Abstract

We report an infrared study on the optimally Te-doped iron-chalcogenide superconductor, Fe$_{1.03}$Se$_{0.5}$Te$_{0.5}$ as a function of pressure at various low temperatures down to 115K. The evolution with pressure and temperature of the mid-IR reflectance spectra shows that by increasing pressure the mid-IR absorption band associated with magnetic order reduces its intensity before it vanishes at 2 GPa. However, overall low temperature reflectance spectral in the mid-IR range indicates drastic changes in the electronic configuration of the system at all pressures up to 5 GPa below 120K. Far IR reflectance measurements at various high pressures show dramatic changes of the IR phonon spectra indicating structural transition below this temperature. Thus our study suggests that structural modification may not be the only parameter establishing the magnetic order in this system.

1. Introduction

Discovery of superconductivity in iron-chalcogenides, with the layered anti-PbO tetragonal structure at room temperature, has raised considerable interest in studying these compounds in more detail because of their simplest crystal structure among various iron-based superconductors (F. C. Hsu et al. 2008). Interestingly, although α-
FeSe exhibits spin-fluctuation driven superconducting ground state (with \( T_c \sim 9K \)), unlike other iron-based superconductors (FeSCs), at ambient pressure no long range magnetic order is established at low temperature (T. Imai et al. 2009). However moderate amount of external pressure drives the system into a state where static magnetic order is realized (M. Bendele et al. 2010). Structurally, due to the absence of alkali ions or charge-reservoir layers between the Fe\(_2\)Se\(_2\) superconducting layers, the system is found to be very much compressible and a strong correlation is noticed between the structural parameters and superconducting transition temperature. (Y. Mizuguchi et al. 2008, K. Miyoshi et al. 2009, H. Okabe et al. 2010). Recent observation of the structural distortion in Te-doped FeSe compounds and the correlated change in the superconducting transition temperature \( T_c \) has stimulated interest to the detailed investigations of the structural and electronic properties of this compound under high pressure. Although, various theoretical investigations have predicted chalcogen height dependent change in magnetic order and electronic properties in Te-doped FeSe compounds (C. Y. Moon et al. 2009, J. Kumar et al. 2012), no experimental report is available for the pressure effect of the magnetic order in these compounds. However, the temperature dependence of magnetic susceptibility has been studied by J. Pietosa et al. 2012 where clear SDW transition is observed at ambient and 1 GPa with no change of transition temperature.

In the present work, we report on synchrotron based infrared investigation on the optimally Te-doped iron-chalcogenide superconductor \( \text{Fe}_{1.03}\text{Se}_{0.5}\text{Te}_{0.5} \) as a function of pressure at various low temperatures above and below the SDW transition temperature (120K). Mid-IR reflectance spectral analysis, particularly the absorption band associated with the magnetic transition and the changes of the far IR phononic spectra suggest that structural modification may not be the only parameter establishing the magnetic order in this system.

![Crystal structure of tetragonal \( \text{Fe}_{1.03}\text{Se}_{0.5}\text{Te}_{0.5} \) and temperature dependence of magnetic susceptibility in the field cooled (FC) and zero-field cooled (ZFC) scheme](image)

2. Experimental

Polycrystalline \( \text{Fe}_{1.03}\text{Se}_{0.5}\text{Te}_{0.5} \) has been prepared by the solid state reaction method. Stoichiometric amounts of Fe (99.9%), Se (99.5%) and Te (99.5%) are mixed, and the pressed powder of this mixture are sealed in an evacuated quartz tube and heated at 700°C for 24 hr. Structural characterization by x-ray diffraction measurements on as-grown sample shows a mixture of tetragonal (\( \alpha \)-phase) and hexagonal (NiAs type \( \beta \)-phase). No trace of excess Fe was detected. Magnetic susceptibility measurement was performed using a SQUID magnetometer (Quantum Design) under an external magnetic field of 10 Oe and the onset superconducting \( T_c \) was found to be \( \sim 13.5 \) K. A clear feature for the SDW like AFM transition is observed at \( \sim 120 \) K. A small positive overall susceptibility above the superconducting transition temperature is due to the presence of paramagnetic hexagonal phase. In order to study the pressure dependence of the superconducting \( T_c \) and the magnetic transition temperature, resistance measurement has been performed using a miniature DAC in the temperature range 2 - 300K. A quasi-four probe resistance measurement technique with in-situ ruby pressure
measurement was employed. The details of the DAC preparation, resistance measurement and sample pressure determination technique have been described elsewhere (S. Karmakar 2013).

