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# A study of the Nb<sub>3</sub>Ge system by Ge K-edge extended x-ray absorption fine structure and x-ray absorption near-edge structure spectroscopy

N L Saini<sup>1</sup>, M Filippi<sup>1</sup>, Ziyu Wu<sup>1,2</sup>, H Oyanagi<sup>3</sup>, H Ihara<sup>3,5</sup>, A Iyo<sup>3</sup>,  
S Agrestini<sup>4</sup> and A Bianconi<sup>4</sup>

<sup>1</sup> Unità INFN, Università di Roma 'La Sapienza', P. le Aldo Moro 2, 00185 Roma, Italy

<sup>2</sup> Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, PO Box 918, Beijing 100039, People's Republic of China

<sup>3</sup> National Institute of Advanced Industrial Science and Technology, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

<sup>4</sup> Unità INFN and Dipartimento di Fisica, Università di Roma 'La Sapienza', P. le Aldo Moro 2, 00185 Roma, Italy

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## Abstract

The local structure of Nb<sub>3</sub>Ge intermetallic superconductor has been studied by Ge K-edge absorption spectroscopy. Extended x-ray absorption fine structure (EXAFS) experiments show two Ge–Nb distances. In addition to the crystallographic distance of  $\sim 2.87$  Å, there exists a second Ge–Nb distance, shorter than the first by  $\sim 0.2$  Å, assigned to a phase with short-range symmetry related to local displacements in the Nb–Nb chains. The x-ray absorption near-edge structure (XANES) spectrum has been simulated by full multiple-scattering calculations considering the local displacements determined by the EXAFS analysis. The XANES spectrum has been well reproduced by considering a cluster of 99 atoms within a radius of about 7 Å from the central Ge atom and introducing determined local displacements.

## 1. Introduction

Until the discovery of high  $T_c$  superconductivity in the cuprate perovskites, the superconducting intermetallic compounds were regarded as high  $T_c$  superconductors, with the highest  $T_c$  in Nb<sub>3</sub>Ge compound having A15 structure [1]. Experimental studies on the A15 superconductors revealed a variety of properties related to the interplay between electron–phonon interactions and superconductivity and their variability with structural parameters [2]. The lattice instability of the A15 structures has been shown by considering structural anomalies as a function of temperature and lattice strain. Indeed the superconducting properties of these materials are

<sup>5</sup> This work is dedicated to the late Dr H Ihara.

found to be strongly dependent on the lattice strain and instability and it had been argued that the higher  $T_c$  in these compounds could be obtained by driving them near lattice instability [2].

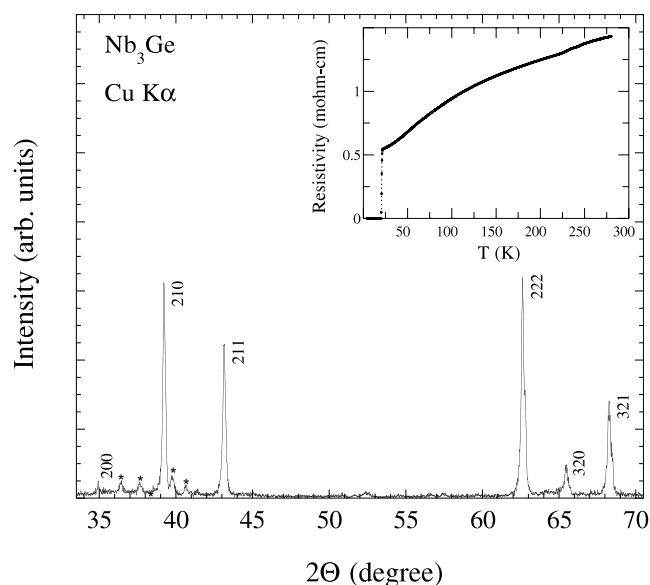
It should be recalled that the superconducting correlation in the A15 compounds appear with a short coherence length of  $\sim 10\text{--}30$  Å, the same order of magnitude as for the high  $T_c$  cuprate perovskites. Therefore local atomic displacements are expected to play an important role in the superconducting and normal state electronic behaviour of these A15 compounds, as evidenced by several experiments for cuprate superconductors [3–6]. Indeed, one of the theoretical approaches based on local electron–phonon interaction was used to discuss high  $T_c$  in A15 superconductors, resulting in an effective double-well potential and anharmonic phonon modes [7].

