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Lattice-dynamical properties of black phosphorus under pressure studied by inelastic neutron scattering

Y. Yamada, Y. Fujii, Y. Akahama, S. Endo, and S. Narita
Faculty of Engineering Science, Osaka University Toyonaka, Osaka 560, Japan

J. D. Axe
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

D. B. McWhan
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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Acoustic-phonon dispersion relations of black phosphorus in its orthorhombic $A11$ phase have been measured along three principal directions mainly at 1 bar and 15.4 kbar. An anomalous softening has been observed on the LA[100] branch whose vibrational patterns (eigenvectors) have been analyzed based on a force-constant-model fit by Kaneta *et al.* It is suggested that this softening is caused through electron-phonon interactions associated with a large change in bonding angles. The $\mathrm{TA}_y[001]$ mode at the zone boundary, which can be assigned to the atomic displacements relevant to the $A11$-to-$A7$ (rhombohedral) structural transition at 45 kbar, does not soften, but at least the hardening shows a tendency to saturate at pressure higher than 15.4 kbar.

I. INTRODUCTION

Black phosphorus (BP) shows interesting structural phase transitions at high pressures. With increasing pressure, it transforms from the $A11$ orthorhombic structure (D_{2h}^{18}, semiconductor) to the $A7$ rhombohedral structure (D_3^5, semimetal) at 45 kbar, and further to the simple-cubic system (O_h^1, metal) at 110 kbar. In order to understand this phase-transition scheme, it is convenient to consider the simple-cubic phase as the "prototype" structure of group-V materials with electronic configuration s^2p^3. Stabilization of the simple-cubic structure is understood by formation of six (fluctuating) orthogonal bonds around each atom constructed out of the three p electrons.[1] Starting from this high-symmetry structure, the low-symmetry phases are described by bond localization which tends to construct three covalent bonds around each atom. The pattern of localized bond is expressed in terms of the following "bond charge fluctuation models":

$$\xi_\nu = |\psi_\nu|^2 \exp(i\vec{K}_1\cdot\vec{r}), \quad \vec{K}_1 = (\tfrac{1}{2},0,0)$$

$$\eta_\nu = |\psi_\nu|^2 \exp(i\vec{K}_2\cdot\vec{r}), \quad \vec{K}_2 = (\tfrac{1}{2},\tfrac{1}{2},0)$$

$$\zeta_\nu = |\psi_\nu|^2 \exp(i\vec{K}_3\cdot\vec{r}), \quad \vec{K}_3 = (\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})$$

where $\nu = x,y,z$, and where ψ_ν denotes the wave function of the p_ν orbital. Among possible charge-density modes which allow three covalent bonds around each atom, we have

$$\delta\rho_1(\vec{r}) = \zeta_x + \zeta_y + \zeta_z, \quad \delta\rho_2(\vec{r}) = \zeta_x + \zeta_y + \xi_z \ .$$

These charge-density modes will be accompanied by small lattice distortion waves whose distorted structures just correspond to the $A7$ structure and (pseudo) $A11$ structure as depicted in Fig. 1.

Therefore, from lattice-dynamical point of view, one might expect anomalies in phonon dispersion relations around $\vec{K} = (\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})$ at the transition from the simple-cubic to the $A7$ structure. On the other hand, the transition from $A7$ to $A11$ structure is quite different because it is different from an "ordered" state to another "ordered" state and, hence, is strongly first order. Recently, however, Kikegawa and Iwasaki[2] pointed out that this transition can be associated with a single phonon assigned to the $\mathrm{TA}_y[001]$ zone-boundary mode, and that there may be softening of this particular mode at the $A11$-to-$A7$ transition at 45 kbar. Apart from investigating the