Pressure dependent reflectance measurements were performed with a moissanite anvil cell (MAC) at the SISSI beamline of Elettra synchrotron facility, with the help of an IR microscope (Hyperion) equipped with liquid nitrogen cooled HgCdTe (MCT) detector and liquid helium cooled Bolometer and coupled to a Bruker IFS66v interferometer. For low temperature measurements, MAC was mounted inside a N$_2$-flow microscope cryostat from Oxford, allowing cooling the MAC down to ~100K. A thin pallet of finely ground sample was placed in the gasket hole (of diameter 200 micron), which was then filled with dry KCl as pressure medium. In the mid-IR range, the reflectance at the sample-moissanite interface was measured in the wide frequency range (700 - 12000 cm$^{-1}$). However, due to strong infrared absorption of the moissanite, sample reflectance can only be recorded in the frequency range 2700-7000 cm$^{-1}$. In the far-IR region, reflectance is measured in the frequency range 250-700 cm$^{-1}$. As the absorption band due to the AFM (SDW) magnetic ordering appears within the above mid-IR range, the magnetic transition has clearly been probed by this study. At each pressure, the intensity of light, $I(\omega)$, reflected from the sample surface is measured and normalized with the light intensity, $I_0(\omega)$, reflected from the external face of moissanite window, to obtain a quantity $r(\omega)=I(\omega)/I_0(\omega)$. At the end of the pressure run, another measurement is performed on the open moissanite surface [$I_m(\omega),I_{0m}(\omega)$] by removing the sample. The ratio $R(\omega)=I_{m}(\omega)/I_{0m}(\omega)$ is assumed to be pressure independent. The reflectance $R_{s-m}(\omega)$ at the sample-moissanite interface is thus obtained from the equation $R_{s-m}(\omega)=[r(\omega)/R(\omega)]*R_m$, where $R_m=\left[(n_m^{-1})/(n_m^{+1})\right]^2$ and $n_m$ being the real refractive index of moissanite in air. For this experiment, pressure inside the DAC was monitored with the in-situ ruby luminescence method (Mao et al. 1986).

3. Results and Discussion

Fig. 2 shows temperature dependence of resistance at 0.3 and 3.5GPa. The sharp drop in resistance at 120K is ascribed to formation of SDW order. Fig. 3(a,c-f) presents the mid-infrared reflectance spectra at temperatures below and above the magnetic transition temperatures (T$_m$~120K) from the sample-moissanite interface, $R_{s-m}$, at various high pressures. At 0.1 GPa, full mid-IR reflectance spectra is shown. Below 2600 cm$^{-1}$ strong IR absorption of the moissanite crystal prevents the measurement of true sample reflectance (Z. Liu et al. 2004). For the measurements at low pressures, sufficient initial pressure was applied to make the sample in good contact with the moissanite surface. The reflectance spectra $R_{s-m}$ is fitted with Drude Lorentz oscillators [applying f-sum rule for auto rescaling] [Equations 1, 2] (Kuzmany 2009) and the optical conductivity at two temperatures have been plotted in figure 3(b).

$$\varepsilon_1(\omega) = \varepsilon_\infty + \left[ \frac{\varepsilon_0}{\omega^2 + \varepsilon_0^2} + \varepsilon_{\text{tot}} \sum_{i=1}^{n} \frac{f_i(\omega^2 - \omega_i^2)}{(\omega^2 - \omega_i^2)^2 + (G_i\omega)^2} \right]$$  \hspace{1cm} \text{(1)}

$$\varepsilon_2(\omega) = \varepsilon_{\text{tot}} \sum_{i=1}^{n} \frac{f_i G_i \omega}{(\omega^2 - \omega_i^2)^2 + (G_i\omega)^2}$$  \hspace{1cm} \text{(2)}

