

Local Structure Instability Across the Martensitic Transition in Nb₃Sn

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Abstract We report x-ray absorption fine structure (XAFS) measurements at the Nb *K*-edge of a Nb₃Sn single crystal, for temperatures across the martensitic structural transition temperature T_m . The Fourier transform amplitude of the peak associated with the second neighbor Nb–Nb and Nb–Sn pairs exhibits hysteresis across the martensitic transition under cooling and heating the sample across the transition. In contrast no such behavior was found for the Nb–Nb nearest neighbor distribution. The observed hysteresis can be attributed to the second neighbor Nb–Nb pairs as only the Debye–Waller factor of these pairs exhibits such a behavior. These results are consistent with a first-order phase transition, which has been previously proposed, and which suggests the possibility of an inhomogeneous ground state similar to other high-temperature superconductors.

Keywords Martensitic transition · Local lattice distortion · First-order phase transition

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1 Introduction

The recent discovery of the high-temperature superconductor family based on Fe compounds [1, 2], resulted in extensive research trying to find similarities between different families of superconductors, which could yield more clues about the nature of high-temperature superconductivity. In this sense the focus on previously studied systems, like A-15 superconductors, has acquired new relevance [3–5] as experimental techniques which have been successfully applied to the study of copper-oxide- and iron-based superconductors can yield new relevant information. The proximity of phases with different structural order in the vicinity of the superconducting transition seems to be one of the common characteristics of the different families of high-temperature superconductors. Although the exact nature of the transition between different phases might differ, e.g. the tetragonal to orthorhombic transition in cuprates, tetragonal to monoclinic transition in iron-based superconductors, and a martensitic cubic-tetragonal transition in A-15 compounds, in all cases such a structural transition is always present in a compound that develops superconductivity or serves as a parent compound to the actual superconducting compound. Another common characteristic of high-temperature superconductors is the presence of two superconducting gaps, originally observed in MgB₂ [6], which now has been demonstrated in cuprates [7], iron compounds [8] and recently also in Nb₃Sn [5]. The presence of multigap superconductivity is naturally explained by two-component superconductivity, which arises from the appearance of an inhomogeneous ground state below some characteristic temperature. In turn the presence of local structural inhomogeneity is a common signature of first-order phase transitions, which lead to hysteresis and metastability [9]. The nature of the martensitic transition

of Nb₃Sn has been the subject of a long term discussion with experimental evidence for a first-order transition [10, 11] and of second-order phase transition [4, 12]. Consequently, we decided to investigate the local atomic structure of Nb₃Sn across the martensitic transition for indications of inhomogeneity or hysteresis, which might give an indication of the order of this structural transition. To this end we performed x-ray absorption fine structure (XAFS) measurements at the Nb *K*-edge of Nb₃Sn, for temperatures across the martensitic structural transition temperature T_m .

In Sect. 2, we present a brief description of the experimental procedure. The results of the analysis of the experimental data are presented in Sect. 3. Finally, in Sect. 4, we present a summary and conclusions.

2 Experimental Procedure

For the x-ray absorption measurements we used an 8 mg. single crystal, whose preparation and diffraction characterization have been described elsewhere [4]. The crystal was attached to a copper cold finger, mounted on an aluminum holder on an open-cycle liquid-helium refrigerator. Measurements of the absorption at the Nb *K*-edge were performed in fluorescence mode at beam line 2–3 at the Stanford Synchrotron Radiation Lightsource, using a Si (220) monochromator, and the temperature was monitored with an accuracy of ~ 1 K. Spectra were taken after cooling the sample from room temperature to 6.5 K during a period of 4 hours. After this, the temperature was increased to 40, 42, 46, and 65 K taking 5 minutes to achieve successive temperature readings and then waiting for 30 minutes at a given temperature before starting a measurement which took 118 minutes. We call this procedure the heating cycle. After this heating cycle the temperature was brought down to 53, 44, and 35 K, using the same time intervals as those taken during the heating cycle. We identify this as the cooling cycle. Similar heating and cooling procedures had been successfully used in x-ray absorption measurements in PrNiO₃ [13] in order to avoid that the system would be quenched in a metastable state as a result of rapid variations of temperature, as it had been previously reported on that system [14]. It is important to note however, that the temperature reported here is that measured at the cold finger of the cryostat and it is possible to have a temperature gradient with an estimated difference of about 3 K. Also if the thermodynamic equilibration time scale of Nb₃Sn is significantly different from that of PrNiO₃ there would be a possibility that the sample would contain domains of a metastable state. Such observation, in any event, would be a signature of a first-order thermodynamical transition.

