several independent measurements such as the thermal conductivity, x-ray,³¹ and neutron³² measurements.

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¹R. J. Gillespie and P. K. Ummat, Chem. Commun. 1168 (1971).

²I. D. Brown, B. D. Cutforth, C. G. Davies, R. J. Gillespie, P. R. Ireland, and J. E. Vekris, Can. J. Chem. 52, 791 (1974).

³B. D. Cutforth, Ph.D. thesis (McMaster University, Hamilton, Ontario, Canada, 1975) (unpublished); B. D. Cutforth, W. R. Datars, R. J. Gillespie, and A. van Schyndel, Adv. Chem. Series 150, 56 (1976).

⁴B. D. Cutforth, W. R. Datars, A. van Schyndel, and R. J. Gillespie, Solid State Commun. 21, 377 (1977).

⁵C. K. Chiang, R. Spal, A. Denenstein, A. J. Heeger, N. D. Miro, and A. G. MacDiarmid, Solid State Commun. 22, 293 (1977).

⁶D. L. Peebles, C. K. Chiang, M. J. Cohen, A. J. Heeger, N. D. Miro, and A. G. MacDiarmid, Phys. Rev. B 15, 4607 (1977).

⁷See, for example, I. F. Shchegolev, Phys. Status Solidi A 12, 9 (1972); *Low Dimensional Cooperative Phenomena*, edited by H. J. Keller (Plenum, New York,

1975).

⁸See, for example, M. Weger and I. B. Goldberg, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1973), Vol. 28, p. 1; L. R. Testardi, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1973), Vol. X, p. 193; L. P. Gor'kov and O. N. Dorokhov, J. Low Temp. Phys. 22, 1 (1976).

⁹N. D. Miro, A. G. MacDiarmid, A. J. Heeger, A. F. Garito, C. K. Chiang, A. J. Schultz, and J. M. Williams (unpublished); A. J. Schultz, J. M. Williams, N. D. Miro, A. G. MacDiarmid, and A. J. Heeger, Inorg. Chem., (to be published).

¹⁰T. Wei, S. Etemad, A. F. Garito and A. J. Heeger, Phys. Lett. A 45, 269 (1973); T. Wei, Ph.D. thesis (University of Pennsylvania, Philadelphia, Pa., 1976) (unpublished).

¹¹J. C. Scott, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 3131 (1974).

¹²E. F. Rybaczewski and L. S. Smith (unpublished); L. S. Smith, Ph.D. thesis (University of Pennsylvania, Philadelphia, Pa., 1976) (unpublished); E. Ehrenfreund, P. R. Newman, A. J. Heeger, N. D. Miro, and A. G. MacDiarmid, Phys. Rev. B (to be published).

¹³B. J. C. van der Hoeven, Jr. and P. H. Keesom, Phys. Rev. 135, A631 (1964).

- ¹⁴F. J. Morin and J. P. Maita, *Phys. Rev.* 129, 1115 (1963).
- ¹⁵D. B. McWhan, J. P. Remeika, S. D. Bader, B. B. Triplett, and N. E. Phillips, *Phys. Rev. B* 7, 3079 (1973); M. E. Sjöstrand and P. H. Keesom, *ibid.* 7, 3558 (1973).
- ¹⁶J. Labbé and J. Friedel, *J. Phys. (Paris)* 27, 153 (1966); 27, 303 (1966); 27, 708 (1966).
- ¹⁷K. Krebs, *Phys. Lett.* 6, 31 (1963); A. M. Clogston, *Phys. Rev.* 136, A8 (1964).
- ¹⁸J. R. Schrieffer, *J. Appl. Phys.* 39, 642 (1968).
- ¹⁹W. F. Brinkman and T. M. Rice, *Phys. Rev. B* 2, 4302 (1970).
- ²⁰P. A. Lee, T. M. Rice, and P. W. Anderson, *Phys. Rev. Lett.* 31, 462 (1973).
- ²¹S. M. Genensky and G. F. Newell, *J. Chem. Phys.* 26, 486 (1957); W. H. Stockmayer and C. E. Hecht, *ibid.* 21, 1954 (1953).
- ²²V. V. Tarasov, *New Problems in the Physics of Glass* (Oldbourne, London, 1963).
- ²³R. L. Greene, P. M. Grant, and G. B. Street, *Phys. Rev. Lett.* 34, 89 (1975).
- ²⁴R. C. Zeller and R. O. Pohl, *Phys. Rev. B* 4, 2029 (1971); R. B. Stephens, *Phys. Rev. B* 13, 852 (1976).
- ²⁵P. W. Anderson, B. I. Halperin, and C. M. Varma, *Philos. Mag.* 25, 1 (1972); W. A. Phillips, *J. Low Temp. Phys.* 7, 351 (1972).
- ²⁶H. B. Rosenstock, *J. Non-Cryst. Solids* 7, 123 (1972).
- ²⁷A. Granato, *Phys. Rev.* 111, 740 (1958).
- ²⁸J. Jäckle, *Z. Phys.* 257, 212 (1972).
- ²⁹D. H. Reneker and B. Fanconi, *J. Appl. Phys.* 46, 4144 (1975).
- ³⁰P. R. Couchman, C. L. Reynolds, Jr., and R. M. J. Cotterill, *Nature* 264, 534 (1976).
- ³¹J. P. Pouget (unpublished).
- ³²G. Shirane (private communication).