Close correlation between magnetic properties and the soft phonon mode of the structural transition in BaFe$_2$As$_2$ and SrFe$_2$As$_2$

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Parent compounds of Fe-based superconductors undergo a structural phase transition from a tetragonal to an orthorhombic structure. We investigated the temperature dependence of the frequencies of transverse acoustic (TA) phonons that extrapolate to the shear vibrational mode at the zone center, which corresponds to the orthorhombic deformation of the crystal structure at low temperatures in BaFe$_2$As$_2$ and SrFe$_2$As$_2$. We found that acoustic phonons at small wavevectors soften gradually towards the transition from high temperatures, tracking the increase of the size of slowly fluctuating magnetic domains. On cooling below the transition to base temperature the phonons harden, following the square of the magnetic moment. Our results provide evidence for close correlation between magnetic and phonon properties in Fe-based superconductors.

I. INTRODUCTION

The parent compounds of the ferropnictide superconductors are metallic but not superconducting, and order antiferromagnetically. Just like the cuprates, they become superconducting upon doping, which gradually suppresses antiferromagnetic order. Density-functional theory (DFT) predicts only very weak electron-phonon coupling, which is not directly contradicted by any experimental result so far. So it is unlikely that superconductivity in these compounds is mediated by conventional electron-phonon coupling, and most theories have focused on the role of spin fluctuations.

On the other hand, there is strong coupling between the magnetic degrees of freedom and the lattice. The most important experimental evidence for this coupling is a structural transition from tetragonal to orthorhombic, which is thought to be driven by magnetism. Further, it was reported that the arsenic A$_{1g}$ mode can generate AFM order dynamically and Raman scattering shows strong splitting of the in-plane E$_g$ mode in the ordered state. These observations have led several groups to suggest enhanced electron-phonon coupling via the spin channel. However, previous work using inelastic x-ray scattering (IXS) found no measurable changes in most optic phonons across the magnetic transition, in contrast to what has been predicted by density functional theory (DFT) calculations making allowance for spin-phonon coupling (although the inclusion of magnetism is required in order to correctly reproduce the structure). Therefore, the importance of spin-phonon coupling for the occurrence of high-$T_c$ superconductivity in the pnictides remains an open question.

The structural transition is accompanied by a transition into an antiferromagnetically ordered state. DFT calculations predict that the AFM state is energetically more stable even in the absence of a structural distortion, and that the structural distortion is the consequence of AFM order via magnetoelastic coupling. The structural transition is above the magnetic one in electron-doped pnictides (it was reported that this is might happen even in undoped BaFe$_2$As$_2$), which has led to the proposition of a nematic phase which does not show static

![Diagram](https://example.com/diagram.png)

FIG. 1. (color online) Lattice deformation and phonon renormalization across the magnetic ordering transition. a) Schematic of spin-phonon coupling in iron pnictides. Dots represent Fe positions. Straight lines/arrows on top are boundaries of the unit cell/unit vectors used for the notation in this paper respectively. Parallel/antiparallel alignment of the spins on near-neighbor Fe sites favor longer/shorter bonds. b) Schematic of scans shown in (c) and (d). c) Constant-energy scans of SrFe$_2$As$_2$ at 2 meV showing that the acoustic phonon peaks move closer to the zone center upon cooling below T$_N$ = 200 K, which indicates that the low-energy dispersion becomes steeper (schematic in (b)). d) constant-Q scans reflecting phonon hardening on cooling through T$_N$ = 135 K (schematic in (b)) in BaFe$_2$As$_2$. 

magnetic order, but where magnetic fluctuations have a preferred direction. Alternatively, the nematic phase might be characterized by orbital ordering with unequal occupations of the $d_{xz}$ and $d_{yz}$ orbitals. The magnetic, orbital, and structural order parameters break the tetragonal symmetry in the same way, but the parameter primarily responsible for the symmetry breaking is still a matter of debate (e.g., recent work has claimed that the nematic state is driven by spin, but strongly enhanced by orbital fluctuations). Although as pointed out in Ref. if the parameters are strongly coupled the “primary” parameter loses some distinction.