Being a fast ( $\sim 10^{-15}$ ) and local (5–10 Å) experimental probe, x-ray absorption spectroscopy has been found to be a suitable tool for investigating the short/medium-range instantaneous structure of materials with such local electron–lattice correlation [8]. While the extended x-ray absorption fine structure (EXAFS) technique provides the atomic pair correlation function, x-ray absorption near-edge structure (XANES) probes the higher-order atomic pair correlation function within the cluster of atoms. However, not many studies have addressed the local structure of the A15 compounds. The local structure of these compounds has been studied by ion channelling [9] and EXAFS measurements [10–13]. Brown *et al* [10] used Ge K-edge EXAFS to characterize thin films of Nb<sub>3</sub>Ge made by two different techniques and Claeson *et al* [11] made an effort to study the local structure at high temperature. Later Cargill *et al* [12] focussed on the lattice dynamics and studied polycrystalline samples of Nb<sub>3</sub>Ge by Nb K-edge EXAFS and revealed large anisotropic vibrational correlations related to the one-dimensional Nb–Nb chains in the structure, much larger in the Nb<sub>3</sub>Ge system than other A15 structures (Nb<sub>3</sub>Al, V<sub>3</sub>Si and Cr<sub>3</sub>Si). More recently, Boyce *et al* [13] used Sn K-edge and Sb K-edge EXAFS to study local structure of the Nb<sub>3</sub>Sn and Nb<sub>3</sub>Sb systems respectively. It was also found that the Debye–Waller factors (DWFs) of the Sn–Nb and Sb–Nb follow a similar temperature dependence without any anomaly, however with a slightly different Einstein temperature. Moreover, it is clear from the above studies that the local structure of the A15 compound is quite different from the one obtained by diffraction experiments.

In this study, we have looked again at the local structure of the Nb<sub>3</sub>Ge compound, the highest  $T_c$  A15 intermetallic superconductor, by temperature-dependent Ge K-edge EXAFS. By exploiting advances in the EXAFS technique with a new experimental approach applied to a number of high-quality thin films of the Nb<sub>3</sub>Ge compound, we have been able to determine temperature-dependent lattice displacements in the vicinity of the superconducting transition temperature showing a similarity with the cuprates [14]. We focus on the local structure of the system by combined analysis of the EXAFS and XANES results. We report high-resolution Ge K-edge EXAFS and XANES measurements on the Nb<sub>3</sub>Ge system ( $T_c = 20.6$  K) to obtain direct information on the local structural displacements. Unlike the diffraction studies, the EXAFS results show two local Ge–Nb distances ( $\sim 2.88$  and  $2.66$  Å). The *ab initio* multiple-scattering theory has been exploited to simulate different features in the Ge K-edge XANES spectrum resulting in consistency with structural displacements determined by the EXAFS.

## 2. Experimental methods

The film of Nb<sub>3</sub>Ge used for the measurements was grown by the chemical vapour deposition (CVD) technique and characterized by its structural and transport properties. Figure 1 shows x-ray diffraction (XRD) pattern of the film along with the temperature-dependent resistivity behaviour revealing a sharp superconducting transition at 20.6 K (inset). The main diffraction lines were well indexed by the A15 structure (space group  $Pm\bar{3}n$ ). The lattice parameters



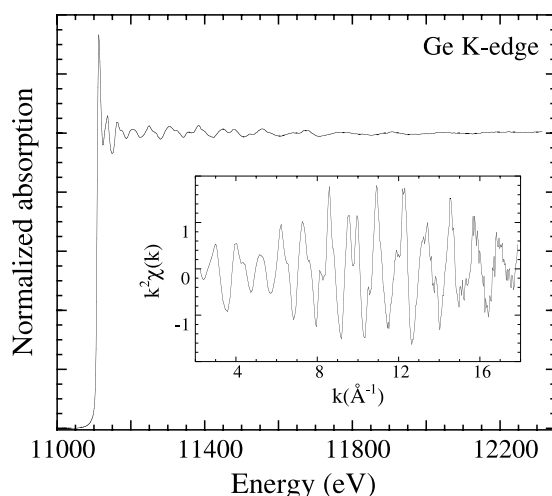
**Figure 1.** XRD pattern of the Nb<sub>3</sub>Ge thin film recorded at 300 K. The main peaks correspond to a cubic structure with space group *Pm3n*. There are some extra weak peaks (marked with \*) due to small impurity of tetragonal phase Nb<sub>5</sub>Ge<sub>3</sub>, estimated to be ~4%. The inset shows resistivity of the Nb<sub>3</sub>Ge film as a function of temperature showing a sharp superconducting transition at a temperature of 20.6 K.

were determined to be  $5.1398(\pm 0.0007)$  Å by refinement of the XRD pattern, consistent with earlier reports [15]. There are also traces of minority phase (estimated to be ~4%) of Nb<sub>5</sub>Ge<sub>3</sub> having tetragonal structure [16].

