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OF THE GeK EDGE

Effect of Intermediate Range Order on the Lineshape of the Ge K Edge

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1 Introduction

EXAFS investigations on a-Ge [1-3] deposited at different temperatures pointed to the nucleation of ordered grains in the amorphous matrix, whose size increases with temperature. This process was revealed by important modifications of the EXAFS spectrum, $\chi(k)$, and consequently of its Fourier transform. Besides these modifications in the EXAFS part of the spectrum, significant changes in the shape of the near edge structure (XANES) occur which should be correlated to the structural evolution of the system. It is the purpose of this paper to show that this is indeed the case and that a careful analysis of the near edge structure (associated with a calculation of the absorption cross section) can elucidate the relation between fluctuations of bond distances and edge shape.

2 Experimental

The samples were obtained by thermal evaporation onto Si(111) crystal substrates. The evaporation temperature, T_S, was varied in the range 130-350°C. The smoothness of the Ge films and the absence of macroscopic inhomogeneities were checked by a Scanning Electron Microscope. The optical thickness of the films ranged from $\mu x = 0.4$ to $\mu x = 0.7$. The crystalline sample was a Ge single crystal polished down to an optical thickness of $\mu x = 1.8$. The X ray spectra at the Ge K edge were taken at the Synchrotron Radiation Facility in Frascati, at LN temperature. The radiation was monochromatized by a Si(220) crystal, and the resolution was $\Delta E \sim 2$ eV. After background removal, the near edge spectra were normalized to the absorption far above the edge in order to eliminate their thickness dependence.

3 Results and discussion

In Fig.1 we report the experimental Ge K edges of several samples, normalized as described above, as well as their first derivatives. The main feature common to all spectra is the strong "white line" peak labelled A, due to the high density of empty p-like states. At $\Delta E \sim 15$ eV from the main peak a second structure B is present which exhibits significant variations as a function of deposition temperature: it is barely visible for the sample grown at T = 130°C, while it shows up more and more clearly at increasing temperature. In crystalline Ge peak B is well defined and prominent. The largest variation of this structure occurs in the temperature range 200 - 240 °C, where the system undergoes the amorphous-to-crystal transition [1].

The question arises, then, about what is the correlation between the local order and this peak. One could argue that other processes (not structural in nature) could be at the origin of this structure. For in-
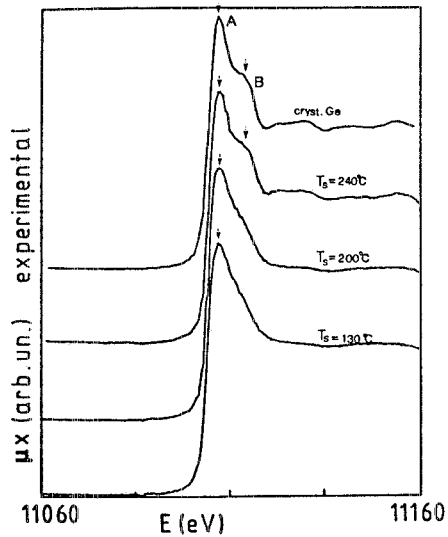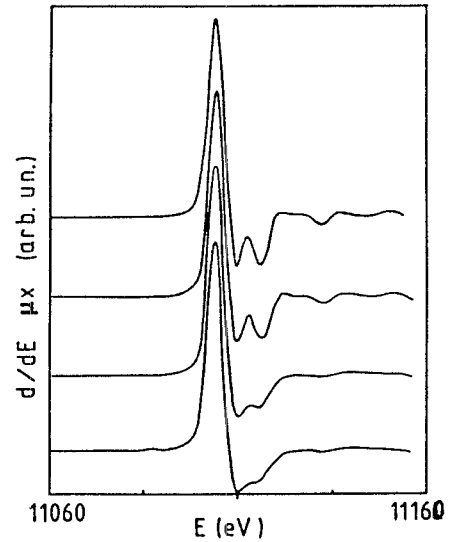
Fig.1 (a)