In this paper, we investigate the coupling of the crystal lattice to the magnetic degrees of freedom by a study of transverse acoustic phonons and the magnetic properties of undoped SrFe$_2$As$_2$ and BaFe$_2$As$_2$. More precisely, phonons were studied whose eigenvectors correspond to the structural distortion in the long-wavelength limit. These phonons propagate along the tetragonal [1 0 0] and are polarized along [0 1 0]. An early IXS study showed a pronounced softening of such phonons at low $q$ on approaching $T_N$ from above. On further cooling, these modes hardened gradually to some extent. The softening on cooling is corroborated by measurements of the elastic modulus by ultrasound technique. The softening was found to be closely correlated with a previous report of magnetic susceptibility as deduced from NMR above $T_N$.

The motivation for our present study was twofold: (i) whereas the behavior of the shear modulus and phonon frequencies above $T_N$ reported so far looks quite plausible, this is not really the case for the behavior below $T_N$: Since the phase transition in undoped pnictides is largely first-order, one would expect strong and sudden changes on cooling below $T_N$, and (ii) to gain a better understanding of the phonon behavior below the Néel temperature (the uncertainties associated with the lowest-temperature points in the previous report were large). We used inelastic neutron scattering for our study which provided data of much better quality. Neutron scattering was further used to explore the magnetic properties of our samples above and below $T_N$ with the aim to correlate the magnetic properties with the phonon properties. We show that the magnetic correlation length above $T_N$ and the magnetic order parameter squared below $T_N$ track the phonon softening at all temperatures.

II. EXPERIMENTAL DETAILS

We investigated two single-crystal samples of BaFe$_2$As$_2$ (Ba122) and of SrFe$_2$As$_2$ (Sr122). The samples were mounted in closed-cycle refrigerators with a temperature range of 10 K - 300 K (BaFe$_2$As$_2$) or 10 K - 350 K (SrFe$_2$As$_2$). The experiments were carried out on the 4F cold triple-axis spectrometer and on the 1T thermal triple-axis spectrometer at the ORPHEE reactor at the Laboratoire Léon Brillouin at Saclay, France. Final energies were chosen between 8 meV and 14.7 meV, depending on the energy resolution needed for the particular part of the experiments. The open collimations of the standard configuration were used for some scans (effectively 35'-35'-35'-35'), but tighter collimations were also often used to improve the resolution in energy and momentum transfer. Measurements of the phonon branch were made in the HK0 plane, and of the magnetic fluctuations in the HHL plane. Peaks were fit to Gaussian functions; error bars are derived from the statistical uncertainty.

III. RESULTS

At room temperature these materials are tetragonal, but as has been amply documented in the literature, they undergo a structural distortion from tetragonal-to-orthorhombic structure at $T_N$. This transition is closely accompanied by a transition to an antiferromagnetically ordered state at $T_N$. $T_N$ is very close to $T_s$, if different at all. We did not observe any splitting of the structural and AFM transitions in our samples. The transitions were observed at $T = 200$ K (SrFe$_2$As$_2$) and 135 K (BaFe$_2$As$_2$). This transition can be understood within the framework of DFT calculations, which show that magnetic order as observed in experiment with antiparallel spin alignment on neighboring Fe sites in one direction and parallel alignment in the other direction leads to a lowering of the total energy. A further energy gain is obtained by shortening

![FIG. 2. (color online) Phonon renormalization in SrFe$_2$As$_2$ and BaFe$_2$As$_2$ as a function of temperature along [1 0 0]. Error bars are drawn in all panels, but are sometimes smaller than the symbol. a) Relative phonon frequency change as a function of temperature in SrFe$_2$As$_2$ and BaFe$_2$As$_2$ b) Relative frequency jump at $T_N$. c) Dispersion of transverse phonons propagating along [1 0 0] with polarization along [0 1 0] in SrFe$_2$As$_2$. Lines are a guide to the eye.](image-url)
the bonds with antiparallel spin alignment and stretching the bonds with parallel spin alignment, as illustrated in Fig. 1h. The transition into the orthorhombic state leads to twinning of the samples, which results in a noticeable broadening of the mosaic distribution. In the following, we will adopt the tetragonal notation, and will make use of the orthorhombic notation only in a few places.