Temperature-dependent Ge K-edge absorption measurements were performed at the beamline BL13B of the Photon Factory at the 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 250–360 mA was monochromatized by a variable-height exit beam, double-crystal Si(111) monochromator and sagittally focused on the sample. Improvements to the storage ring lattice and a better monochromator cooling system achieved 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 [17]. The emphasis was to measure the spectra with a high signal-to-noise ratio, up to a high momentum transfer. For this purpose we measured several scans, with each scan averaged over 19 channels (see e.g. figure 2). A standard procedure was used to extract the EXAFS signal from the absorption spectrum [8] which was corrected for the x-ray fluorescence self-absorption before the analysis [18].

### 3. Calculation details

The calculations for the Ge K-edge XANES were carried out using one-electron, full multiple-scattering theory [19–21]. We have used the Mattheiss prescription [22] to construct the cluster electronic density and the Coulomb part of the potential (by superposition of neutral atomic charge densities obtained from the Clementi–Roetti tables [23]) and the screened  $Z + 1$  approximation (final state rule) [24] for simulating the charge relaxation around the core hole.



**Figure 2.** Normalized Ge K-edge x-ray absorption spectrum measured in fluorescence mode on a thin film sample of the  $\text{Nb}_3\text{Ge}$  at 12 K. The inset is the EXAFS spectrum multiplied by  $k^2$ .

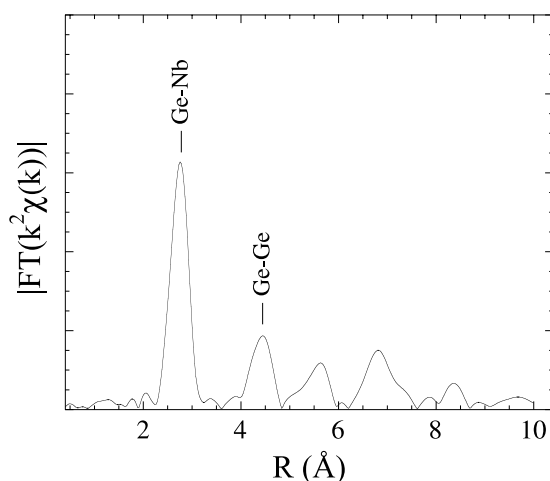
The energy-dependent complex Hedin–Lundqvist exchange potentials were used, followed by a Lorentzian convolution ( $\sim 3.5$  eV, consistent with core hole life time and experimental resolution) to account for the inelastic losses of the photoelectron in the final state and the core hole width. We chose the muffin-tin radii allowing a 10% overlap between the contiguous spheres to simulate the atomic bonds [25].

#### 4. Results and discussion

Figure 2 shows the Ge K-edge x-ray absorption spectrum measured at 12 K using fluorescence mode on a thin film sample of the  $\text{Nb}_3\text{Ge}$ . The EXAFS spectrum is shown as an inset, displaying oscillations up to  $k = 18 \text{ \AA}^{-1}$  with high signal to noise ratio. The spectrum is multiplied by  $k^2$  to enhance the EXAFS modulations at the high  $k$  region. The Fourier transform of the  $k^2$  multiplied EXAFS spectrum is shown in figure 3. The Fourier transform is performed for  $k = 3\text{--}18 \text{ \AA}^{-1}$  and not corrected for the phase shifts.

The Fourier transform represents the global atomic distribution of the nearest neighbours around the absorbing Ge atom in the  $\text{Nb}_3\text{Ge}$  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 peaks do not appear at the real atomic distances and the position should be corrected for the photoelectron back-scattering phase shifts to find the quantitative value of the atomic positions with respect to the central Ge.