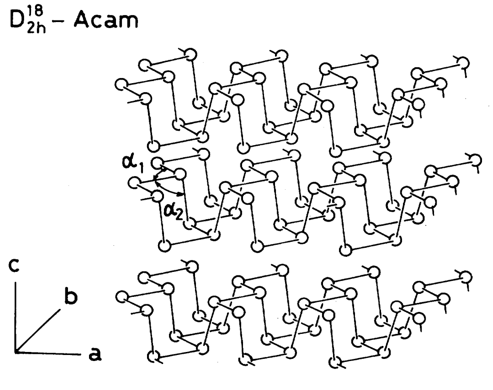

FIG. 1. $A11$ crystal structure of black phosphorus consisting of puckered layers stacking in the [001] direction. The middle layer is displaced by $\vec{b}/2$ with respect to the adjacent ones. Space group D_{2h}^{18}-$Acam$; $a = 4.374$ Å, $b = 3.313$ Å, and $c = 10.473$ Å at 1 bar and room temperature (Ref. 7).

behavior of this particular phonon mode, it is interesting to observe the overall behavior of the phonon dispersion relations under pressure. It is considered that in this material the valence-electron—phonon interaction is the key quantity in understanding its electronic as well as structural properties. The effect of pressure on the phonon dispersion relations should directly manifest these electron-phonon interactions.

In our previous work,[3] we already measured the acoustic-phonon dispersion relations at atmospheric pressure (1 bar) and the results were compared with the force-constant model of Kaneta *et al.*[4] The purpose of the present paper is to extend the previous work to observations at higher pressures and directly investigate the pressure dependence of the phonon dispersion relations. Unfortunately, the highest pressure achievable with our inelastic-neutron-scattering experiments (about 30 kbar) is still significantly below the critical pressure to drive the phase transitions. Nevertheless, from the viewpoint described above, it will provide useful information on the dynamical properties of valence-electron fluctuations.

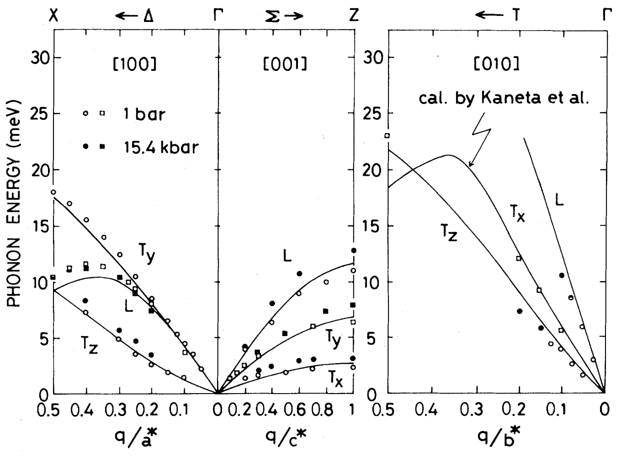

FIG. 2. Acoustic-phonon dispersion relations of black phosphorus along its three orthorhombic principal axes. Open and solid symbols represent the present observation at 1 bar and 15.4 kbar (room temperature), respectively. Solid curve is a force-constant-model fit to the data at 1 bar carried out by Kaneta *et al.* (Ref. 8). A suffix to the mode T (transverse) or L (longitudinal) denotes polarization direction of the phonon.

II. EXPERIMENTS

Black phosphorus single crystals were grown from melt at about 1100 °C and 10 kbar as previously reported.[5] A large crystal, $8\times4\times2$ mm^3, was used in the measurement at 1 bar of the $\mathrm{TA}_z[100]$ and $\mathrm{TA}_x[010]$ branches, which were not observable in the previous experiment.[3] For measurements under pressure, crystals were trimmed by a string saw so as to fit a pressure cell 4 mm in diameter and 10 mm high. In order to measure a complete set of acoustic branches along the three orthorhombic principal directions as sketched in Fig. 1, crystals having three different zones—(100), (010), and (001)—were prepared. The mosaic spread of these crystals was found to be 0.5°—1° full width at half maximum in the (001) plane and 2°—5° along the [001] axis, the layer-stacking direction.

Measurements of phonon energies were performed on a triple-axis spectrometer at the Brookhaven High Flux Beam Reactor. Neutron energies of $E_i=14$ and 30 meV were used for a constant-incident-energy—mode operation, while $E_f=24$ and 30.5 meV were used for a constant-final-energy—mode operation. Monochromator and analyzer crystals were of pyrolytic graphite. Horizontal collimators (in-pile, monochromator-sample, sample-analyzer, and analyzer-detector) were either 20″ or 40″ depending on resolution and intensity requirements. Higher-order contamination of the incident beam was removed by a graphite filter in the constant-E_i measurement.

