Phonons in the New Iron-Based High-Temperature Superconductors

The new iron-pnictide superconductors discovered by Hosono and coworkers [1] present a fantastic opportunity for new science. With transition temperatures in excess of 50 K, they are interesting systems both in themselves, and as compared to the only other system with $T_c > 50$ K, the copper oxides, which remain poorly understood, even after 20 years of concerted research. The very first question, then, is if the new superconductors are phonon mediated, like MgB_2? or if their mechanism is more complex? Calculations of phonon properties appeared very quickly, and suggested superconductivity in these new materials was not phonon mediated [2]. However, our experimental results [3], as discussed below, show that the phonon properties differ significantly from simple calculations, suggesting conclusions based on those calculations that the phonon role in superconductivity should be considered cautiously.

Our technique of choice for these measurements was inelastic X-ray scattering (IXS) at beamline **BL35XU**, as it allows access to small samples: phonon densities of states (DOS) were measured using ~50 mg powder samples, and while phonon dispersion was measured using a small (~20×100×150 μm^3) single crystal. The powder samples of LaFeAsO (non superconducting) and $LaFeAsO_{0.9}F_{0.1}$ (T_c = 27 K) were synthesized at Tokyo Institute of Technology, while powder and a single crystal of $PrFeAsO_{1-y}$ (T_c = 48 K for powder and 36 K for the single crystal) were prepared at AIST using high-pressure synthesis.

IXS measurements from powder samples give an approximation to the phonon DOS, which we call a "pseudo-DOS." While not being precisely the DOS, which requires incoherent scattering, this provides similar information, which can be compared against various models. Figure 1 shows the results of *ab initio* GGA (general gradient approximation) pseudo-potential calculations for the tetragonal non-magnetic structure as compared against measurements from several samples. First, looking only at the calculations, we can see that most of the features of the DOS (Fig. 1(a)) are preserved in the pseudo-DOS (Fig. 1(b)). Meanwhile, the measurements are similar across all materials, and like the calculation, have a triplet peak structure. However, again, across all materials, the highest energy peak is ~5 meV softer than the calculation, a discrepancy that is very large by the standards of modern pseudo-potential calculations. This difference is also consistent with other work [2,4].

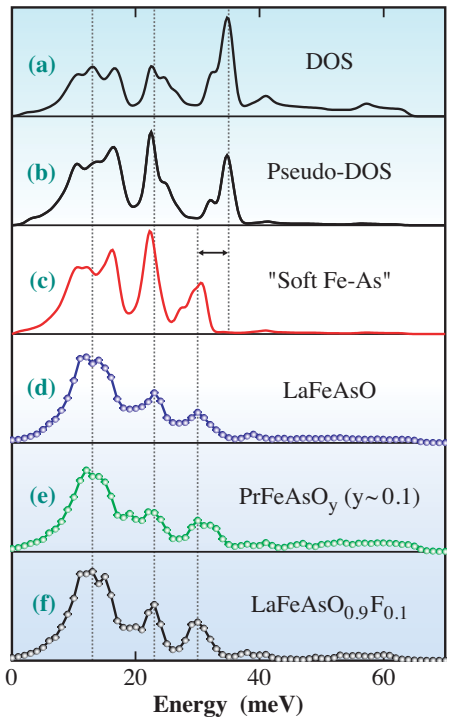

Fig. 1. Calculated and measured densities of states (DOS). **(a)** The DOS, **(b)** pseudo-DOS and **(c)** the effect of softening only the Fe-As bond (see text). **(d)**-**(f)** The pseudo-DOS extracted from measurements of three samples at room temperature. Vertical lines are at 13, 23, 30 and 35meV, which clearly shows the improved agreement with the soft Fe-As model.

In order to understand the origin for the softening, we examined the calculations in more detail, and measured dispersion from a single crystals. The calculated dispersion relation near 35 meV, the third phonon DOS peak, is somewhat complex (Fig. 2). The relevant bands consist primarily of in-plane FeAs motion at zone center (Γ), but apart from Γ point they begin to mix with the *c*-axis polarized motion of the FeAs layers, and across the fast-dispersing oxygen modes. However, the peak in the pseudo-DOS is nearly entirely from Fe-As motion. This can be demonstrated by softening *only* the Fe-As force constant matrix in the calculations. By a reduction of the nearest neighbor interactions by 30%, the third peak of the "soft Fe-As" pseudo-DOS falls to near the experimental value. Moreover, this reduction has only small effect on other peaks, and the total spectrum agrees reasonably well with the experiment as shown in Fig. 1(c). This model, at least in first approximation, is supported by measurements of a single crystal of $PrFeAsO_{1-y}$ (y~0.1). Figure 3 compares the spectra along Γ-X between the experiment and the soft