Fig. 2. Temperature dependent resistance at two different pressures. T$_c$ indicates the superconducting transition temperature. T$_m$ is magnetic transition temperature. For sake of clarity, two resistance plots have been shifted arbitrarily.
Low frequency Drude extrapolation has been performed with our room temperature measurements in a diamond anvil cell at lowest pressure. (P. S. Malavi et al. 2013).

In Fig. 3(a), we see that with decreasing temperature, below the magnetic transition at 120 K, a new peak emerges at 3000 cm\(^{-1}\), which is associated with the magnetic ordering. This feature was first observed in FeAs based superconductors below the SDW transition by Hu et al. 2008. Fig. 3(b) shows the fitted optical conductivity based on the DL fitting of the reflectance spectra. Apart from the broad high energy oscillator at 4500 cm\(^{-1}\), a new absorption band at 3000 cm\(^{-1}\) due to magnetic origin is apparent. With increasing pressure this band in the reflectance spectra decreases in intensity and vanishes at 2 GPa. However, in the low temperature reflectance spectra at all pressures in this investigation, a sudden spectral change is noticed. Also anomalous temperature dependence of the energy (\(\omega\)) and intensity (oscillator strength) of the high energy oscillator at 4500 cm\(^{-1}\) was noticed below 130K along with the decrease in the intensity of magnetic feature at 1 GPa. This electronic change indicates a low temperature structural change below 130K causing the changes in magnetic order.

In order to understand the origin of these mid-IR spectral changes, we have also investigated this compound in the FIR region. Fig. 4 shows the FIR reflectance spectra at two pressures (2 GPa and 3 GPa) at various low temperatures. Although the magnetic order vanishes at these pressures, the emergence of a new phonon peak at around 500 cm\(^{-1}\) at both the pressures at the lowest temperature clearly indicates structural transition below 120K. The phonon mode at 500 cm\(^{-1}\) in the high temperature tetragonal phase starts softening with lowering temperature indicating instability of the structure below 120K. This agrees with the reported low temperature structural transition (\(P4/nmm \rightarrow Cmma\)) in this compound. Also intensity of the corresponding mode in low
temperature (orthorhombic) phase has increased significantly.

The structural phase transition around 120K significantly affects the phonon frequencies as previously observed in SmFeAsO and SrFe$_2$As$_2$ (C. Marini et al. 2008, Hanckock et al.2010). It is widely believed that structural distortion is driven by the magnetic instability (T. Yildrim 2008, C. Fang et. al. 2008) but our results show that this is not true at high pressures, as with increase in pressure we observe that structural transition occurs irrespective of SDW order in the system.

4. Conclusions

Infrared spectroscopic measurements on Fe$_{1.03}$Se$_{0.5}$Te$_{0.5}$ have been carried out at high pressure below magnetic ordering temperature. A mid-IR absorption band at ~3000 cm$^{-1}$ has been identified as of magnetic (SDW like) origin. Upon increasing pressure this peak vanishes above ~2 GPa, indicating pressure-induced suppression of the magnetic order. However, the mid IR spectral change and the IR phonon anomaly below 120K prominently indicate the structural transition at least up to 5 GPa (the highest pressure of this investigation). Our study suggests that structural modification may not be the only parameter establishing the magnetic order in this system.