As was discussed in the introduction, the long-wavelength transverse acoustic phonons are expected to soften on approaching $T_N$ from above, followed by a gradual and moderate hardening on cooling below $T_N$. To our surprise, we observed a strong and sudden hardening of these phonons in SrFe$_2$As$_2$. The previous investigation made by IXS was, however, performed on BaFe$_2$As$_2$. In order to see whether the two compounds behave in a different way, or whether the effect observed in SrFe$_2$As$_2$ is a generic feature of the ferropnictides, complementary measurements were performed on BaFe$_2$As$_2$. It turned out that the two compounds show very similar behavior. The phonon effect is clearly evident from both constant-$Q$ and constant-energy scans through the phonon dispersions. (See Fig. 1c,d) The constant-$Q$ scan in Fig. 1c illustrates that in BaFe$_2$As$_2$ the phonon hardens strongly on cooling across $T_N = 135$ K by just 10 K from 140 K to 130 K. The same effect is reflected in the constant-energy scan on Sr122 in Fig. 1f. Here $q = 0$ is the zone center and the peaks on both sides at $q = 0.07$ originate from acoustic phonons dispersing on both sides of the zone center. The steeper (shallower) the dispersions, the closer (further) the peaks in the constant-energy scan are to the zone center (see schematic in Fig. 1f). On cooling through $T_N = 200$ K, the peaks move closer together, which reflects the same hardening as observed in Fig. 1f.

Fig. 2a shows varying behavior at different $q$. For small $q$, the phonon softens substantially upon cooling towards $T_N$, which is followed by abrupt hardening at lower temperature. At intermediate $q$ (e.g. $q = 0.25$) there is no softening above $T_N$, but there is still the hardening below $T_N$. And at high $q$ (e.g. $q = 0.45$), no temperature dependence is observed across $T_N$. The ratio of the frequency just below $T_N$ divided by the frequency above $T_N$ increases strongly towards the zone center (Fig. 2a,b). As is evident from Fig. 2a, the hardening below $T_N$ not only undoes the softening above $T_N$, but overshoots it by a substantial amount (see Fig. 2a). Further, the hardening below $T_N$ extends much farther in $q$, pointing to a different origin of the two phenomena.

Since we expected the phonon effect to be related to the formation of magnetic order, we carefully investigated the temperature dependence of magnetic Bragg peak intensity below $T_N$ and of magnetic fluctuations above $T_N$ in the same samples. In order to correlate the phonon softening above $T_N$ with magnetic properties, we measured the width in momentum transfer of the magnetic fluctuations at several low energies (up to 6 meV). The $q$-resolution at each energy was determined empirically from the spin wave spectrum below $T_N$ (which is nearly resolution-limited at the energies considered). We found that the temperature behavior of the linewidths was essentially the same at all energies investigated. The data shown in the following are those for which we obtained the best quality. Fig. 3 shows that well-defined peaks from magnetic scattering at 4 meV are already present at 300 K. They become much sharper on approaching $T_N$ from above, although they never become resolution-limited, even close to $T_N$. As generally expected, the in-plane widths are considerably smaller than those measured along c, but even in the c-direction, linewidth narrowing begins already at 300 K (Fig. 3b). This highlights the three-dimensional character of low energy magnetic fluctuations, and is in qualitative agreement with previous reports on the spin dynamics in the BaFe$_2$As$_2$ and SrFe$_2$As$_2$ systems. None of the widths, taken alone, correlates well with the phonon softening above $T_N$. However, the product of all three does (Fig. 3b).

