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HIGH TEMPERATURE RESISTIVITY AND LOW TEMPERATURE SPECIFIC HEAT OF THE MERCURY CHAINS IN $Hg_{3-\delta}AsF_6$

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We discuss the high temperature phonon limited resistivity and the low temperature specific heat of the mercury chains in $Hg_{3-\delta}AsF_6$, in a model where the acoustic longitudinal phonons are highly anisotropic. The anisotropy is characterized, in our model, by the parameter $\alpha=v_\perp/v_\parallel$ where $v_\perp$ and $v_\parallel$ are the sound velocities perpendicular and along the chain direction. The second order contribution to the electrons' scattering rate is largely enhanced for 1-d electrons localized on the mercury chains when $\alpha << 1$. It is shown that the expression following our model $\rho=AT+BT^2$ can account for the experimental data in the temperature range 235K-430K with a value $\alpha=0.015$. With this small α we calculate the low temperature specific heat and obtain excellent agreement with experiment.

PHONON LIMITED HIGH TEMPERATURE RESISTIVITY

The resistivity of $Hg_{3-\delta}AsF_6$(1-2) in the ab plane poses a dilemma. Its temperature dependence is found to deviate significantly from linearity at high temperatures, and its value at T=300K, $\rho=60\mu\Omega$-cm, gives by the Hopfield relation $\hbar/\tau=2\pi\lambda T$ a value $\lambda\simeq 1$. This value is extremely high when compared with that deduced from the superconducting transition ($T_S=0.3$ K$\Rightarrow\lambda=0.15$) and with that of liquid mercury($\lambda=0.4$).

The mean free path, obtained from the room temperature resistivity, is about 20 lattice constants, thus, suggesting that the electron is described by extended Bloch states along the chain. The large resistivity perpendicular to the chain $\rho_\perp/\rho_\parallel = 250(1)$, induces a strongly localized description in that direction.

If we denote the mercury ions' sites by X_ℓ, Y_m, Z_n an electron localized on the m,n'th chain is described by the wave function:

$$|k\rangle_{mn} = (1/\sqrt{Nb})e^{ikx}\delta(y-Y_m)\delta(z-Z_n) \tag{1}$$

and the Hamiltonian:

$$H_e^{mn} = \sum_k \varepsilon(k) a_k^{\dagger mn} a_k^{mn} \tag{2}$$

where $\varepsilon(k) = \hbar^2k^2/2m$ and $a_k^{\dagger mn}$ (a_k^{mn}) create (annihilate) an electron in state k localized on the m,n'th chain.

The AsF_6 lattice probably does not couple strongly to the electrons since there are 6% vacancies in this lattice and no measurable residual resistance (3). As for the coupling to other chains, the number of crossing chains is small and does not contribute much to the electron-phonon interaction. Thus, we assume the electron to interact only with the chain on which it is localized (at low temperatures, an alternative description is given by Ehrenfreund and Kaveh (4)), the interaction being given by:

$$V = \sum_\ell v_{mn}(x - X_{\ell mn} - u^x_{\ell mn}) = \sum_\ell v_{mn}(x - X_{\ell mn}) - \sum_\ell \frac{\partial v(x-X_{\ell mn})}{\partial x} u^x_{\ell mn} \tag{3}$$

where $u_{\ell mn}$ are the longitudinal vibrations along the chain. The first term in eq. (3) is the usual chain potential which we assume not to change $\varepsilon(k)$ for $k<k_F$. The second term, when written in second quantized form, gives the e-ph interaction:

$$H_{mn} = \frac{1}{N^{3/2}b} \sum_{k,q,\vec{q}_\perp} iqv(q) e^{i\vec{q}_\perp \cdot \vec{r}_{\perp mn}} u_{-q,\vec{q}_\perp} a_{k+q}^{\dagger mn} a_k^{mn} \tag{4}$$

Here, N and b are the number of sites and lattice constant along the chain respectively, and $v(q)$ is the 1-d Fourier transform of $v_{mn}(x)$. $q=q_x$, $\vec{q}_\perp$ and $\vec{r}_{\perp mn}$ are the transverse phonon wave-vector and radius vector of the m,n'th chain respectively, and $u_{q,\vec{q}_\perp}$ are the 3-d amplitudes of the normal mode expansion of the phonons polarized along the chain.