The Nb *K*-edge was calibrated using Nb metal foil, fixing the first inflexion point as 18990 eV for all spectra, this

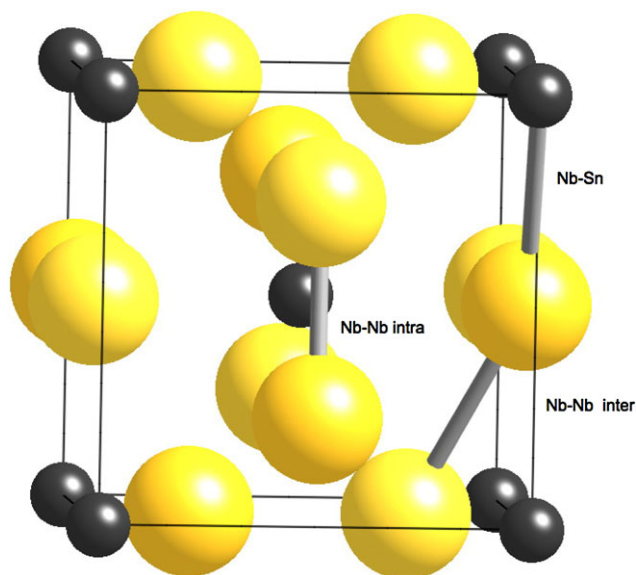


Fig. 1 Nb₃Sn cubic unit cell, indicating the Nb–Nb inter, Nb–Sn and Nb–Nb intra pair average distances

value was also used as the energy reference, E_0 . Spectra were normalized by setting the difference between a first-order polynomial fit to the pre-edge region and a three component fourth-order spline in the post-edge region to one. The XAFS signal was obtained using standard procedures, by minimizing the signal of the magnitude of the Fourier transform below $R = 1 \text{ \AA}$ by varying the parameters of the spline coefficients [15]. Fourier transforms of the spectra were taken over the range $2 \text{ \AA}^{-1} < k < 16 \text{ \AA}^{-1}$ with a k^3 weight using a Gaussian window. In order to extract structural parameters from the spectra these were fitted in k -space using contributions from the Nb–Nb nearest neighbor (subsequently referred to as Nb–Nb intra), Nb–Sn and Nb–Nb second neighbors (subsequently referred to as Nb–Nb inter) in the region $2 \text{ \AA}^{-1} < k < 16 \text{ \AA}^{-1}$. See Fig. 1 for a schematic view of the structure and corresponding labeling of the pairs. Photoelectron backscattering amplitudes and phases were generated with the code feff7 [16], using as a reference structural model the cubic structure of NbSn₃ obtained from neutron diffraction experiments [17]. For the fits to the spectra at different temperatures the number of nearest neighbors, N_i , was fixed to their crystallographic value for each shell. Also an overall scale factor S_0 and energy shift ΔE_0 were fixed to the value obtained in the fit for the spectra at 6.5 K. In this manner only pair distances to the absorbing Nb atoms, R_i , and corresponding Debye–Waller factors, σ_i , were allowed to vary as a function of temperature. A typical comparison between the experimental spectra and the generated fit in real space is shown in Fig. 2.

