Resistivity of high pressure phosphorus phases

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Simple cubic (sc) “black phosphorus” (denoted “BP”), stable at \( P > 10 \text{GPa} \), seems an ordinary metal. It has electron-phonon-driven superconductivity at \( T_c \approx 5 \text{-} 10 \text{~K} \). The A17 phase, stable at atmospheric pressure, has a narrow gap, becomes semimetallic at \( P \approx 1 \text{~GPa} \), and has a smooth transition to topological metal behavior at \( P \approx 5 \text{~GPa} \). The A7 phase, stable for \( 5 < P < 10 \text{~GPa} \), is metallic, superconducting, and less conventional than the sc phase. Some insights are extracted from analysis of resistivity \( \rho(T) \) at various pressures. A surprising order-of-magnitude disagreement between theory and experiment is discussed.

INTRODUCTION

Black phosphorus (BP) becomes metallic under pressure \( (P) \) \cite{1, 2}. The absolute resistivity was recently measured by Li et al. \cite{3} at pressures up to \( 15 \text{GPa} \), from \( T = 1.5\text{~K} \) to \( 300\text{~K} \). The simple cubic phase (stable from \( P = 10 \) to \( 137 \text{~GPa} \) \cite{4}) seems a normal metal, and superconducts, at least in the lower \( P \) range, at \( T \approx 10\text{~K} \). Analysis of resistivity, with input from density-functional (DFT) band theory, provides a way to extract the electron-phonon coupling constant \( \lambda \) \cite{5, 6}.

Our analysis for black phosphorus, reported here, indicates that this goes seriously wrong. Therefore it is important to ask how reliable are resistivity measurements at such pressures. The paper by Guo et al. \cite{7} gives relative resistivities at various pressures. These are compared with the absolute resistivities of Li et al. in Fig. 2. There is general agreement about the shape of the \( T \) dependence. Higher \( T \) measurements at \( 13.8 \text{~GPa} \) were published by Okajima et al. \cite{8}. These are shown in Fig. 2. The data are encouragingly similar to the recent results of Li et al. \cite{3}. One can tentatively accept Li’s data as a realistic standard.

The Bloch-Grüneisen formula \cite{10, 11} for electrical resistivity of a metal is a variational approximation for the solution of the Bloch Boltzmann equation \cite{10} for electrons scattering from phonons in metals. It uses a Debye model. The formula is

\[
\rho_{\text{BG}}(T) = \rho_0 + \rho_1 f_{\text{BG}}(T/\Theta_D) \tag{1}
\]

where \( \rho_0 \) is the residual resistivity from impurity scattering, \( \Theta_D \) is the Debye temperature, and \( \rho_1 \) is given by

\[
\frac{1}{\rho_1} = \left( \frac{n}{m} \right)_{\text{eff}} e^2 \tau_D, \tag{2}
\]

The factor \( (n/m)_{\text{eff}} \) from DFT computations will be explained shortly. The term \( \tau_D \) is a normalization factor for the scattering lifetime \( \tau_T(T) \); \( 1/\tau_T \) is \( 1/T_D \) times a dimensionless factor that, in Bloch-Grüneisen theory is explained shortly. The term \( \tau_T \) is a normalization factor for the scattering lifetime \( \tau_T(T) \); \( 1/\tau_T \) is \( 1/T_D \) times a dimensionless factor that, in Bloch-Grüneisen theory is

\[
\frac{1}{\tau_D} = \frac{2\pi \lambda_T k_B \Theta_D}{\hbar}, \tag{3}
\]

where \( \lambda_T \) is the transport version of the dimensionless electron-phonon coupling constant \( \lambda \). The dimensionless function \( f_{\text{BG}}(T/\Theta_D) = f_{\text{BG}}(y) \) is

\[
f_{\text{BG}}(y) = 4y \int_0^1 dx x^3 \left( \frac{x/2y}{\sinh(x/2y)} \right)^2 \tag{4}
\]

This assumes a three-dimensional Debye spectrum for the phonons. At large \( y = T/\Theta_D \), the factor in parentheses in Eq. 4 goes to 1 and \( f_{\text{BG}} \rightarrow T/\Theta_D \), giving the familiar high \( T \) linear resistivity. At low \( T \),
the function $f_{\text{BG}}$ becomes $64(T/\Theta_{D})^{5}$ times the integral $\int_{0}^{\infty}dzz^{5}/\sinh^{2}z = 15\zeta(5)/2$. This gives the familiar $T^{5}$ temperature dependence. Finally, the factor $(n/m)_{\text{eff}}$ is

\[
\frac{(n)}{(m)}_{\text{eff}} = \frac{1}{V} \sum_{k} \frac{1}{\hbar^{2}} \frac{\partial^{2} \epsilon_{k}}{\partial k_{x}^{2}} f_{k} = \frac{1}{V} \sum_{k} \frac{v_{kx}^{2}}{\hbar^{2}} \left( -\frac{\partial f_{k}}{\partial \epsilon_{k}} \right) .
\]

