SIGNATURE OF LOCAL STRUCTURE ANOMALY AT $T_c$ IN THE Nb$_3$Ge SUPERCONDUCTOR

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Received 10 January 2002
Revised 27 March 2002

We report local structure of Nb$_3$Ge intermetallic superconductor by Ge K-edge extended X-ray absorption fine structure (EXAFS) measurements performed in the temperature range of 6–300 K, with an emphasis to determine the local and instantaneous atomic displacements across the superconducting transition temperature $T_c$. We find that the temperature dependent correlated Debye-Waller factor of the Ge-Nb bonds shows a drop at the $T_c$ while cooling the sample, similar to the one observed in the high-$T_c$ cuprate superconductors. The results provide a clear indication of an intimacy between the local atomic displacements and the short coherence superconductivity, and suggests that local electron-lattice interaction should be considered to explain the high-$T_c$ superconductivity in these materials.

Keywords: Superconductivity; A15 superconductors; local structure and high-$T_c$.

1. Introduction

Recent experiments are converging on the importance of lattice excitations in the pairing mechanism to give superconductivity at high temperature.$^{1-3}$ The credit also goes to the studies aimed to reveal information on the local structure$^{4-8}$ since the local structure is expected to play a distinct role in the superconductivity with short coherence length as the case of the high-$T_c$ superconductors.

Recent technical developments in the field of extended X-ray absorption fine structure (EXAFS) have made this an important tool of local and instantaneous displacements in the condensed matter, supported by high brilliance and polarized X-ray synchrotron radiation sources allowing directional information around a
selective site. Indeed, the EXAFS studies have revealed some key information on
the local structure of the high-\(T_c\) materials, including an evidence for a specific local
structural distortion mode of the CuO\(_2\) plane, that seems to be common in these
superconductors.\(^7\)\(^,\)\(^8\) Here we have applied EXAFS to explore local displacements in
the superconducting Nb\(_3\)Ge as a function of temperature.

It should be recalled that until the discovery of high-\(T_c\) superconductivity in
the cuprate perovskites, the superconducting intermetallic compounds with A15
type structure were called high-\(T_c\) superconductors. The highest \(T_c\) was found in
Nb\(_3\)Ge compound belonging to the A15 structural family. These superconductors
were widely studied for their characteristic properties, well reviewed by J. Muller.\(^9\)
The structural aspects of these systems are focussed in the review by Testardi.\(^10\)
There were some efforts to study the local structure of this class of superconductors
by EXAFS measurements.\(^11\)\(^−\)\(^14\) While Brown \textit{et al.}\(^11\) used Ge K-edge EXAFS to
classify thin films of Nb\(_3\)Ge made by two different techniques, Claeson \textit{et al.}\(^12\)
made an effort to study the local structure at high temperature. Later Cargill
\textit{et al.}\(^13\) focussed on the lattice dynamics and studied polycrystalline samples of
Nb\(_3\)Ge by Nb K-edge EXAFS and revealed large anisotropic vibrational correlations
related to the one-dimensional Nb-Nb chains in the structure, which were much
larger in the Nb\(_3\)Ge system than others A15 structures (Nb\(_3\)Al, V\(_3\)Si and Cr\(_3\)Si).
More recently, Boyce \textit{et al.}\(^14\) used Sn K-edge an Sb K-edge EXAFS to study local
structure of the Nb\(_3\)Sn and Nb\(_3\)Sb systems respectively and found that the Debye–
Waller factors of the Sn-Nb and Sn-Nb follow the similar temperature dependence
without any anomaly, however, with slightly different Einstein temperatures. In
this work, we report evolution of the local structure of the Nb\(_3\)Ge in a temperature
range of 6–300 K by high \(k\)-resolution fluorescence EXAFS, focussing in the region
of superconducting transition temperature to explore possible local displacements.
The Ge K-edge EXAFS reveals signature of a clear change in the correlated Debye–
Waller factor of the Ge-Nb bonds at the superconducting transition temperature
\(T_c\), similar to the case of high-\(T_c\) cuprate superconductors. The anomaly in the local
structure at \(T_c\), suggests that the local displacements have an intimate relationship
with the superconductivity at high temperature.

