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Phonon spectrum of single-crystalline FeSe probed by high-resolution electron energy-loss spectroscopy☆

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ABSTRACT

Utilizing high-resolution electron energy-loss spectroscopy (HREELS) we measure the phonon frequencies of β–FeSe(001), cleaved under ultra-high vacuum conditions. At the zone center ($\bar{\Gamma}$–point) three prominent loss features are observed at loss energies of about $\simeq 20.5$ and 25.6 and 40 meV. Based on the scattering selection rules we assign the observed loss features to the A_{1g}, B_{1g}, and A_{2u} phonon modes of β–FeSe(001). The experimentally measured phonon frequencies do not agree with the results of density functional based calculations in which a nonmagnetic, a checkerboard or a strip antiferromagnetic order is assumed for β–FeSe(001). Our measurements suggest that, similar to the other Fe-based materials, magnetism has a profound impact on the lattice dynamics of β–FeSe(001).

1. Introduction

Investigation of superconductivity in Fe-based materials has been a major research topic during the last decade, after the discovery of high temperature superconductivity in pnictides [1]. Among all Fe-based high temperature superconductors β–FeSe is the most simplest one and has been discovered almost at the same time of pnictides [2]. The discovery of of high transition temperature of up to 100 K in the FeSe monolayer grown on $SrTiO_3$ has created lots of excitements in the field of high temperature superconductivity [3]. β–FeSe is composed of square planar sheets of Fe atoms which are tetrahedrally coordinated, very similar to the other Fe-based high-T_c superconductors [4]. Inelastic neuron scattering experiments with polarization analysis have revealed that the Cooper pairing mechanism in this material is likely mediated by spin fluctuations [5,6], similar to the other Fe-based high-T_c materials [7–10]. It is now generally believed that FeSe also belongs to the category of unconventional superconductors, which the underlying mechanism of Cooper pairing is not directly mediated by the electron-phonon coupling. However, the isotope effect has been reported in this material [11]. This question that what is the impact of the lattice dynamics on superconductivity? has still remained as an open question [12–15].

The lattice dynamics in FeSe and other Fe-chalcogenides has already been investigated by several techniques [15–21]. A large part of those investigations is carried out on polycrystalline or powder samples. This might be due to the fact that preparing large single crystals of β–FeSe is still a challenge. The experiments performed on the single-crystalline samples are mainly performed by means of Raman scattering which can only probe the Raman active modes [15,18–20,22].

Here we present our results of phonon measurements at the surface of β–FeSe(001) obtained using low-energy electron scattering. We probe all the three possible A_{1g}, B_{1g} and A_{2u} phonon modes at the $\bar{\Gamma}$–point. We demonstrate that these modes originate from the atomic displacements of Se and Fe atoms along the c-axis, normal to the surface and hence can be easily excited by means of electrons. We will comment on the impact of magnetism on the phonon frequencies in this material.

2. Results and discussions

β–FeSe single crystals were grown using the standard method, explained in Ref. [23]. As precursor Fe and Se powders were mixed in an atomic ratio 1.1 to 1 and sealed in an evacuated SiO_2 ampoule together with a eutectic mixture of KCl and $AlCl_3$. The crystals were mounted on a sample holder and were transferred into the ultra-high vacuum (UHV) chamber, where they were cleaved under UHV conditions (pressure better than 1×10^{-10} mbar) at room temperature. In this material Fe atoms are covalently coordinated with Se atoms above and bellow the

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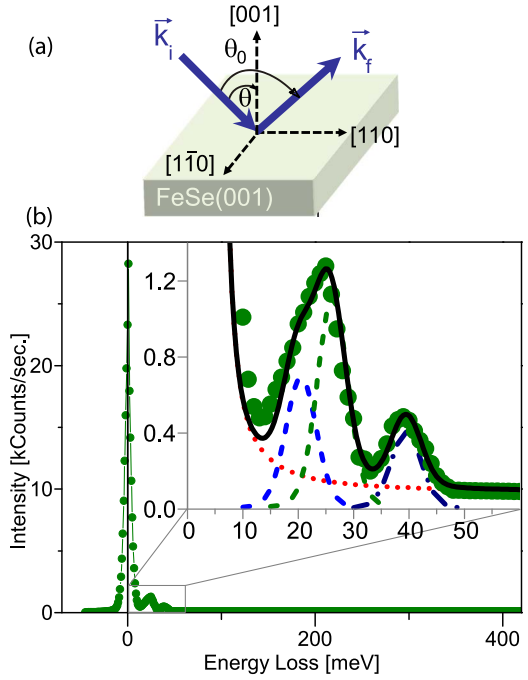

Fig. 1. (a) A schematic representation of the scattering geometry used in our experiments. $\mathbf{k_i}$ and $\mathbf{k_f}$ denote the wave vector of incident and scattered beam, respectively. The scattering plane was parallel to the [110]-direction. θ_0 denotes the total scattering angle and was 80°. The angle of the incident and scattered beam with respect to the surface normal was 40°. (b) High-resolution loss spectrum recorded on the β–FeSe surface at 15 K. The spectrum is recorded with an incident energy of 4.08 eV at the specular geometry. Insets shows a magnified part of the spectrum where different phonon modes are observed.