We now use an anisotropic Debye model for the dispersion law of the phonons:

$$\omega^2(\vec{q}) = v_s^2(q_x^2 + \alpha^2 q_\perp^2) \tag{5}$$

with $|q_x| \leq \pi/b$ $|q_y|, |q_z| \leq \pi/a$, a being the transverse lattice constant. The parameter $\alpha=v_\perp/v_{//}$ introduced here is the ratio of the sound velocities perpendicular and along the chain direction. We also define the dimensionless e-ph coupling constant:

$$\lambda(q) = \frac{2|g_q|^2\rho(\varepsilon_F)}{\hbar\omega_q} = \frac{q^2|v(q)|^2}{M\omega^2(q)} \frac{m}{2\pi\hbar^2 k_F b} \tag{6}$$

where $\rho(\varepsilon_F)$ is the density of states at ε_F for one spin direction.

With these definitions we calculate the high temperature phonon limited conductivity along the mercury chains within the quasistatic limit for ions' vibrations ($\omega\tau<<1$, where ω is the phonon frequency and τ the electron scattering time) using both first and second Born approximations. We also assume the intrachain interaction of the mercury ions, to be much larger than the interchain one, thus, taking $\alpha<<1$. We obtain (2):

$$\hbar/\tau^{(1)} = 2\pi\lambda(2k_F)T \tag{7}$$

$$\hbar/\tau^{(2)} = (4\pi)^{3/2}(k_F b)\frac{\lambda(o)\lambda(2k_F)}{\tilde{\alpha}} \frac{(k_B T)^2}{\varepsilon_F} \tag{8}$$

where $\tilde{\alpha}=\alpha(b/a)$. The ratio $\tau^{(2)}/\tau^{(1)} \propto (\lambda(o)/\alpha)(k_B T/\varepsilon_F)$ which is usually small since $k_B T << \varepsilon_F$, is now enhanced when the anisotropy is large ($\alpha<<1$). The resistivity obtained from this model is now given by:

$$\rho = \frac{\pi^2/n_\perp}{e^2 v_F}\lambda(2k_F)\, k_B T \left\{1 + \frac{2\pi^{1/2} k_F b\lambda(o)}{\tilde{\alpha}} \frac{k_B T}{\varepsilon_F}\right\} = AT + BT^2 \tag{9}$$

where $n_\perp$ is the number of chains per unit area.

In fig. 1 we plot σ/T vs. T. For high temperatures T>235K we get a straight line, confirming the law $\rho=AT+BT^2$ in that temperature region, with A=0.09μΩ-cm/K and $B=0.35 \times 10^{-3}$μΩ-cm/K^2. We now apply our model eq. (9) with the following parameters: ε_F =3.74 eV, b = 2.64Å, a = 7.5 Å, $k_F = (5/6)\pi/b$, $n_\perp = 2.17 \times 10^{-2}$Å^{-2} and $v_F = 1.1 \times 10^8$

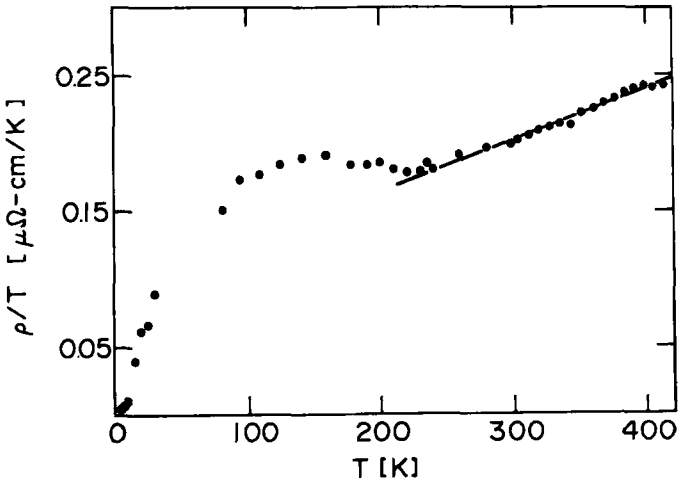

FIGURE 1 ρ/T vs. T. The points are experimental results of Spal(1) (T<300K) and Moses (2) (T>300K). The line is the fit to our model. (Note the anomaly in the resistivity around 234K)

cm/sec. Assuming $\lambda(0) = \lambda(2k_F) = \lambda$ we can solve for λ and α from A and B and get $\lambda = 0.3$ and $\alpha = 0.015$.

In the next section we show that this small value of α perfectly explains the low temperature specific heat results of Moses et al. (5).

THE SPECIFIC HEAT OF $Hg_{3-\delta}AsF_6$

The density of phonon states $D(\omega)$ is given by $D(\omega) = dN(\omega)/d\omega$ where $N(\omega)$ is the number of phonon states with frequency less than or equal ω.