3 Results and Discussion

In Fig. 3 we plot the height of the peaks of the Fourier transform magnitude of the Nb *K*-edge XAFS associated with the closest neighbors to the Nb absorbing atom. In the case of the peak associated with the closest Nb neighbors (Nb–Nb intra) a very small variation is observed between the measurements during the heating and cooling cycles (Fig. 3a). These changes fall within the variation due to the statistical uncertainty of the analysis and measurements, reflected in the estimated error bars of the peak height. However, the height of the second peak, associated with the Nb–Sn and Nb–Nb inter pairs, shows a variation above the estimated uncertainties (Fig. 3b). In this case, the peak height

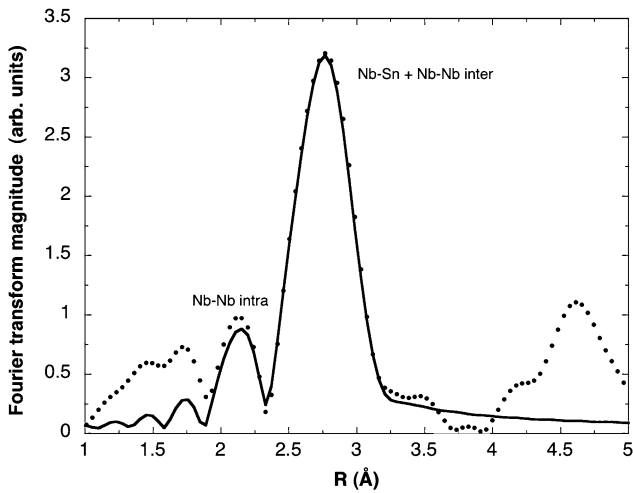
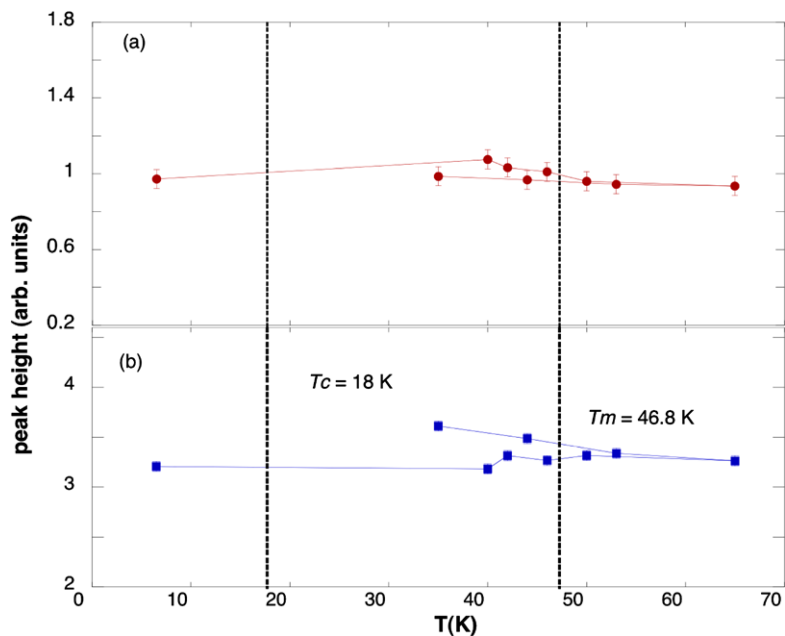


Fig. 2 Magnitude of the Fourier transform of the Nb *K*-edge XAFS, $k^3 \chi(k)$, at $T = 6.5$ K, solid line experiment, dashed line fit

Fig. 3 (a) Height of the maximum of the magnitude of Fourier transform peak associated with Nb–Nb inter pairs as a function of temperature. (b) Height of the maximum of the magnitude of Fourier transform peak associated with Nb–Sn and Nb–Nb intra pairs as a function of temperature



of the Fourier transform magnitude for measurements taken during the cooling cycle has larger values than those presented for the measurements performed during the heating cycle. This difference starts around the martensitic transition temperature, T_m . We note that all temperatures at which the measurements were performed are well below the Debye temperature of the material, ~ 300 K [18]. Hence one should not expect a variation in the Fourier transform magnitude at these low temperature if the system behaved in a harmonic manner.

In order to understand the observed variation in the Fourier transform magnitude peak heights we performed fits as indicated above. In this case variations in the peak height should be reflected in the behavior of the Debye–Waller factor as a function of temperature. In Fig. 4a the extracted value of the Debye–Waller factor, for the Nb–Nb intra pairs is shown. In consistency with the result presented in Fig. 3a, σ_i shows a constant behavior, within the uncertainty in the experiment, in the temperature range studied. The same behavior is observed in σ_i for the Nb–Sn pairs (Fig. 4b). However, σ_i for the Nb–Nb intra pairs takes smaller values during the cooling cycle than the values it has during the heating cycle (Fig. 4c). The observed behavior is consistent with the one exhibited by the Fourier transform magnitude peak height, and clearly shows a hysteretic behavior. We note that the average distances of all pairs included in the fit show no significant variation in the temperature interval studied.