The EXAFS spectrum due to the Ge–Nb was simulated by a standard least squares approach using curved wave theory [8]. The starting parameters were taken from the diffraction studies on the system. We attempted to model the EXAFS following diffraction studies, considering a single distance for the coordination shell, where the effective DWF includes all distortion effects, both static and dynamic. However, we could not obtain a satisfactory fit using either a Gaussian or non-Gaussian approach. In addition, a large Ge–Nb distance broadening suggested another coexisting Ge–Nb distance. The results indicated a distance of  $\sim 2.66 \text{ \AA}$ , compared to the crystallographic distance of  $\sim 2.87 \text{ \AA}$ , shown by an earlier EXAFS study [10]. This led us to use a starting model with two Ge–Nb distances, improving the fit index by  $\sim 40\%$  with respect to the model with one Ge–Nb distance.

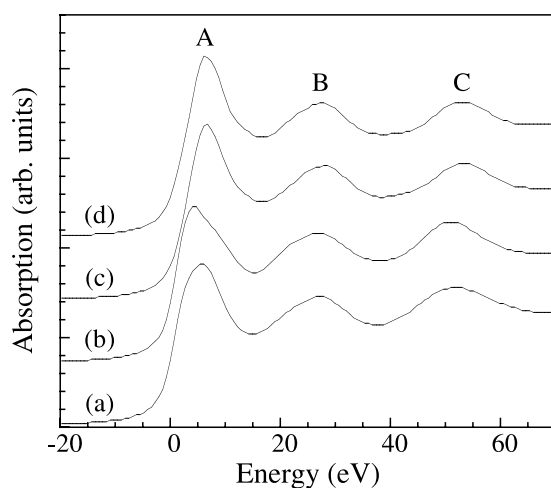


**Figure 3.** Fourier transform of the EXAFS spectrum shown in figure 1. The Fourier transform has been performed for  $k = 3\text{--}18 \text{ \AA}^{-1}$  using a Gaussian window and not corrected for the phase shifts.

The number of parameters which may be determined by EXAFS is limited by the number of independent data points,  $N_{ind} \sim (2\Delta k \Delta R)/\pi$ , where  $\Delta k$  and  $\Delta R$  are the respective ranges in the  $k$  and  $R$  spaces over which the data are analysed. In our case,  $\Delta k = 15 \text{ \AA}^{-1}$  and  $\Delta R = 2 \text{ \AA}$  give  $N_{ind} \sim 20$  for the EXAFS due to the Ge–Nb [8]. In the present analysis, we have allowed variation of the two Ge–Nb bond lengths and the distance broadening, determined by the correlated DWFs. The two distances at 12 K were determined to be  $\sim 2.66 \pm 0.01$  and  $2.880 \pm 0.005 \text{ \AA}$ , with the probability of  $0.33 \pm 0.03$  and  $0.67 \pm 0.03$  respectively. The correlated DWFs for the two distances were found to be  $0.0045 \pm 0.00032 \text{ \AA}^2$  and  $0.0032 \pm 0.00027 \text{ \AA}^2$  respectively. As a matter of fact the relative probability remains temperature independent [14] within the experimental uncertainties.

While the longer Ge–Nb distance is similar to the one found in the diffraction experiments, the shorter distance was seen only in the local structure [10]. The present results are therefore consistent with the earlier EXAFS work where two Ge–Nb distances were found. We have measured several samples where the diffraction studies have shown only one distance while EXAFS measured two Nb positions. The shorter distance appears to be due to the presence of a phase with short-range order, characterized by the distortion of the Nb–Nb chains, in which two Nb in a chain are getting closer while the other two in the orthogonal Nb–Nb chain are getting further apart. Indeed this distortion has been found to exist in Nb<sub>3</sub>Sn, appearing below a temperature tens of kelvin above the  $T_c$  and assigned to a martensitic-like transition [26, 27]. We believe that the presence of the Ge–Nb distance in Nb<sub>3</sub>Ge is related to the coexisting phase with short-range order due to local displacements in the Nb–Nb chains. Since XRD does not show any evidence of such coexistence, it seems that  $\sim 2/3$  of the Ge–Nb bonds are ordered while  $\sim 1/3$  may be disordered.