Since each linewidth is proportional to the inverse of a correlation length in a particular direction, the product of the linewidths is proportional to the inverse of the volume of the correlated domains.

Below $T_N$, we determined both the temperature dependence of the magnetic order parameter and that of

![FIG. 3. (color online) Magnetic fluctuations in SrFe$_2$As$_2$ and BaFe$_2$As$_2$. a) Constant-energy (E = 4 meV) scans through the magnetic superlattice peak at two temperatures. Lines are fits with a Gaussian. The blue arrow denotes the experimental resolution. b) Resolution-corrected widths (in units of (H,0,0)) of spin fluctuation peaks measured at E = 4 meV versus temperature. The labeling assumes that the spin fluctuations locally break the tetragonal symmetry in the same manner as the static magnetic order does below $T_N$. The values for the c-axis are also given in the same units to make them directly comparable (in terms of absolute units) with the other data. c) Constant-energy scans from which the spin gap was determined d) Spin gap and the square of the magnetic order parameter versus temperature. $M^2$ has been scaled to match the value of the spin gap.](image-url)
the spin gap. For the magnetic order parameter, we measured the intensity of the magnetic Bragg peak at \( Q = (2.5, 0.5, 1) \) (or \( 5.0.1 \)) in orthorhombic notation). To determine the spin gap, we made a series of constant-energy scans through the magnetic Bragg peak at \( Q = (0.5, 0.5, 2) \) (or \( 10,0.5 \)) in orthorhombic notation, see Fig. 3). On approaching the spin gap energy from above, the peak intensities decrease sharply for reasons of phase space. We made careful measurements of the spin gap energy, and found that the temperature dependence of the spin gap tracks the square of the magnetic moment quite closely, for both \( \text{SrFe}_{2}\text{As}_{2} \) and \( \text{BaFe}_{2}\text{As}_{2} \) (see Fig. 3).

**IV. DISCUSSION**

In the \( q = 0 \) limit, vibrations associated with the investigated phonon modes correspond to the shear vibrational mode of the crystal, whose frequency squared is proportional to the shear modulus that was previously reported for \( \text{BaFe}_{2}\text{As}_{2} \) based on resonant ultrasound experiments (RUS)\(^{15}\). Our data are qualitatively consistent with the RUS results above \( T_N \). A quantitative comparison is not possible, however, because the softening is strongly dependent on \( q \), and insufficient \( q \)-resolution does not allow us to probe \( q \)-values which are very close to \( q = 0 \). On the other hand, it is clear that the neutron results disagree with the RUS results below \( T_N \): RUS shows only a small hardening on cooling compared to the softening above \( T_N \), whereas our data show a very large hardening that exceeds the softening above \( T_N \). This disagreement is likely due to the twin domain boundaries inside the crystal in the orthorhombic phase, which are known to interfere with RUS measurement, but not with phonon measurements (beyond a slight broadening).

Our data are qualitatively consistent with the IXS results for \( \text{BaFe}_{2}\text{As}_{2} \) above \( T_N \) reported in Ref. 12. However, there is a significant disagreement between our data and the previous report for \( T < T_N \), in that the low-\( q \) IXS results for \( q \leq 0.1 \) do not capture the sudden and very strong increase of phonon frequencies just below \( T_N \). One possible explanation for this disagreement is that the IXS beam size is extremely small (50 \( \mu \)m by 350 \( \mu \)m), and it is possible to obtain data from a single domain. Neutron beams (and samples) are significantly larger, and obtain data from an average of both twinned domains. If this phonon branch became strongly split in the orthorhombic phase, neutrons would see a contribution from both domains, appearing as an extremely broad peak. But we do not see any obvious indication of such an effect, so consider this explanation unlikely. We do not have any other plausible explanation for the disagreement, but emphasize that the strong and sudden increase of phonon frequencies below \( T_N \) is proved beyond doubt by our data (see, e.g., Fig. 1).

