•

M. Federico, G. Galli, S. Magazù, D. Majolino, E. Burattini

STUDY OF THE GLASS TRANSITION REGION IN AMORPHOUS SELENIUM BY EXAFS

•

•

Study of the Glass Transition Region in Amorphous Selenium by EXAFS.

M. Federico, G. Galli, S. Magazù and D. Majolino

Istituto di Fisica dell'Università and G.N.S.M.-C.I.S.M. - Messina, Italia

E. Burattini

C.N.R.-I.N.F.N., Laboratorio Nazionale - Frascati (Roma), Italia

Summary. — EXAFS spectra of amorphous bulk selenium and $Se_{80}Te_{20}$ alloy have been analysed in the temperature range of the glass transition region (-15 to $37\,°C$). a-Se shows an unexpected behaviour because the modulated part of the X absorption increases with the temperature, irrespectively of the action of the EXAFS Debye-Waller factor from which one expects an opposite behaviour. Analogous features do not appear in the $Se_{80}Te_{20}$ alloy, probably because of the role played by the intramolecular covalent Se-Te bond strength, weaker than the corresponding Se-Se. In the absence of suitable models for the temperature dependence of the microscopic processes occurring in glasses near T_g, a tentative explanation is proposed in terms of the temperature dependence of the backscattering amplitude function $F(k)$.

PACS. 78.70. – Other interactions of matter with particles and radiation.

The increasing interest the amorphous materials have aroused, because of their eventual use for various types of devices, has also increased the need to completely understand all their features and behaviours. Among these, one of the least known is the existence of a class of phenomena that takes place when the amorphous materials undergo temperature variations across the region, typical of each one, known as «glass transition region», labelled by a particular value T_g. Normally one refers to it as to the separation temperature between glass and supercooled liquid, the amorphous material being a glass below T_g, where it is in a state of metastable equilibrium characterized by the existence of

425

only local motions of its elementary constituents. Crossing T_g, towards higher temperatures, the amorphous solid acquires, more and more rapidly, the availability of thermodynamic states lying on the extrapolated equilibrium liquid curve. Contemporary collective motions of the molecules begin to occur, allowing new modes to contribute to the density of vibrational states.

Together with the thermodynamic parameters, from which one usually defines and measures the glass transition temperature, also the dynamics of the systems changes. In particular, by an inelastic incoherent neutron scattering experiment[1], we have shown that the low-energy density of states, to which «acoustic» as well as lattice vibrational modes contribute, becomes strongly temperature dependent through T_g. From the low-energy region (up to 2.7 meV) of the vibrational density of states we also noted that, for a-Se, the Debye-Waller factor sharply increased over T_g. As also indicated in ref. [1], since the Debye-Waller factor can be assumed as a disorder parameter, to which the entire vibrational dynamics contributes, other than the static disorder, more appropriate information is necessary, involving elastic and anelastic scattering experiments.

On this basis we will properly discuss an EXAFS experiment we have carried out on amorphous selenium and a selenium-tellurium alloy, as a function of the temperature, in the glass transition temperature region.

As far as we know, this is the first time an investigation of this kind has been carried out and its results, largely unexpected, could be useful for the better understanding of the phenomena occurring in the glass transition region.

1. – Experimental procedure and results.

Samples of a-Se and $Se_{80}Te_{20}$ were obtained by cutting thin sheets (1 mm thick) from ingots produced by a technique already discussed[2]. The sheets (10 mm diameter) were then processed to reduce their thickness to 80 μm. Before the mechanical processing they were reinforced at one end by sticking them onto films of kapton by cyanacrilate adhesive. The choice of cyanacrilate and kapton was due to their transparency to X-ray in the energy range of our interest (12.4 to 13.6 keV). The amorphous state was finally tested by X-ray diffraction and the samples stored for two months at room temperature.

The EXAFS measurements were carried out using the PWA facility at the Frascati National Laboratories in Italy. The X-radiation was obtained from the Wiggler ondulators, in line with the Adone storage ring, through the Si

[1] G. GALLI, P. MIGLIARDO, R. BELLISSENT and W. REICHARDT: Solid State Commun., 57, 195 (1986).
[2] G. CARINI, M. CUTRONI, M. FEDERICO and G. GALLI: J. Non-Cryst. Solids, 64, 29 (1984).

monocromator of the facility. The samples were mounted on a thermostated loader and alternatively exposed to the incoming X photons. To allow the samples to reach their thermodynamic equilibrium at each temperature, the EXAFS spectra were collected starting from the lowest ($-15\,°C$) up to the highest ($37\,°C$), waiting two hours for preliminary thermostatation at each intermediate temperature. The experimental absorption data have been analysed in the framework of the almost standardized procedure [3] from which one obtains, from the experimental $\chi(k) = \Delta\mu/\mu_0$ curves, the $k\chi(k)$ shown in fig. 1. It is possible to recognize in the set of the six curves, relative to a-Se, some interesting features:

1) all curves have the same period in k and are strictly in phase;

2) all the $k\chi(k)$ are sinusoidal without evident beat revealing (as is shown in fig. 2a), as an example) the existence of a unique feasible peak in the distribution function $P(r)$ [4];

3) the envelope of the $k\chi(k)$, for increasing temperatures below T_g, increases too [5] showing an abrupt damping at the highest temperature $T = 37\,°C$.