A clamp device specially designed for neutron scattering at high pressure[6] was used in the present experiment. The crystal was mounted with a pressure-transmitting fluid (Fluorinert FC-75) in an aluminum cell of 4 mm i.d. and 10 mm high. The cell was sealed with beryllium copper extrusion rings and cap, and then mounted inside a barrel-shaped alumina cylinder. A series of tungsten carbide pistons inserted into the cylinder and back-up blocks transmitted load applied by a small hydraulic press to the sample. After the load was locked by an aluminum locking sleeve and mating steel support pieces, the clamp device was transferred onto the neutron spectrometer. Pressure was determined from the measured lattice constants based on the previous data on compression.[7] All measurements were carried out at room temperature.

III. EXPERIMENTAL RESULTS

Phonon dispersion relations measured along the three orthorhombic principal directions are displayed in Fig. 2. Each branch is denoted by T or L instead of TA or LA because only acoustic branches were measured. Open symbols represent data at 1 bar. The $\mathrm{T}_z[100]$ and $\mathrm{T}_x[010]$ branches, which were not considered in the previous experiment[3] were observed in the present measurement. The present, more complete set of acoustic branches was recently fitted by a force-constant model by Kaneta *et al.*[8] Solid curves in Fig. 2 show the results of the best-fit calculations. Also shown by solid symbols in the same figure are phonon energies measured at 15.4 kbar. One can see a remarkable hardening for all branches along [001], the layer-stacking direction. No appreciable change in energy was observed in the [010] direction, which is the hardest axis. In the [100] direction, on the other hand, an unexpected softening was observed for the L[100] branch. In contrast, the $\mathrm{T}_z[100]$ branch shows a normal hardening. Figure 3 gives more detailed behavior of these two branches. A speculation on this softening mechanism is given in the next section. The pressure dependence of the $\mathrm{T}_y[001]$ branch was investigated carefully because atomic displacements for the *A*11-to-*A*7 transition analyzed by Kikegawa and Iwasaki[2] correspond to this phonon branch at its zone boundary ($q/a^*=1$). According to a lattice-dynamical analysis, this mode shows the adjacent puck-

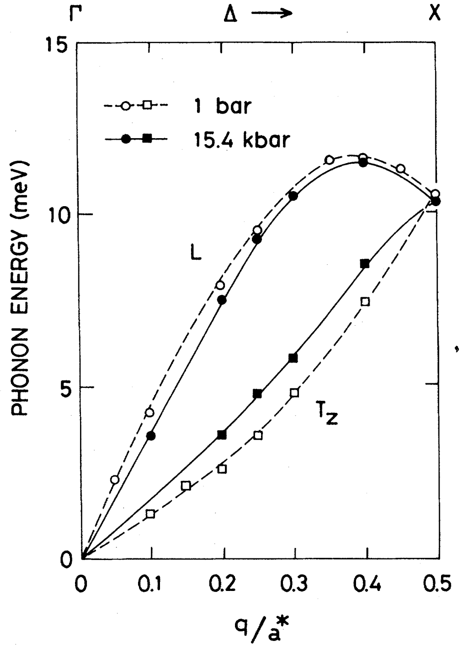

FIG. 3. Pressure dependence of acoustic-phonon dispersion relations along [100]. The mode L shows the definite softening in contrast to the normal hardening observed in T_z.