Fig.1 (b)
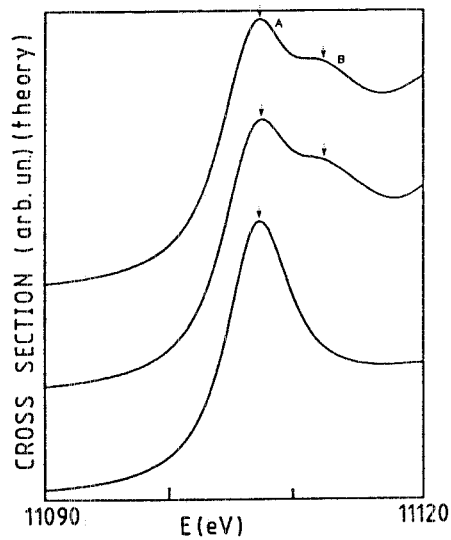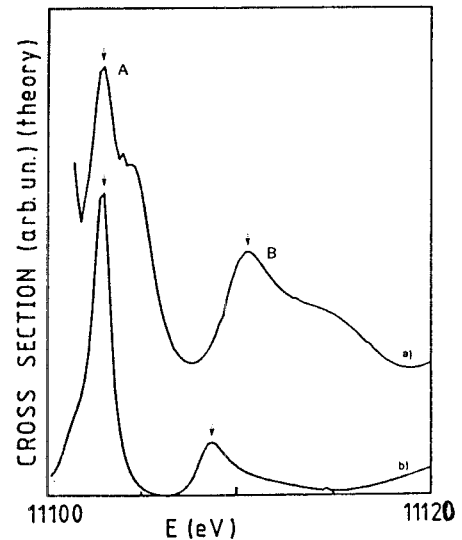

Fig. 2

Fig. 3

Fig. 3 Theoretical cross section obtained for a two shells cluster with
a) 2nd shell"compressed" and b) "elongated". The spectra are
not convoluted with a lorentzian function.

stance, it has been shown [4] that a similar structure occurring in some
transition-metal chlorides can be explained in terms of multielectron exci-
tations, as due to shake up and shake off processes. We believe though,
that this is not the case for Ge: in fact, were a multielectron process at
the origin of peak B, there is no way to explain why it should appear in
crystalline and not in amorphous Ge. In order to ascertain the effect
which originates that structure, we performed a calculation of the absorp-
tion cross section following the multiple scattering approach already used

in Ref.5. The calculations were made for the following clusters:

a) absorbing atom + 1st coord. shell (5 atoms)
b) absorbing atom + 1st + 2nd coord. shell (17 atoms)
c) absorbing atom + 1st + 2nd + 3rd coord. shell (29 atoms)

As a first step, the known crystallographic distances, namely $R_1 = 2.45$ Å, $R_2 = 4.00$ Å, $R_3 = 4.69$ Å, were used as bond lengths. The calculated cross sections were convoluted with a Lorentzian function whose width, Γ, was assumed to be the sum of the core hole lifetime (1.9 eV) plus the experimental broadening function. The results are shown in Figs. 2 and can be summarized as follows:

i)   the 1-shell cluster gives rise to a strong resonance, corresponding to peak A in the experimental spectra, without any further structure.
ii) Both the 2-shells and 3-shells clusters with T_d symmetry and crystallographic distances, give origin to peak B, shifted with respect to the main peak by an amount in good agreement with the experimental one.

Then a two-shell calculation was repeated with bond distances varied according to the estimated distortion of dihedral angles in a-Ge. The chosen values were:

$$R_1 = 2.45 \text{ Å} \qquad\qquad R_1 = 2.45 \text{ Å}$$
$$R_2 = 3.89 \text{ Å} \qquad\qquad R_2 = 4.22 \text{ Å}$$

The symmetry of the cluster (T_d point group) was not distorted in order to save on the already long computer time. We believe that even this crude scheme can give much insight into the relationship between the geometrical arrangement and the edge shape. The results, not convoluted, are reported in Fig.3. The 2-shells cluster, with shorter or longer bond distances again gives peak B, but shifted towards higher or lower energies, as expected in similar situations [6]. Notice that the curve (a) of Fig.2, corresponding to 1-shell calculation compares closely with the experimental spectrum of a-Ge (Fig.1). A naive interpretation of this result could suggest that the amorphous sample is formed by tetrahedral units largely uncorrelated over distances as short as the second coordination shell. As is well known, this oversimplified scheme is not the correct one: the amorphous state in this class of materials is represented by a continuous random network, where correlations exist well beyond the 1st coordination shell. Rather, we think that the explanation of the apparent absence of peak B in the amorphous films lies in the distortion of the second shell, with a consequent large spread of bond distances. The results on the "compressed" and "elongated" clusters bear out clearly this idea: peak B is originated by a transition to empty scattering states, due to the presence of the second (and third) coordination shell. When these shells are distorted, the total absorption cross-section can be visualized as the superposition of several contributions corresponding to different distorted clusters, each of them contributing a B-like structure at a different energy. If the spread of bond distances is large enough, the resulting peak will be smeared out.

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