The index $k$ is short for $(\vec{k}n\sigma)$, the wavevector, band index, and spin needed to label a state. The derivative $-\partial f/\partial \epsilon$ of the Fermi function is accurately replaced by a delta function, $\delta(\epsilon - \mu)$, so $(n/m)_{\text{eff}} = N(\epsilon_{F})(v_{F}^{2})$, where $N(\epsilon_{F})$ is the density of states (per unit volume) at the Fermi level $\epsilon_{F} = \mu$, and $\langle v_{F}^{2} \rangle = \frac{1}{V} \sum_{k} v_{kx}^{2} \delta(\epsilon_{k} - \mu)/\sum_{k} \delta(\epsilon_{k} - \mu)$ is the Fermi surface average of the squared $x$ component of the electron’s group velocity. In an anisotropic material, a first guess would be that the conductivity tensor $\sigma_{\alpha\beta}$ is given by the same formula, except $\langle v_{F}^{2} \rangle$ is replaced by $\langle v_{\alpha}v_{\beta} \rangle$. The older terminology “optical mass” is still sometimes used for the mass in the denominator of $(n/m)_{\text{eff}}$. The reason for abandoning this terminology is that $n$ and $m$ are not separately definable except in semiconductors with small carrier densities in a parabolic band. For phosphorus, the choice $n = 5$ electrons per atom works fairly well for the sc phase, but not so well for lower $P$ phases, or for high $P$ phases where 3$d$ electron states start to be occupied.

A more complete theory is also available, using a variational solution of the Bloch-Boltzmann equation 

\[
\rho(T) = \frac{1}{n/m} \int_{0}^{\infty} d\omega \alpha_{\text{eff}}^{2}(\omega)^{2} \left( \frac{\hbar\omega/2k_{B}T}{\sinh(\hbar\omega/2k_{B}T)} \right)^{2} .
\]

Here $\alpha_{\text{eff}}^{2}(\omega)$ is a modified version of the function $\alpha^{2}F$ used in Eliashberg theory of electron-phonon superconductors [13]. The additional information in $\alpha_{\text{tr}}F$ will not overcome the discrepancy between theory and experiment.

Mass renormalization by interactions is another worry. Coulomb renormalization is usually well incorporated in the DFT band masses. Electron-phonon renormalization is seen in ac conductivity [15], $\sigma(\omega) \approx (n/m)_{\text{eff}} e^{2}/(1/\tau + i\omega\Lambda(\omega))$, but drops out in the dc limit.

### FITTING EXPERIMENTAL RESISTIVITY

Resistivity measurements by Li et al. [3] cover $0 < T < 300$K, and $P$ up to 15 GPa. The sc phase at $P > 10$ GPa is the most conventional. Resistivity $\rho(T)$, and Bloch-Grüneisen fits, are shown in Fig. [5]. The fits is as good as normally expected. An even better fit is shown in Fig. [6]. In principle there should be deviations from Bloch-Grüneisen because of deviations of the phonon spectrum from Debye. The deviations are particularly small, probably because the sc crystal structure has simple and rather Debye-like phonons.

At 12 GPa, the Bloch-Grüneisen fit, shown in Fig. [6], is not as good as normally expected, but not totally bad. In the A7 phase at 8 GPa, shown in Fig. [7], the fit doesn’t work. The choice $\Theta_{D}=300$K fits at low $T$ but...
probably persists in the lower harmonic phonon-phonon interactions change or even in-<P<
portance of anharmonicity to dynamically stabilize the approximation for <P< [16] find the sc structure unstable in harmonic
Coulomb or impurity scattering would not help. Chan
does not work well at either end. What is the reason?
fails at higher T. The choice Θ_D=500K fits near room
temperature but fails at low T. The choice Θ_D=400K
does not work well at either end. What is the reason?
Coulomb or impurity scattering would not help. Chan
et al. [16] find the sc structure unstable in harmonic
approximation for <P< [16] compute

\[ \rho_1 = \frac{2\pi \lambda_T k_B \Theta_D}{h}, \]

where \( \omega_p^2 = (n/m)_{\text{eff}} e^2/\epsilon_0 \) is the square of the Drude
plasma frequency. For the \( P=15 \) GPa data of Li et al. [3],
values of \( \rho_1 \sim 45 \mu \Omega \text{cm} \) and \( \Theta_D \sim 575 K \) give good fits to
\( \rho(T) \) data. This requires \( \omega_p^2 / \lambda_T = 5.15 \text{ (eV)}^2 \). The value of \( \lambda_T \approx \lambda \) can be estimated from the
superconducting \( T_c \) to be \( \sim 0.5 - 0.8 \). Chan et al. [16] compute \( \lambda \sim 0.7 - 0.8 \)
and diminishing as \( P \) increases, for \( P > 20 \) GPa. Flores-
Livas et al. [17] and Wu et al. [9] compute \( \lambda \sim 0.5 - 0.65 \). These numbers are well in line with the measured
superconducting \( T_c \)'s. If such values are used to fit \( \rho(T) \) data, they require a Drude plasma frequency \( \omega_p \sim 5 - 6 \)
eV. The next section tests this by band calculations. The
results for the 15 GPa sc phase are similar to free electron
values, with \( \omega_p > 20 \) eV. Then \( \lambda_T \) should be higher by
\( \sim 16 \), i.e. \( \lambda \sim 10 \), an unphysically large value.

