Extended X-ray Absorption Fine Structure Spectroscopy in Co$_{0.013}$NbSe$_2$

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Abstract. We present a study of the local environment of the Co atom in single crystalline Co$_x$NbSe$_2$, $x=0.013$, via Extended X-ray Absorption Fine Structure (EXAFS) measurements at the Co K-edge (7.7 keV) at various temperatures. Co intercalation quickly suppresses superconductivity and the charge-density wave (CDW) present in pure NbSe$_2$. In order to study the effect of impurities on superconducting and CDW states one has to verify the random distribution of the intercalated atoms in contrast to possible clustering which could lead to additional, e.g. magnetic, interactions in the case of Co intercalation. Our measurements show that the Co atoms are indeed randomly distributed in Co$_{0.013}$NbSe$_2$.

1. Introduction

Recently, detailed resistance measurements in manganites [1] and scanning tunneling microscopy in cuprates [2] indicated that charge density waves (CDW) are at the origin of stripe and checkerboard phases, which are observed in these materials and thought to be linked to exotic behaviors such as colossal magnetoresistance [3] and high temperature superconductivity [4]. It is therefore extremely important to understand the fundamental nature of such phases. However, even in the canonical CDW systems like the dichalcogenides many questions remain. For example, the competition between the coexistent CDW and superconducting phases in 2H-NbSe$_2$, already discovered in 1963 [5], is still poorly understood. Recently, it was shown that TiSe$_2$, too, shows superconductivity when intercalated with Cu atoms [6]. The proposed phase diagram similar to the canonical one of high temperature superconductors [7] (antiferromagnetism replaced by charge-density wave) has again strengthened scientific interest in the dichalcogenides.

We embarked on an investigation of Co$_x$NbSe$_2$ in order to study the effect of impurities to CDW and superconductivity on an atomic scale. Co intercalation quickly suppresses both CDW and superconductivity [8] and, thus, the influence of disorder/impurities on CDW and superconductivity can be studied as a function of $x$ at an atomic scale. In order to ensure the random distribution of the Co atoms in our samples we performed EXAFS experiments on the Co K-edge investigating the local structure around the Co atoms in a radius of a couple of Å.

2. Experiment and Data Analysis

Crystal growth and characterization of our sample are described in Ref. [8].

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Synchrotron measurements were performed at beamline 20-BM-B at the Advanced Photon Source (APS) at Argonne National Laboratory. Si(111) was used as monochromator and data was collected in x-ray fluorescence detection mode. The energy dependence of the x-ray absorption coefficient $\mu(E)$ at the Co K edge was measured detecting the intensity of the Co K$\alpha$ fluorescence line by means of a 13-element Ge solid-state detector. The sample was mounted in a closed-cycle refrigerator allowing us to measure various temperatures, i.e. $T = 15$ K, $50$ K, $180$ K and $300$ K. The $c$-axis was at an angle of $30^\circ$ with respect to the polarization of the incident x-rays. This was included in the ab initio calculations. The measured data were analyzed using the program packages ATHENA (data reduction) and ARTEMIS [10] (fitting EXAFS data using theoretical standards from FEFF [11, 12] with input files generated in ATOMS [13]).

3. Results and Discussion

The XAFS absorption coefficient $\mu(E)$ of Co$_{0.013}$NbSe$_2$ at $T = 50$ K is shown in fig. 1. The sharp rise at $E_0 = 7715$ eV is the Co K absorption edge. Above this energy, electrons are excited from the Co 1s core into the continuum. Oscillations in $\mu(E)$ above the edge are due to interference effects between backscattered and outgoing photoelectron waves and contain informations about the local structure around the Co atom.

In this work we focus on the energy range far above the absorption edge (50-1000 eV). First, a smooth background function representing the absorption of an isolated Co atom $\mu_0(E)$ (dashed curve in fig. 1) is subtracted. Thus, we obtain the extended x-ray absorption fine structure (EXAFS) function $\chi(E) = [\mu(E) - \mu_0(E)]/\Delta \mu_0$, where $\Delta \mu_0$ is the jump in $\mu(E)$ at $E = E_0$. The extracted $\chi(k)$ using ATHENA multiplied by $k^2$ as a weighing function is shown in the inset of fig. 1.