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References

F.C. Hsu, J.Y. Luo, K.W. Yeh, T.K. Chen, T.W. Huang, P. M. Wu, Y.C. Lee, Y.L. Huang, Y.Y. Chu, D.C. Yan, M. K. Wu, 2008, Superconductivity in the PbO-type structure α-FeSe, Proc. Natl. Acad. Sci., 105, 14262.
T. Imai, K. Ahilan, F. L. Ning, T. M. McQueen, R. J. Cava, 2009, Why Does Undoped FeSe Become a High-Tc Superconductor under Pressure? Phys. Rev. Lett., 102, 177005.
M. Bendele, A. Amato, K. Conder, M. Elandler, H. Keller, H.-H. Klauss, H. Luetskens, E. Ponomarkushha, A. Raselli, and R. Khasanov, 2010, Pressure Induced Static Magnetic Order in Superconducting FeSe$_{1.3}$,Phys. Rev. Lett., 104, 087003.
Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, Y. Takano, 2008, Superconductivity at 27 K in tetragonal FeSe under high pressure, Appl. Phys. Lett., 93, 152505.

K. Miyoshi, Y. Takaichi, E. Mutou, K. Fujiwara, J. Takeuchi, 2009, Anomalous Pressure Dependence of the Superconducting Transition Temperature in FeSe, Studied by DC Magnetic Measurements, J. Phys. Soc. Jpn., Vol. 78, No. 9, 093703.

H. Okabe, N. Takeshita, K. Horigane, T. Muranaka, J. Akimitsu, 2010, Pressure-induced high-Tc, superconducting phase in FeSe: Correlation between anion height and Tc, Phys. Rev. B, 81, 205119.

C. Y. Moon and H. J. Choi, Chalcogen-Height Dependent Magnetic Interactions and Magnetic Order Switching in FeSe,Tc, 2010, Phys. Rev. Lett., 104, 057003.

J. Kumar, S. Auluck, P. K. Aithwalia, and V. P. S. Awana, 2012, Chalcogen height dependence of magnetism and Fermiology in FeTe, Science and Technology, 25, 095002.

J Pietosa, D J Gawryluk, R Puzniak, A Wisniewski, J Fink-Finowicki, M Kozlowski, M Berkowski, 2012, Pressure-induced enhancement of the superconducting properties of single-crystalline FeTe0.5Se0.5, J. Phys.: Condens. Matter, 24, 265701.

S. Karmakar, 2013, High Pressure Research, 33, 381.

H. Mao, J. Xu, and P. Bell, Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions, 1986, J. Geophys. Res., 91, 4673.

Z Liu, J Xu, HP Scott, Q Williams, H Mao, R. Hemely, 2004, Moissanite (SiC) as windows and anvils for high-pressure infrared spectroscopy, Review of scientific instruments, 75,11.

H. Kuzmany, 2009, Springer-Verlag, in 'Solid-State Spectroscopy', Ch. 6.

P. S. Malavi, S. Karmakar, N. Patel, S. M. Sharma, 2013, arXiv: Cond-Mat 1308.3367.

W. Z. Hu, J. Dong, G. Li, Z. Li, P. Zheng, G. F. Chen, J. L. Luo, and N. L. Wang, 2008, Origin of the Spin DensityWave Instability in AFe2As2 (A =Ba, Sr) as Revealed by Optical Spectroscopy, Phys. Rev. Lett 101, 257005.

C. Marini, C. Mirri, G. Profeta, S. Lupi, D. Di Castro, R. Sopracase, P. Postorino, P. Calvani, A. Perucchi, S. Massidda, G. M. Tropeano, M. Putti, A. Martellini, A. Palenzona and P. Dore, 2008, The optical phonon spectrum of SmFeAsO, arXiv:0810.2176v1 [cond-mat.supr-con].

J. N. Hancock, S. I. Mirzaei, J. Gillett, S. E. Sebastian, J. Teysier, R. Viennois, E. Giannini, D. van der Marel, 2010, Strong coupling to magnetic fluctuations in the charge dynamics of iron-based superconductors, Phy. Rev. B 82,014523.

T. Yildirim, 2009, Frustrated magnetic interactions, giant magneto–elastic coupling, and magnetic phonons in iron–pnictides Physica C 469, 425–441.

Chen Fang, Hong Yao, Wei-Feng Tsai, JiangPing Hu, Steven A. Kivelson, 2008, Theory of electron nematic order in LaFeAsO, Phy. Rev. B, 77, 224509.