ELECTRONIC STRUCTURE CALCULATIONS

Electronic structure calculations have been done for
the simple cubic phase by Aoki et al. [18], Rajagopalan
et al. [19], Chan et al. [16], Flores-Livas et al. [17], and
Wu et al. [9]. Their results show that a free electron gas
model describes the general features of the bands. This
is illustrated in Fig. 6. Numerical results are in Table 1.
These show that sc black phosphorus is reasonably well
modeled as a free electron gas. The density of electrons is
5 per atom, with one atom per cell of lattice constant \( a \).
Values of \( a \) near \( a = 2.44 \) at \( P \sim 15 \) GPa were measured
by many authors [4, 7, 20, 21].

Density functional theory (DFT) calculations were per-
formed on the sc phase with the projector augmented
wave method [22, 23], as implemented in the Vienna Ab
Initio simulation package VASP [24, 25]. A \( 47\times 47\times 47 \)
\( k \)-point mesh, a plane wave cutoff of 500 eV, and a
force convergence tolerance of 2.5 meV/\( \text{Å} \) were employed in
structural relaxation and density of states calculations.
The sc phases were simulated under pressures of 12 and
15 GPa. The \( (n/m)_{\text{eff}} \) values were calculated using the
code BoltzTrap [26] based on band structure from VASP
calculations.

If we choose a reasonable value \( \lambda_T \sim 0.8 \), then the
BoltzTraP result \( \omega_p = 20.5 \) eV predicts at \( T=300 K \),
using the high \( T \) limit, resistivity \( \rho(300K) - \rho(0) \sim 2.3 \mu \Omega \text{cm} \).
This is about 8 times smaller than the measured value
shown in Figs. 2 and 3. The small theoretical resistivity
is a result of the large theoretical value of \( \omega_p \). Alt-
ernatively, if we use the experimental \( \rho_1 \) of Figs. 2 and 3 and

FIG. 4. At 12GPa, the structure of BP is still sc. The
resistivity [3] is fitted less well by a Bloch-Grüneisen formula
than at 15GPa.

FIG. 5. At 8GPa, the structure of BP is A7. The resistivity
[3] deviates significantly from a Bloch-Grüneisen formula.
the BoltzTrap value of $\omega_p$, then $\lambda_{tr} \geq 6$, an unrealistic range. All known values of $\lambda_{tr}$ are close to $\lambda [5, 6]$ which has never been observed greater than 2. Large $\lambda$ may reflect small phonon frequencies, driven toward lattice instability, as is indeed found in computations [16] for sc BP when the pressure decreases toward 10GPa. Large $\lambda$ would cause the superconducting $T_c$ to be much larger than seen in BP.

Agreement in shape between measured $\rho(T)$ and Bloch-Grüneisen theory is usually a good confirmation of the applicability of the theory. This would suggest that the measured value of $\rho(T)$ is somehow too large by a factor $\sim 8$. But the similarity in magnitude and shape of the Li et al. data to other experiments argue against this. Also the downward curvature of $\rho(T)$ (seen by Okajima et al. and shown in Fig. 2 at higher $T$) would be very unusual if the actual $\rho(T)$ were 8 times smaller than reported. It should be mentioned that Wu et al. [9] compute $\rho(T)$ from first principles. The numerical values shown in Fig. 12 of their paper are only a factor $\sim 2$ smaller than experiment. However, they apparently use a free electron choice of $(n/m)$, and values of $\lambda_{tr}$ similar to those used here. Therefore the plotted magnitude of $\rho(T)$ seem to have been incorrectly enhanced by a factor $\sim 5$.

**SPECULATIONS**

Electronic structure calculations [3, 16] show that in the sc phase, harmonic phonons are not stable unless $P > 20$GPa. This can have two interpretations. Either there is a DFT problem, and a correct harmonic theory would have stable phonons, or else, more likely, DFT is correct about the instability of harmonic phonons, and the sc phase is stabilized by anharmonic interactions when 10GPa $< P < 20$GPa. The sc phase is rare in nature. P atoms have small masses and lose packing in the sc phase. Thus one expects large zero-point vibrations. These factors likely require anharmonic interactions to be included in a correct zeroth order theory. In such a situation, the large displacements can not only stabilize a harmonically unstable phase, but also alter the electron-phonon coupling. Coupling beyond first-order $(\partial U/\partial u_{\alpha})u_{\alpha}$ will affect $\rho(T)$ in a way that alters the Bloch-Boltzmann theory from Bloch-Grüneisen form. Then probably one needs to invent a "strongly coupled" theory of lattice vibrations and their interaction with electrons. Numerous thoughts in this direction are available, for example, refs. [27] and [28].

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