Let us now discuss the XANES spectrum of the Nb<sub>3</sub>Ge system. The XANES technique is very sensitive to small local displacements being a probe of a higher-order pair correlation function and hence expected to add useful information on the local structure of the target compound. We have used multiple-scattering calculations to reproduce the experimental features in the Ge K-edge XANES spectrum. Here we recall that the Nb<sub>3</sub>Ge system has a body-centred cubic structure, with lattice constant  $\sim 5.14 \text{ \AA}$ , having the space group  $Pm\bar{3}n$ . The Ge atoms form a body-centred cubic sub shell with Ge atoms sited at the edges and at



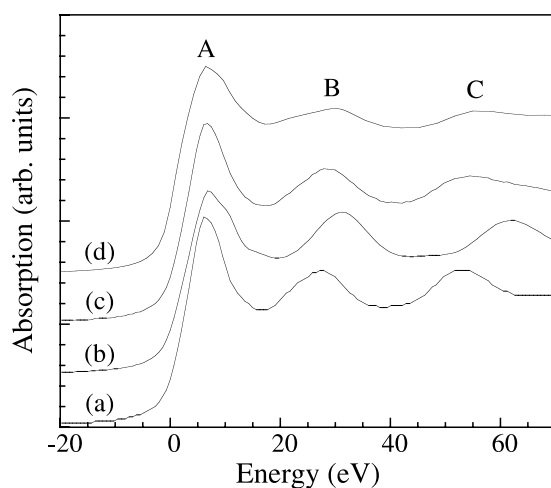
**Figure 4.** Multiple-scattering calculations for the Ge K-edge XANES with increasing cluster size. The spectra for 13-atom (a), 33-atom (b), 63-atom (c) and 99-atom (d) clusters are shown. The main transition features are denoted by A, B and C (see text).

the centre of the cube, while Nb atoms form three orthogonal chains sited on the faces of the cube [1, 2].

Figure 4 shows Ge K-edge XANES spectra, calculated using full multiple scattering with a relaxed final-state potential for clusters of increasing size up to the convergence (13, 33, 63 and 99 atoms, respectively). The cluster of 99 atoms contains all atoms within a radius of  $\sim 7$  Å from the central Ge. The calculated spectrum for a minimum size of the cluster (central Ge atom surrounded by 12 neighbouring Nb atoms at a distance  $\sim 2.88$  Å) shows three transition peaks (denoted by A, B and C). When the cluster size is increased (central Ge, 12 Nb atoms, 8 Ge atoms, 12 Nb with a total of 33 atoms) the spectrum shows small change, in particular around the white line feature A.

When the cluster size is further increased (about five shells including 66 atoms around the central Ge), the spectrum looks quite similar to the experimental one. We have calculated a spectrum for a larger cluster (about six shells including 99 atoms around the central Ge) which is similar to that for the 66-atom cluster, indicating that the cluster size has reached convergence. The cluster dependence of the calculated XANES spectrum (figure 4) suggests that the main features are mostly contributed by the first shell. Therefore, following the EXAFS results, we have calculated the Ge K-edge XANES spectrum for a cluster with a  $\text{Nb}_3\text{Ge}$  structure containing the shorter Ge–Nb distance (i.e. 2.66 Å). Figure 5 shows the two calculated spectra using different  $\text{Nb}_3\text{Ge}$  structural parameters (the longer Ge–Nb distance of 2.88 Å (a) and the shorter Ge–Nb distance of 2.66 Å (b)) for the 99-atom cluster. The linear combination of the two spectra with probabilities, determined by the EXAFS analysis (0.67 times the spectrum (a) and 0.33 times the spectrum (b)) is also plotted (curve (c)) along with the experimental XANES spectrum (curve (d)) in figure 5. The agreement between the calculated spectrum and the experimental spectrum is very good and consistent with the EXAFS findings.

In summary, we have studied the local structure of the  $\text{Nb}_3\text{Ge}$  intermetallic superconductor by Ge K-edge EXAFS and XANES measurements. A combined analysis of EXAFS and XANES allowed us to determine the quantitative local structure of the target system. The EXAFS shows two coexisting phases at the local scale, one characterized by a Ge–Nb distance of  $\sim 2.88$  Å close to that determined by diffraction and the other characterized by a Ge–Nb



**Figure 5.** Multiple-scattering calculations for different Nb<sub>3</sub>Ge structures: (a) with a Ge–Nb distance of 2.88 Å, a distance close to that measured by diffraction; (b) with shorter Ge–Nb distance of 2.66 Å and (c) linear combination of the two spectra with probabilities of 0.67 and 0.33 respectively, compared with the experimental spectrum (d).

distance of  $\sim 2.66$  Å related to a phase with short-range order. The XANES spectrum has been modelled by full multiple-scattering calculations considering the two coexisting phases determined by the EXAFS analysis. The XANES results are found to be consistent with the EXAFS findings, confirming the presence of a phase without any long-range crystallographic symmetry due to local displacements in the Nb–Nb chains, coexisting with the normal crystallographic structure.

### Acknowledgments

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