ESRF	**Experiment title:** **^{57}Fe NFS and NIS studies of superconducting $Fe_{1.01}Se$ as function of temperature and pressure**	**Experiment number**: HS-3978
Beamline: ID18	**Date of experiment**: from: 25. Aug. 2009 to: 1. Sept. 2009	**Date of report:** 16. Oct. 2009
Shifts: 18	**Local contact(s)**: Dr. Aleksandr Chumakov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Vadim Ksenofontov*, Teuta Gasi*, Claudia Felser (University of Mainz)

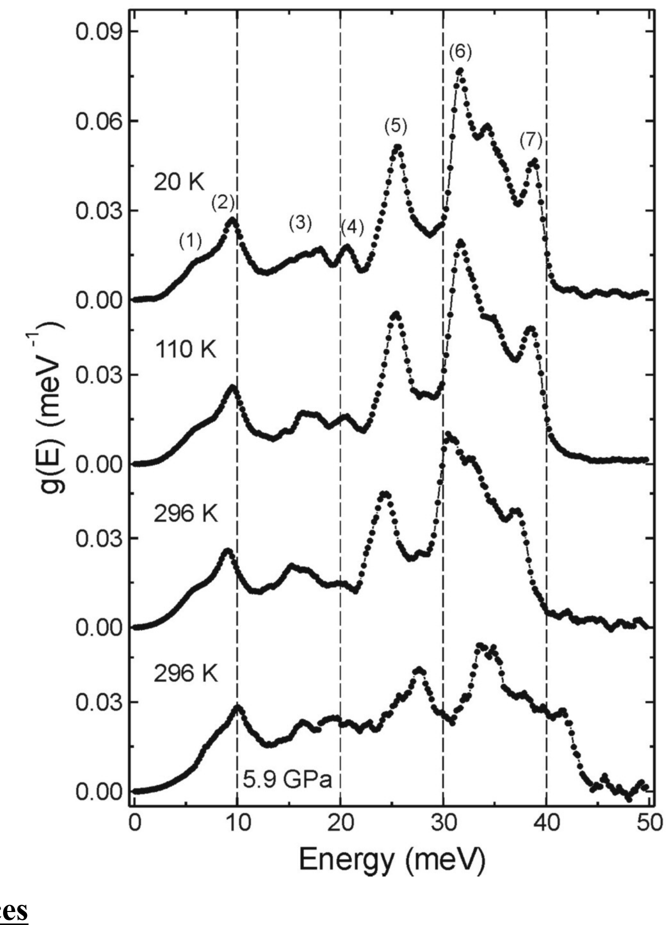
Gerhard Wortmann* (University of Paderborn)

Report:

The FeSe system, investigated in this beamtime, is a model system for the new high-T_C superconductors with Fe_2As_2 or Fe_2Se_2 layers. Here we studied a $Fe_{1.01}Se$ sample, which was previously characterized and intensively investigated by the applicants in cooperation with Princeton University and Max-Planck Institute of Chemistry, Mainz, as documented in recent publications [1-5]. FeSe could be a clue compound [6] for the understanding of the principal mechanisms of superconductivity in these layered systems. In particular, the dramatic increase of T_C from 8 K at ambient pressure to 37 K at 9.0 GPa [2] points towards a common pressure modulated mechanism for superconductivity in these systems. For the superconducting FeAs systems $Ba_{1-x}K_xFe_2As_2$ and $SmFeAsO_{1-x}F_x$, large isotope effect on the T_C values, here an increase of T_C for the lighter ^{54}Fe isotope, has been detected [7]. Even it is evident that superconductivity is not originating from standard electron-phonon coupling, phonons are involved in the “unconventional” mechanisms, e.g. connected with spin fluctuations. Therefore a detailed study of the local phonon density-of-states (DOS) at the Fe sites (which are here the “players”) is of actual scientific interest.