The magnitude and the real part of the Fourier transform of the Co K-edge EXAFS $k^2 \chi(k)$ function, $|\chi(R)|$ and $Re[\chi(R)]$, at $T = 50$ K are shown in fig. 3. The nearest neighbor Se(2) dominates the spectra and scattering from the Se(3) shell and Nb(2) places are visible as peaks in $|\chi(R)|$ just below 4 Å and at 4.5 Å, respectively. The signal from Nb(1) is fairly small and only visible as high energy shoulder in the Se(2) intensity. Note that the observed distances $R$ in the Fourier transform are slightly smaller than that of the real structure due to contributions...
Figure 3. Magnitude (top) and real part (bottom) of the Fourier transform of the Co K-edge EXAFS function $\chi(k)$ at $T = 50\, \text{K}$. Solid black lines are experimental data. Dotted/dashed lines are model calculations including/excluding scattering from the Co(1) atoms shown in fig. 2 done with the ARTEMIS analysis package [10]. The rectangular shaped lines denote the fitting range in R, $1.7\, \text{Å} \leq R \leq 4.7\, \text{Å}$.

Figure 4. Fit parameters $\Delta R$ (top) and $\sigma^2$ (bottom) for the different scattering paths as function of temperature. Results shown here were obtained excluding scattering from Co(1) atoms (red dashed lines for $T = 50\, \text{K}$ in fig. 3).

from scattering phase shifts to the phase of EXAFS. This is taken into account by the modeling. As input we used the structure of NbSe$_2$ as determined in Ref. [14]. Positions of Nb, Se and Co atoms are $(0, 0, \frac{1}{2})$, $(\frac{3}{4}, \frac{3}{4}, \frac{1}{2})$ and $(0, 0, 0)$, respectively (fig. 2).

We performed an ab initio modeling of the absorption cross section using the cluster shown in fig. 2 with $R \leq 4.7\, \text{Å}$. Only single scattering paths were included in the fits. We used the program FEFF for calculating the theoretical backscattering amplitudes and phase shifts and ARTEMIS for fitting. In the fitting process the distances for each group of atoms at a certain distance were refined by $\Delta R$. The EXAFS Debye Waller factors (DWFs) $\sigma^2$ were refined as well. However, we assumed that $\sigma^2$ is similar for atoms at similar distances and thus refined only two different values. Parameters were independently fitted for the measured temperatures as shown in fig. 4. The overall amplitude and energy shift $\Delta E$ were treated as global parameters which are the same for all temperatures.

Calculated and experimental $|\chi(R)|$ and $Re[\chi(R)]$ are shown in fig. 3. We see a very good agreement between the ab initio calculation and experiment if we do not take into account scattering from the Co(1) atoms (red dashed lines), what is indicated by a R-factor$^2$ of less than 1% for all temperatures. The obtained values of $\Delta R$ and $\sigma^2$ are shown in fig. 4 and show on overall normal temperature dependence according to lattice expansion and increased thermal

$^2$ R-factor is a measure of the difference between calculated and measured $\chi(R)$
atomic movements at higher temperatures. The negative value of $\Delta R$ for scattering from Nb(1) is in contrast to the positive ones for the Nb(2) scattering. In case of size effects one would expect the same sign for both. In earlier EXAFS measurements [15] in Ru$_x$NbSe$_2$ it was found that the Nb - Nb distance in the ab plane increases and the Se - Se distance along the c-axis shrinks on intercalation whereas the Nb - Se distance was more or less unchanged. Such a behavior could lead to opposite signs for $\Delta R$ of Nb(1) and Nb(2) scattering in our experiment. However, the absolute values are much bigger in our case despite a far lower concentration of the intercalated atom. Further investigations and in particular comparisons with EXAFS results on the Se edge (planned) are necessary to clarify this issue.

The fact that $\sigma^2_{Se(3)/Nb(2)} > \sigma^2_{Se(2)/Nb(1)}$ is due to the fact that atoms at greater distances are less correlated and their thermal motion is therefore more out of phase than at shorter distances. A second possibility, anisotropic atomic DWFs with dominant components in the ab-plane, is unlikely as x-ray diffraction [14] actually found a 66% enhanced value along the c-axis.

If we include the full scattering from all Co(1) positions a strong additional signal is predicted at around 3.3 Å which is in contrast to experiment (blue dotted lines in fig. 3). We note that this discrepancy cannot be remedied by varying the involved scattering parameter $\sigma^2$ separately for each atomic group. As an upper limit we found that not more than every twentieth Co(1) site is occupied, i.e. Co(0) has not more than 0.3 Co(1) neighbors in average.

4. Conclusion
In conclusion, we performed EXAFS experiments on Co$_{0.013}$NbSe$_2$ at the Co K-edge at various temperatures. An upper limit of 0.3 Co neighbors per Co atom was found and the results could even be well described by ab initio calculations disregarding any contributions from Co - Co scattering. Hence, the intercalation of Co atoms in Co$_x$NbSe$_2$ can be indeed used to study the effect of impurities on the CDW and superconducting states in NbSe$_2$.

The authors thank D. Haskel for helpful discussions and S. Heald and M. Balasubramanian for help with the experimental setup. This research was supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract No. DE-AC02-06CH11357.

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