2. Experimental

Well-characterized thin films of Nb\(_3\)Ge superconductor, grown by the chemical
vapour deposition (CVD) were used for the measurements. The film shows sharp
superconducting transition below 20.6 K. Temperature dependent Ge K-edge
absorption measurements were performed at the beamline BL13B of Photon Factory
at High Energy Accelerator Research Organization in Tsukuba. The synchrotron
radiation emitted by a 27-pole wiggler source (maximum field \(B_0\) of 1.5 T) inserted
in the 2.5 GeV storage ring with a maximum stored current of 360–250 mA was
monochromatized by a variable exit beam height double crystal Si(111) monochro-
mator and sagittally focused on the sample. Improved lattice of the storage ring
and better monochromator cooling system allowed to get a very stable beam on the sample. The spectra were recorded by detecting the fluorescence yield (FY) using a 19-element Ge X-ray detector array, covering a large solid angle of the X-ray fluorescence emission. The emphasis was given to measure the spectra with a high signal to noise ratio, up to a high momentum transfer, and for the purpose we have measured several scans, with each scan averaged over 19 channels. The oriented crystal was mounted on a Huber 420 goniometer. The sample temperature was controlled and monitored within an accuracy of ±1 K. A standard procedure was used to extract the EXAFS signal from the absorption spectrum and corrected for the X-ray fluorescence self-absorption before the analysis.

3. Results and Discussion

The Fourier transforms (FT) of the Ge K-edge EXAFS spectra (multiplied by $k^2$) recorded on a thin film of the Nb$_3$Ge at some representative temperatures are shown in Fig. 1. The Fourier transforms are performed between $k = 3 - 18$ Å$^{-1}$ and not corrected for the phase shifts (representing the raw experimental data). An EXAFS spectrum is shown as an inset to the Fig. 1, showing oscillations up to $k = 18$ Å$^{-1}$. The FT represents the global atomic distribution of nearest neighbors around the absorbing Ge atom in the system. The main peak is denoted by Ge-Nb, representing the scattering of the ejected photoelectron at the Ge site with the nearest Nb atoms. The peak does not represent the real atomic distances and the position should be corrected for the photoelectron back-scattering phase shifts to find the quantitative value to the atomic positions with respect to the central Ge.

Fig. 1. Fourier transform of the EXAFS spectra (multiplied by $k^2$) recorded on the Nb$_3$Ge superconductor at several temperatures. The Fourier transforms have been performed between $k = 3-18$ Å$^{-1}$ using a Gaussian window and not corrected for the phase shifts. The inset shows EXAFS oscillations at a representative temperature.
We have used the “standard procedure” for the analysis of EXAFS data for the Ge-Nb shell. We made an attempt to model the EXAFS by a single Ge-Nb distance following direction studies, however, unsatisfactory fit to the experimental data suggests another coexisting Ge-Nb distance. In fact a smaller Ge-Nb distance of \(2.66 \text{ Å}\) was indicated to coexists with the crystallographic distance of \(2.87 \text{ Å}\). Therefore, we used a starting model with two Ge-Nb distances, where the effective Debye–Waller factor (DWF) includes all distortion effects, taking into account both static and dynamic distortions. The EXAFS spectra due to the Ge-Nb were simulated by a standard least square approach using curved wave theory. The starting parameters were taken from the direction studies on the system. The number of parameters which may be determined by EXAFS is limited by the number of independent data points: 

\[
N_{\text{ind}} \sim (2\Delta k\Delta R)/\pi,
\]

where \(\Delta k\) and \(\Delta R\) are respectively the ranges in \(k\) and \(R\) space over which the data are analyzed. In our case \(\Delta k = 15 \text{ Å}^{-1}\) and \(\Delta R = 2 \text{ Å}\) give \(N_{\text{ind}} \sim 20\) for the EXAFS of due to the Ge-Nb. In the present analysis, we have allowed to vary the two Ge-Nb bond lengths and their Debye–Waller factors as a function of temperature. While the shorter Ge-Nb distance \((\sim 2.66\text{ Å})\) shows a small but gradual increase with decreasing temperature, the longer bond length remains temperature independent \(\sim 2.88 \pm 0.005\text{ Å}\), in the temperature range studied here, and hence this was fixed in the final iteration. Also, the relative probability of the two Ge-Nb bonds \(32:68\) was found to be temperature independent within the experimental uncertainties, and hence kept fixed for the final analysis.

Temperature dependence of the Debye–Waller factors of the Ge-Nb pairs, \(\sigma_{\text{Nb1}}^2\) and \(\sigma_{\text{Nb2}}^2\), that takes into account both static and dynamic displacements around the Ge atoms, determined from the above analysis, are shown in Fig. 2. The \(\sigma_{\text{Nb1}}^2\) and \(\sigma_{\text{Nb2}}^2\) measures the correlated displacements between Ge and Nb, and not the same as the DWF determined in direction experiments where they account for the mean-square deviation of a given atom from its average site in the crystal. The DWF follows smooth behavior for both Ge-Nb bonds as a function of temperature, at least down to \(\sim 50\text{ K}\). Below this temperature there seems some divergence from this smooth behavior. The temperature dependence of the DWF for the two bonds could be fitted with an Einstein model of harmonic oscillator with Einstein temperatures \(\theta_E = 230^\circ\text{C}\) and \(\theta_E = 210^\circ\text{C}\) respectively for the \(\sigma_{\text{Nb1}}^2\) and \(\sigma_{\text{Nb2}}^2\) with constant values \(0.003\) and \(0.0015\) respectively for the zero-point energies. While the value of \(\theta_E = 230^\circ\text{C}\) for the \(\sigma_{\text{Nb1}}^2\) is consistent with the earlier reports,\cite{12,13} we find distinct \(\theta_E = 210^\circ\text{C}\) for the \(\sigma_{\text{Nb2}}^2\). This difference may be due to the fact that the earlier studies used a single shell fit for the Ge-Nb shell.