Using our anisotropic Debye model eq.(5) for the phonons' dispersion law we obtain:

$$D(\omega) = \frac{V\omega^2}{2\pi^2 v_s^3 \alpha^2} \begin{cases} 1 & ; \tilde{\omega} < a^* \\ 1-\sqrt{1-(a^*/\tilde{\omega})^2} & ; a^* < \tilde{\omega} < b^* \\ b^*/\tilde{\omega}-\sqrt{1-(a^*/\tilde{\omega})^2} & ; b^* < \tilde{\omega} < \sqrt{a^{*2}+b^{*2}} \end{cases} \quad (10)$$

where: $\tilde{\omega} = \omega/v_s$, $a^{*2} = 4\pi\alpha^2/a^2$ and $b^* = \pi/b$.

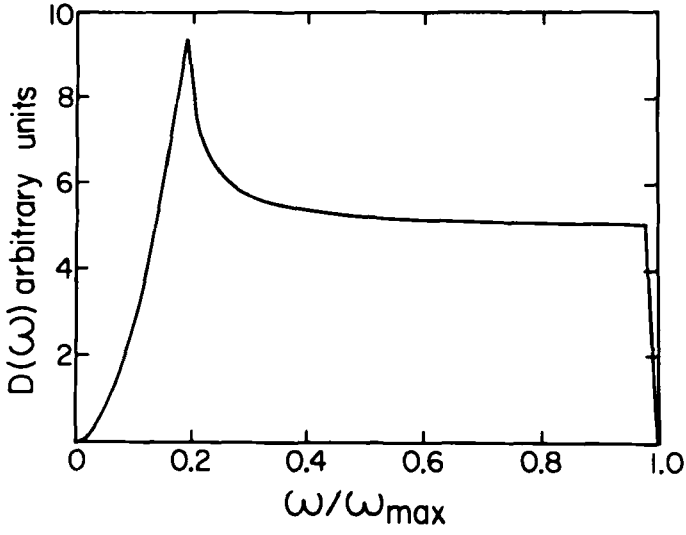

FIGURE 2 The density of states eq. (10)

The density of states is plotted in fig. 2 and we see there three frequency regions: (i) the low frequency region where $D(\omega) \propto \omega^2$ i.e. 3-d region, (ii) the high frequency 1-d region $D(\omega) \simeq$ const. and (iii) the cutoff region where $D(\omega)$ decreases to zero.

Using the density of states eq.(10) with $V/a^2b = N_o$ the specific heat per mole of $Hg_{3-\delta}AsF_6$ is given by:

$$C = (3-\delta)k_B \int \frac{(\hbar\omega/k_BT)^2 \exp(\hbar\omega/k_BT)}{[\exp(\hbar\omega/k_BT)-1]^2} D(\omega)d\omega + \beta T^3 \qquad (11)$$

where the first term is the specific heat of the longitudinal mode of the mercury chains and the second term βT^3 is the usual specific heat of the 3-d AsF_6 lattice. The specific heat may be separated into these two independent contributions because of the weak coupling between the mercury and AsF_6 sublattices related to the incommensurate lattice structure. The conduction electrons' contribution is negligible (see Moses et al. (5)).

The specific heat obtained is in excellent agreement with experiment (fig. 3) the parameters being: $\alpha = .016$, $v_s = 5 \times 10^5$ cm/sec and $\beta = .015$ J/mol K^4.

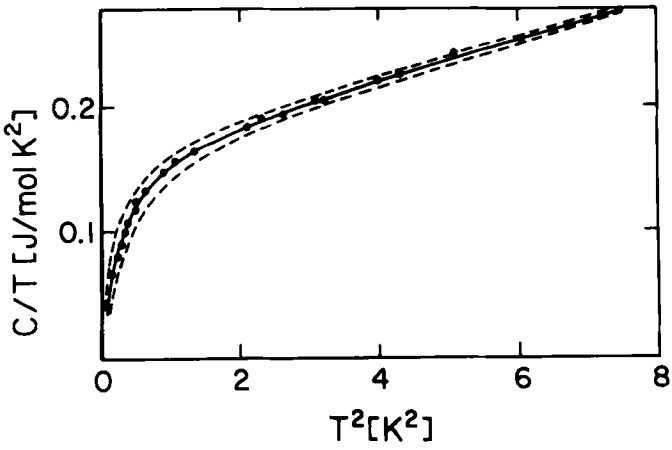

FIGURE 3 C/T vs. T^2. The points are experimental results of Moses et al.(5), the solid line is the fit to our model with α=.016,the upper(lower) dashed line represent α=.014(α=.018).

Moses et al. (5) analyzed the results using Tarasov's phenomenological theory (6) for weakly interacting 1-d chains. Our model is closely related to Tarasov's one, since the weak interaction between chains leads to $v_\perp \ll v_\parallel$. Indeed, our expression for the density of phonon states is similar to that of Tarasov.

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