We used ^{57}Fe nuclear inelastic scattering (NIS) spectroscopy with a high energy resolution of 0.7 meV, provided at beamline ID18, to study the Fe phonon-DOS in $Fe_{1.01}Se$, enriched with 20% ^{57}Fe, as function of temperature (at 20 K, 67 K, 110 K, and 296 K) as well as at a pressure of 5.9 GPa. Fig. 1 shows the phonon-DOS, *g(E)*, of $Fe_{1.01}Se$ at various temperatures in the tetragonal (296 K and 110 K) and in the orthorhombic phase (20 K). The high energy resolution for the whole spectral range allows an unambiguous assignment of characteristic acoustic and optical branches by comparison with theoretical calculations [8] as well as with neutron studies [9]. We could observe spectral details not analysed before such as a shift of all modes to higher energies (by ~4%) and sharpening of the optical modes with decreasing temperature, as exemplified by the DOS spectra at 296 K, 110 K and 20 K. These well-resolved spectra allow at low temperature a graphical analysis of the mode energies with accuracies down to 0.2 meV. The optical modes in the energy range 20 – 40 meV can be attributed to certain symmetry points in the calculated phonon DOS, e.g. the well-resolved mode at 25 meV (signed (5) in Fig.1) to the A_{1g} Raman mode [8, 9]. While the theoretical calculations [8] describe the principal positions of the optical modes quite well, the low-energy part of the phonon-DOS is not described correctly. Of special interest are, to our opinion, the acoustic modes observed in this low energy range, where we tentatively attribute a structure at 5 meV (signed (1) in Fig.1), well-resolved in the so-called reduced form of the DOS, $g(E)/E^2$, to transversal acoustic modes (see Fig. 2) and the well-resolved structure around 9 meV (signed (2) in Figs. 1) to longitudinal acoustic modes. We found no evidence for low-lying modes at 2.5 meV connected with the Γ-Z point of the BZ [8]. Comparison of the well-resolved phonon-DOS spectra of FeSe obtained at 110 K (tetragonal phase) and at 67 K (orthorhombic phase, not shown here) does not indicate any difference originating from this subtle structural phase transition around 95 K [3]. Our present data are in principal agreement with the phonon-DOS derived from the neutron data [8], using three different types of monochromators, in any case with considerably less resolution than in the present NIS study. Since we measure the whole spectral range of the DOS with the same 0.7 meV resolution, we can derive from the NIS spectra (after subtraction of elastic line, subtraction of multi-phonon excitations, etc.) a normalized presentation of the phonon-DOS (total area equals unity) with the actual contributions of all Fe modes. This allows, as shown in a related ^{119}Sn-NIS study of SnO [10], a compound with the same layered PbO-structure as FeSe, to derive elastic and thermodynamic parameters of the Fe sublattice, such as the Mössbauer-Lamb factor f_{LM}, the mean force constant D, the Debye temperature $\Theta_{D,HT}$ and vibrational energy F_{vib} . These data will be presented in a forthcoming publication of the present data.

Fig. 1 (bottom) shows also the phonon DOS of $Fe_{1.01}Se$ at 5.9 GPa measured at 296 K with a special high-pressure cell for NIS spectroscopy developed in Paderborn [11]. At 5.9 GPa, the present sample exhibits superconductivity with T_C = 32 K [2] and is free from the hexagonal phase, which start to appear at 7 GPa and increases in amount at higher pressures [2]. Beside the strong increase of the spectral features towards higher energy (by ~10%) due to the reduction of the molar volume by ~14% [2], clearly evident for the optic modes from 20 – 40 meV, we observe significant modifications in the low-energy range, especially for the transverse acoustic mode, being shifted from ~5 meV to ~7 meV, while the longitudinal mode at 9 meV shifts only to 10 meV. This different behaviour of the low-energy modes is exemplified in the plot of the reduced phonon-DOS, $g(E)/E^2$, indicating also that the sound velocity and therewith the binding strength has considerably increased under pressure. We tentatively attribute these strong modifications of the acoustic modes with the observed strong increase of T_C and want to prove this assumption in further ^{57}Fe-NIS studies of FeSe under pressure as well as of related systems, e.g. $FeSe_{1-x}Te_x$.



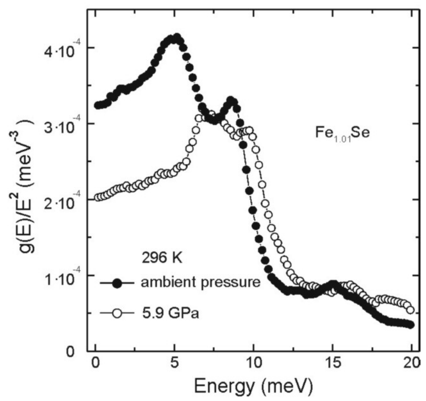


Fig 1: Fe phonon-DOS *g(E)* for $Fe_{1.01}Se$ at different temperatures (above) and at a pressure of 5.9 GPa at 296 K (below).

Fig.2: Fe phonon-DOS for $Fe_{1.01}Se$ presented in the reduced form, $g(E)/E^2$, for the low energy range demonstrating the strong modifications of the acoustic modes.

References

1. T.M. McQueen, V. Ksenofontov, C. Felser, R.J. Cava et al., Phys. Rev. B 79, 014522 (2009). **2.** S. Medvedev, T.M. McQueen, I. Trojan, T. Palasyuk, M.I. Eremets, R.J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann, C. Felser, Nature Mater. 8, 630 (2009). **3.** T.M. McQueen, V. Ksenofontov, F. Casper, C. Felser, R. J. Cava, et al., Phys. Rev. Lett. 103, 057002 (2009). **4.** T. Imai, K. Ahilan, F.L Ning, T.M. McQueen and R.J. Cava, Phys. Rev. Lett. 102, 177005 (2009). **5**. A.J. Williams, T.M. McQueen, V. Ksenofontov, C. Felser, R.J. Cava, J. Phys. Cond. Mat. 21, 305701 (2009). **6.** B. Büchner and Ch. Hess, Nature Mater. 8, 615 (2009). **7.** R.H. Liu et al., Nature 459, 64 (2009). **8.** A. Subedi et al., Phys. Rev. B 78, 1345514 (2008). **9.** D. Phelan et al., Phys. Rev. B 79, 014519 (2009). **10.** R. Lübbers, H.F. Grünsteudel, A.I. Chumakov, Science 287, 1250 (2000). **10.** H. Giefers, S. Koval, G. Wortmann, W. Sturhahn, E.E. Alp, M.Y. Hu, Phys. Rev. B 74, 094303 (2006). **11.** R. Lübbers, H.F. Grünsteudel, A.I. Chumakov, G. Wortmann, Science 287, 1250 (2000).