When trying to correlate the temperature dependence of the phonon frequencies with that of the magnetic properties, we found that the hardening below \( T_N \) tracks the square of the magnetic order parameter very closely in both \( \text{SrFe}_{2}\text{As}_{2} \) and \( \text{BaFe}_{2}\text{As}_{2} \) (Fig. 4). Since we found that the temperature evolution of the spin gap is quite similar to that of the square of the magnetic order parameter, the correlation seen in Fig. 3 could also be related to the opening of the spin gap. It is also well known that in the undoped 122-compounds, the magnetic and the structural order parameters are biquadratically coupled\(^{16-19}\). Since phonon frequencies are biquadratically coupled to the magnetic order parameter as well, it is essentially linearly coupled to the structural order parameter. There thus seem to be three possibilities for the correlation observed in Fig. 4: that the phonon hardening could track either the square of the structural distortion,
the square of the magnetic order parameter, or opening of the spin gap. To determine which is this case, further studies are necessary on samples where the structural and the magnetic order parameters do not follow the same temperature dependence, as in, e.g., Co-doped Ba122.

Above $T_N$ we found the closest correlation between the volume of the short-lived magnetic domains and the phonon frequencies (Fig. 4). Only a slight uniaxial strain is required to produce a resistivity anisotropy in the paramagnetic state, which corresponds to the soft phonon seen here. This indicates the strong coupling between the lattice and the electronic degrees of freedom, although this coupling might be indirect: short-range nematic order will induce some local lattice distortion via magnetoelastic coupling, and the phonons might couple to the lattice distortion. In this context it may be illuminating to consider the $q$-dependence of phonon softening, as its correlation with the $q$-dependence of magnetic or orbital fluctuations make it possible to differentiate between the two mechanisms. This question requires a theoretical investigation that is outside the scope of the current work. Since any local lattice distortion will entail an elastic strain field, which is inherently long-range in 3D, it is plausible that the volume of the dynamic domains is most closely correlated to the phonon frequencies. It follows that in order to understand coupling of magnetic (and for that matter nematic) fluctuations to the atomic lattice, it is necessary to consider not only the in-plane magnetic correlation length but also the correlation length along the c-axis.

Previous theoretical work found that the electron-phonon coupling was significantly stronger in the stripe AFM state than in the paramagnetic state. It is difficult for us to determine if the electron-phonon coupling for this mode (as measured by the energy linewidth) has become significantly enhanced in the AFM phase. This is because the orthorhombic distortion causes a significant broadening of the mosaic spread, which in turn causes a broadening of the TA phonon. Separating these effects is challenging.

V. CONCLUSIONS

We found that in undoped 122 compounds, the TA phonons propagating along [1 0 0] with polarization along [0 1 0] soften gradually on approaching $T_N$ from above, followed by an abrupt hardening just below $T_N$ and further gradual hardening on cooling to very low temperatures. Interestingly, the hardening below $T_N$ exceeds significantly that of the softening above $T_N$ in both magnitude and $q$-range, which remains to be understood. While the softening above $T_N$ was known already from previous publications at least qualitatively, the pronounced hardening below $T_N$ was not. The temperature evolution of the phonon frequencies both below and above $T_N$ correlates closely with that of magnetic properties observed on the same samples. However, this correlation does not necessarily imply a direct spin-phonon coupling. The coupling between the phonons and the static/dynamic magnetic order might only be indirect via magnetoelastic coupling.

The most promising candidates for further insight into this issue are samples where magnetic order and structural distortions do not appear at the same temperature, as in Ba122 samples lightly doped with Co. In such samples, $T_\sigma > T_N$. Just like in the undoped sample, we can expect gradual softening of the phonons on cooling towards the structural transition. It is, however, difficult to predict how the phonon frequencies will evolve on further cooling through the magnetic transition. Answering this question will be a subject of a different paper, which will provide additional insight into understanding the coupling of phonons to magnetic properties in Fe-based superconductors.

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