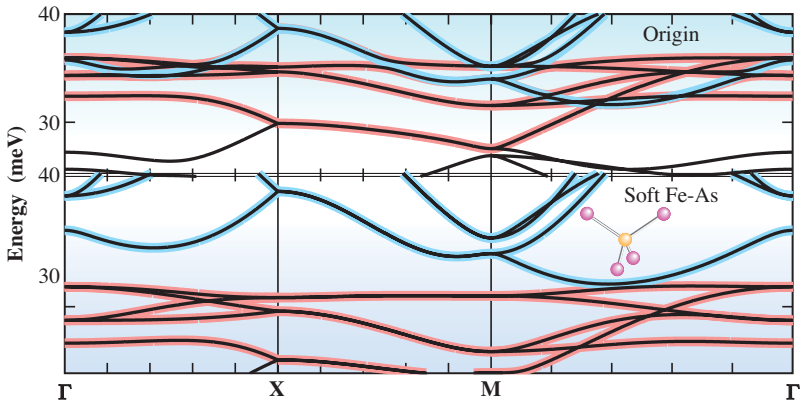

Fig. 2. Original LDA (top) and the "soft Fe-As" (bottom) calculated dispersions around the third peak, 35 meV, of the phonon DOS. Red (blue) shading indicates Fe-As (oxygen) modes. The effect of the soft Fe-As bond is primarily to shift the Fe-As modes to lower energy, as compared to the original calculations.

Fe-As model calculation in the (300) Brillouin zone. Though the low energy region has a slightly complex structure, the high energy part clearly shows the softening of the longitudinal optical modes from ~35 to 30 meV, essentially as expected from our model (see also Fig. 2).

The discrepancy between the measurement and the calculations suggests the existence of some interaction that is not properly included in the calculations. It is known that the LDA (local density approximation) calculations of the Fe-based layered system usually under-estimate the lattice constant *c* and Fe-As bond distance (Fe-As calculated bond distance 2.337 Å *vs.* 2.4 Å measured), and this tendency is consistent with the soft Fe-As model. We also note that another large discrepancy between the calculations and experiments is known about the amplitude of the magnetic moment on the iron atoms (calculation: 1- 2 μ_B, and the measured: ~0.3 μ_B). In fact our recent detailed phonon measurements with single crystals show that the measured dispersion along many symmetrical directions including Γ-X are in reasonable agreement with calculations of the *magnetically ordered* parent compound. This has interesting implications for the presence of short-lived magnetism. Taken together, this work suggests that the phonon system of thismaterial is not yet understood, and that conclusions about the relation between phonons and superconductivity based on simple calculation should be considered with caution.

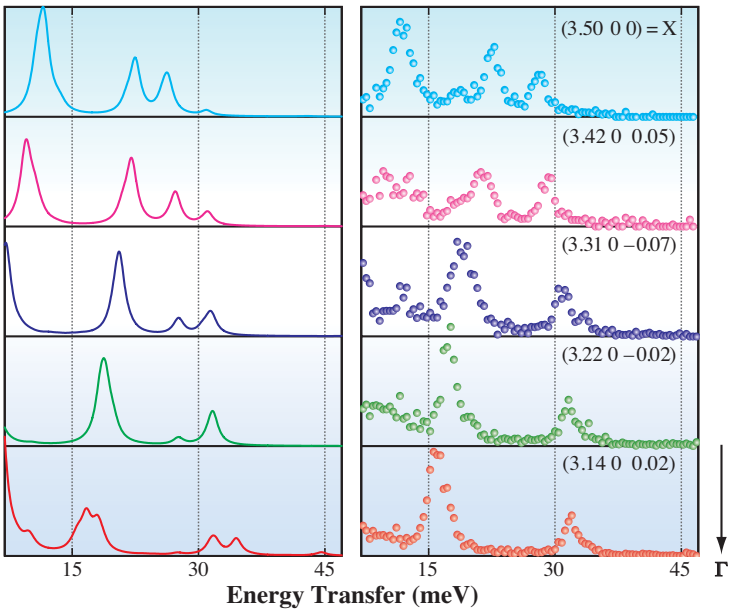

Fig. 3. Comparison of the measured dispersion for $PrFeAsO_{1-y}$ (y~0.1) at room temperature (right panel) and "soft Fe-As" calculation (left).

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References

[1] Y. Kamihara *et al.*: J. Am. Chem. Soc. **130** (2008) 3296; H. Hosono *et al.*: J. Phys. Soc. Jpn. **77** (2008) Supp. C 1.
[2] D.J. Singh and M.-H. Du: Phys. Rev. Lett. **100** (2008) 237003; L. Boeri *et al.*: Phys. Rev. Lett. **101** (2008) 026403.
[3] *T. Fukuda, A.Q.R. Baron, S. Shamoto, M. Ishikado, H. Nakamura, M. Machida, H. Uchiyama, S. Tsutsui, A. Iyo, H. Kito, J. Mizuki, M. Arai, H. Eisaki, and H. Hosono: J. Phys. Soc. Jpn. 77 (2008) 103715.*
[4] A.D. Christianson *et al.*: Phys. Rev. Lett. **101** (2008) 157004.