Fe plane. Since these FeSe planes are weakly bonded by the van der Waals force, the crystal can easily be cleaved along the *c*-axis. The cleaving process leads to a well-ordered β–FeSe(001)–(1 × 1) surface. The structural and chemical characterizations of the surface were performed by means of standard surface science characterization tools such as low-energy electron diffraction and Auger electron spectroscopy.

Our spin-resolved high-resolution electron energy loss spectrometer [24] was utilized to probe the phonon spectrum. The incident electron energy was set on 4.08 eV. The full width at half maximum of the elastic peak was about 6.3 meV. The scattering plane was aligned along the [110]-direction. The scattering geometry is schematically sketched in Fig. 1(a), where $\mathbf{k_i}$ and $\mathbf{k_f}$ denote the wave vector of incident and scattered beam, respectively. This geometry corresponds to the $\bar{\Gamma}$–$\bar{\mathrm{M}}$ direction of the surface Brillouin zone. According to the scattering selection rules, it should be possible to probe all the possible phonon modes which have a polarization along the main crystallographic directions (all modes with polarization along [100]- or [010]-direction shall be observed in the experiment). The total scattering angle was set on $\theta_0 = 80°$. This means that in the specular geometry the angle of the incident and scattered beam with respect to the surface normal was $\theta = 40°$. We used a spin polarized electron beam for these experiments. However, no spin dependency was observed as phonons are spin independent collective excitations. Thus the spectra were recorded in the so-called spin integrated mode. A typical spin integrated spectrum recorded at K and at the specular geometry (with no parallel momentum transfer, $\Delta k_{||} = 0$) is shown in Fig. 1(b). The elastic peak appears at the energy loss of zero and dominates the spectrum. However, beside the elastic peak one can clearly observe the loss features due to the inelastic scattering of electrons with phonons.

At the specular geometry we observe three different phonon modes with the highest phonon energy of about 40 meV. Fitting the spectrum with a set of Voigt functions results in the phonon frequencies. The result of such a fitting procedure is shown in Fig. 1(b) by the black solid line. The fit includes four components (the components are plotted separately in Fig. 1(b)). The dotted curve is the contribution of the elastic peak. The phonon contributions are shown by dashed and dashed-dotted curves in Fig. 1(b). For each phonon mode we assume a Voigt profile. In the Voigt profiles the Gaussian part represents the experimental broadening and was chosen to be the experimental energy resolution and the Lorentzian part is associated with the intrinsic phonon signal. The experimental broadening is the linewidth of the elastic peak at the energy loss of zero. One may first subtract the elastic peak and then fit the remaining spectrum with Voigt profiles. However, such analysis would result in the same values for the phonon frequencies as the influence of the elastically scattered electrons on the inelastic part of the scattering is very small in our experiments.

In phonon spectroscopy using inelastic electron scattering one of the important selection rules is regarding the modes observed at the specular geometry ($\bar{\Gamma}$-point). In fact at this high symmetry point, only the phonon modes which have a polarization perpendicular to the surface are allowed to be excited. Such phonon modes are assigned to the atoms which exhibit an out-of-plane motion. In this geometry a large contribution to the scattering intensity is caused by the so-called dipole scattering mechanism. Generally, while scattering of an electron from a metallic surface, the components of the electric dipole moments normal to the surface are screened by the presence of their image dipoles. As a result the interaction of the electrons is only with the phonon modes that exhibit a finite dipole moment in the direction normal to the surface. It is obvious that this selection rule holds perfectly for metallic surfaces. However if a nonmetallic surface possesses a finite electric permittivity this selection role holds as well. It is important to mention that the dipolar active phonon modes can also be excited using infrared spectroscopy. In this case the coupling of the electric field of the incoming light couples to the electric dipole moment associated with these modes and thereby these modes are excited. Such modes are commonly referred to as infrared active modes and are not usually observed in the Raman experiments.

The possible phonon modes of a crystal can be predicted based on simple symmetry arguments. Fig. 2 shows the possible phonon modes of

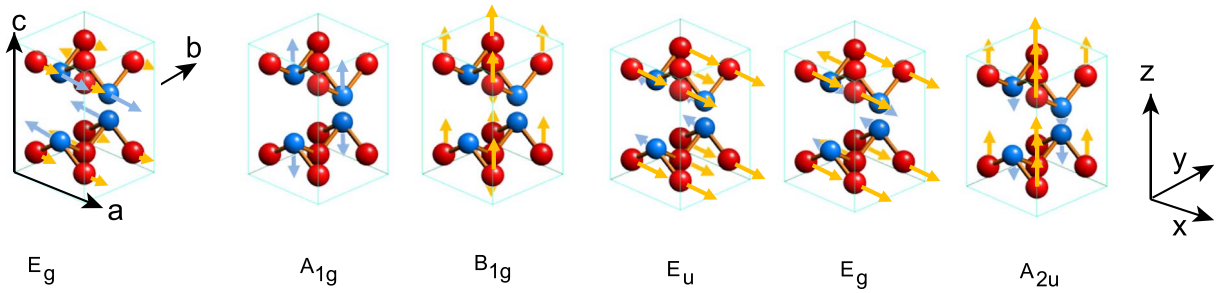

Fig. 2. All possible phonon modes of the β–FeSe with *P4/nmm* symmetry. The Fe atoms are represented by the red colour while the Se atoms are represented by the blue colour. The displacement direction is represented by the small arrows on the Fe and Se sublattices. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)