The Debye–Waller factor is associated with the dynamics of the atomic pairs, assuming that the static disorder remains constant [19]. Consequently we can relate our observations to a change in the dynamics of the Nb–Nb intra pairs in the vicinity of the martensitic transition temperature, T_m . This

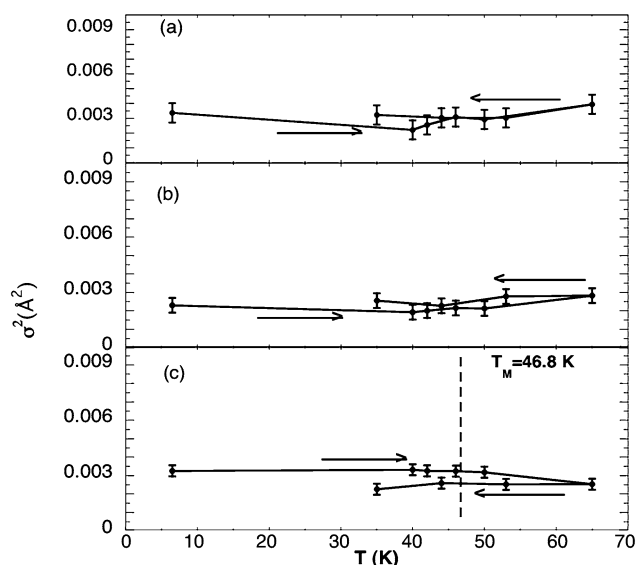


Fig. 4 (a) Debye–Waller factor, s_i , of the Nb–Nb inter pairs as a function of temperature, (b) Debye–Waller factor, s_i , of the Nb–Sn pairs as a function of temperature, (c) Debye–Waller factor, s_i , of the Nb–Nb intra pairs as a function of temperature. Error bars are estimated from the variation of individual spectra with respect to the average, and the uncertainty estimated in the fitting procedure [15]

behavior is consistent with theoretical models that predict the transformation of an anharmonic two-site potential to a shallow single site potential at low temperatures, [18] as a change of the potential will change the dynamics of the pair in question.

The hysteretic behavior of the Nb–Nb intra Debye–Waller factor suggests that the martensitic transition does have a first-order transition character. We note however, that its signature might be subtle as other quantities involved in the martensitic transition such as the pair distances and other Debye–Waller factors do not exhibit hysteretic behavior. Therefore its observation through specific heat experiments might be difficult as this anomalous contribution is expected to be very small compared to that arising from other degrees of freedom which contribute to the specific heat and do not exhibit hysteretic behavior at the martensitic transition.

This result highlights the importance of local structural techniques like XAFS which can focus on specific local vibrational modes that although might have a negligible contribution to macroscopic properties such as specific heat or resistivity, might be crucial to understand the origin of high-temperature superconductivity, e.g., the Cu–O bond stretching mode in cuprates [20, 21].

We note that anomalies in the Debye–Waller factors of Nb_3Ge across the superconducting transition have been previously reported [3]. We expect that similar anomalies characteristic of systems in which there is a strong interaction between charge carriers and the lattice should be present in Nb_3Sn .

4 Conclusions

In summary, we have presented measurements of the Nb *K*-edge extended x-ray absorption fine structure of Nb_3Sn across the martensitic transition. We find an anomalous behavior of the Nb–Nb intra Debye–Waller factor exhibiting hysteresis across the martensitic transition. This result suggests that the martensitic transition has a first-order character, implying that inhomogeneity at the local level should be present, as well as the possibility of metastable phases in similarity with other high-temperature superconductors. The recent report of multigap superconductivity in Nb_3Sn suggests the possibility of two-component superconductivity [22] with implications as anomalous isotope effects, [23] strong sensitivity of T_c to strain and exact stoichiometry as it has been observed in other high-temperature superconductors [24].

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