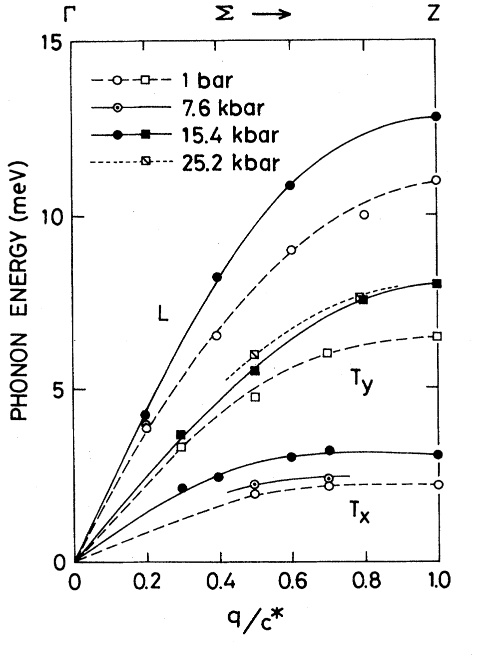

FIG. 4. Pressure dependence of phonon dispersion relations observed along [001] being the layer-stacking direction. The T_y mode at the zone boundary ($q/c^* = 1$), corresponding to atomic displacements relevant to the A 11-to-A 7 transition at 45 kbar, shows a tendency to saturate its hardening at pressure higher than 15.4 kbar.

ered layers moving in an opposite direction, i.e., $\pm\vec{b}$. As seen in Fig. 4, the energy of this zone-boundary phonon increases normally upon compression from 1 bar to 15.4 bar; however, with further increasing pressure up to 25.2 kbar the hardening seems to be saturate. At present it is not known whether this phonon softens at high pressure closer to the critical point of 45 kbar.

IV. CONCLUSION AND DISCUSSION

We studied phonon dispersion relations of black phosphorus at various pressures. The results are summarized as follows:

(i) Supplementary data at 1 bar T_z[001] and part of T_x[010] have been obtained.

(ii) Acoustic-phonon branches at $P = 15.4$ kbar have been observed along [100] and [001] except for the T_y mode along [100]. In general, the phonon energies show hardening as pressure is applied. However, the L mode along [100] shows definite softening with increasing pressure.

(iii) The special mode which is expected to have particular relevance to the A 11-to-A 7 phase transition does not show any softening within the (0—14)-kbar region. When the pressure is increased to 25.2 kbar, hardening of the mode shows the tendency to saturate. It may be possible that this branch would soften when the pressure is further increased towards the critical pressure.

It is remarkable that the L mode along the [100] direction shows softening throughout the whole branch. In Fig. 5 we give the actual displacement patterns of the L mode along [ξ00] with $\xi = 0.25$. These lattice vibrational patterns drawn with thick solid lines on the (010) and

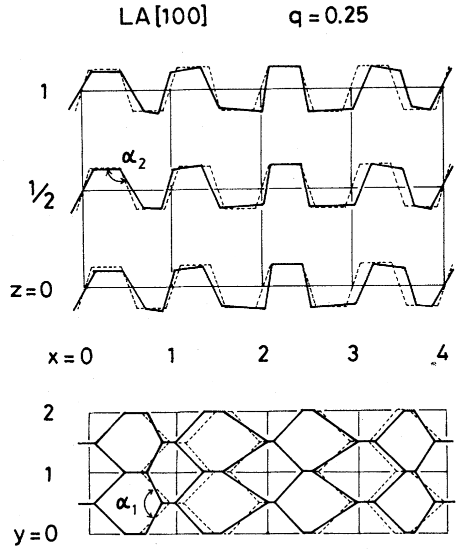

FIG. 5. Calculated lattice-vibrational patterns for LA[100] at $q/a^* = 0.25$ in which the anomalous softening was observed (Fig. 3). Eigenvectors were obtained from a force-constant model which was fitted to the present data at 1 bar by Kaneta *et al.*[8] In the lower figure, only puckered layer located at $z = \frac{1}{2}$ is shown.

(001) planes are obtained from eigenvectors calculated by the force-constant model giving the eigenvalues shown in Fig. 2.[8] Dotted lines represent the time-averaged bonding which corresponds to the static structure as shown in Fig. 1. Properties of the local distortion may be mainly ascribed to the bending of the bond angles α_1 and α_2 (also see Fig. 1). We may therefore characterize the overall property of this particular branch as the "accordion motion" of each puckered layer. On the other hand, it is known that the electronic configurations at the narrowest gap are mainly composed of bonding and antibonding of the p_z orbital, the energy of which should be strongly affected by the change of the bond angle. We may speculate that the energy associated with this accordion motion may be very sensitive to the change in band nature through electron-phonon interactions. Numerical calculations of electron-phonon interactions, with the aim of verifying the origin of softening of the accordion motion along the [100] direction, are planned.

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