What appears clear from the present data is that the divergence from the normal behavior of the DWFs with anomalies in the local structure of the system. There seems an anomalous drop at the superconducting transition temperature \(T_c\) that appears similar to the one observed in the high-\(T_c\) cuprate superconductors by Cu K-edge EXAFS.\cite{7,18} The drop is much clear in the \(\sigma_{\text{Nb2}}^2\). Incidentally, similar drop was observed in the cuprate superconductors by ion channeling experiments.\cite{4}
Fig. 2. Temperature dependence of the correlated Debye–Waller factors (symbols) of the Ge-Nb pairs, $\sigma^2_{\text{Nb1}}$ (upper) and $\sigma^2_{\text{Nb2}}$ (lower). The expected temperature dependence of the Debye–Waller factors for a fully correlated motion of Ge and Nb, calculated by Einstein model, are shown by the dotted lines. The $\sigma^2_{\text{Nb1}}$ and $\sigma^2_{\text{Nb2}}$ are well described by the Einstein model with $\theta_E = 230$ K and 210 K respectively above $\sim 50$ K (see text).

Fig. 3. Superconducting transition temperature has been plotted as a function of the drop in the Debye–Waller factors ($\Delta \sigma^2$) at the $T_c$ for the cuprates, and compared with the drop for the Nb$_3$Ge.
Interesting enough, the drop in the cuprates was found to depend on the critical temperature $T_c$, being larger while the $T_c$ higher. Figure 3 shows the relationship between the superconducting transition temperature and the value of the drop in the DWF ($\Delta \sigma^2$) at the $T_c$ for the cuprates, plotted with the drop in the DWF for the Nb$_3$Ge. While DWF for the Cu-O bonds are used, being the main electronic component, the DWF for the Ge-Nb is given considering the fact that the orthogonal Nb chains are the important structural elements for the electronic structure of the Nb$_3$Ge system. Interesting enough, the figure indicates that the two parameters, the $T_c$ and $\Delta \sigma^2$ have proportionality kind of behavior. This result suggests an intimate relationship between the local lattice fluctuations and superconductivity in the short coherence superconductors having high transition temperature. At this stage it is rather hard to predict on the precise role of the local lattice displacements, however, it appears that these displacements control the fundamental electronic band structure near the singularity point (M point in the cuprates and Γ point in the A15 intermetallics).

In summary, we have used Ge K-edge EXAFS spectroscopy to explore local lattice displacements in the Nb$_3$Ge superconducting system. The temperature dependent local and instantaneous atomic displacements across the superconducting transition temperature, determined by the correlated Debye–Waller factor of the Ge-Nb bonds ($\sigma^2_{Nb}$), indicate a small but clear divergence from their normal temperature dependence. This change, appearing as a drop in the $\sigma^2_{Nb}$ at the superconducting transition temperature $T_c$, is similar to the one found for the Debye–Waller factor of the Cu-O bonds, $\sigma^2_{CuO}$ in the high-$T_c$ cuprate superconductors. The comparison of the drop at $T_c$ in the Nb$_3$Ge intermetallic with the one observed in the cuprate superconductors reveals that the local displacements are tied to the superconductivity of the materials with small coherence length. Also, we find a second distance, shorter by $\sim 0.2$ Å from the average one, that seems to be related with the phase without any long-range crystallographic symmetry. In conclusion, the results suggest that local displacements are the key to the high-$T_c$ superconductivity and in our opinion, one needs to focus on short-range correlation of electron-lattice interactions in the short coherence superconductors as doped cuprates and the A15 compound to explain their superconductivity.

**Acknowledgments**

The authors thank the PF staff for their cooperation during the experiments. This work is supported by “Istituto Nazionale di Fisica della Materia” (INFM), by cofinanziamento MURST under the project “Leghe e composti intermetallici: stabilità termodinamica, proprietà fisiche e reattività” and by “Progetto 5% Superconduttività” of Consiglio Nazionale delle Ricerche (CNR).

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