From the best fit of the experimental data with the EXAFS formula

(1) $$k\chi(k) = \frac{NF(k)}{R^2} \exp\left[-2\sigma^2 k^2\right] \exp\left[-2\frac{R}{L}\right] \sin\left(kR + \phi(k)\right)$$

written here for the unique shell, the following picture for the a-selenium in the explored temperature range emerges:

1) The distance R between the absorber and the nearest neighbours proves to be independent of the temperature and equal to 2.33 Å. Such a value agrees with the distance evaluated from various other experiments [6] and can be confirmed as the radius of the first coordination shell of the amorphous bulk selenium.

2) The coordination number obtained at $T = -15$ and $37\,°C$ is revealed to be $N = 2.05$ in good agreement with values previously [6] obtained. Such a result

[3] P. A. LEE, P. H. CITRIN, P. EISENBERGER and B. M. KINCAID: Rev. Mod. Phys., **53**, 769 (1981).

[4] The values of the scattering amplitude function $F(k)$ and phase shifts $\phi(k)$, used here, have been calculated from BOON-KENG TEO, P. A. LEE, A. L. SIMONS, P. EISENBERGER and B. M. KINCAID: J. Am. Chem. Soc., **99**, 3854 (1977); P. A. LEE, BOON-KENG TEO and A. L. SIMONS: J. Am. Chem. Soc., **99**, 3856 (1977); BOON-KENG TEO and P. A. LEE: J. Am. Chem Soc., **101**, 2815 (1979).

[5] An analogous experimental behaviour on the X-ray structure factor of As_2S_3 has been found by L. E. BUSSE and S. R. NAGEL: Phys. Rev. Lett., **47**, 1848 (1981); C. LIN, L. E. BUSSE, S. R. NAGEL and J. FABER: Phys. Rev. B, **29**, 5060 (1984).

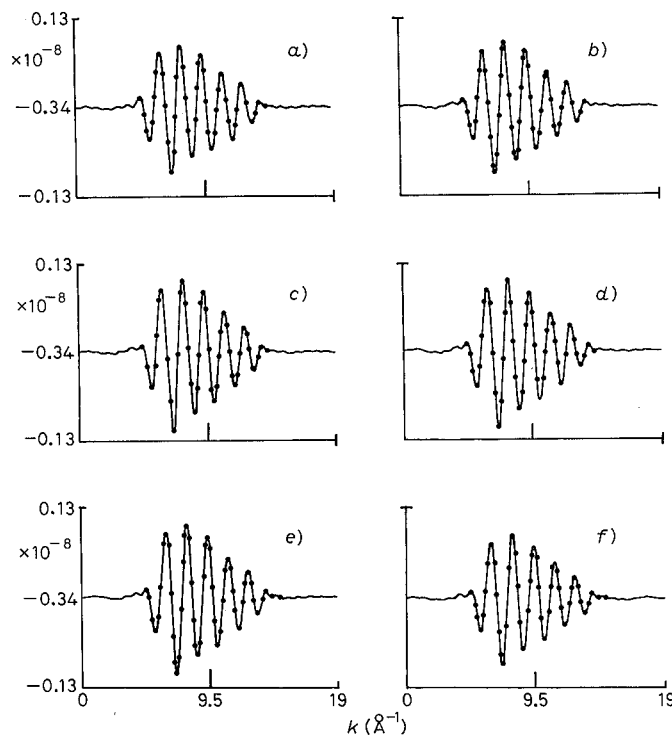[6] R. BELLISSENT: Nucl. Instrum. Methods, **199**, 289 (1982).

Fig. 1. – $k\chi(k)$ plots for amorphous selenium at the various indicated temperatures. Dots represent the experimental points; the lines result from the theoretical fitting. a) $-15\,°C$, b) $-5\,°C$, c) $5\,°C$, d) $15\,°C$, e) $25\,°C$, f) $37\,°C$.

confirm, also by EXAFS, the structural hypothesis of a chain arrangement of the selenium atoms; but it is again unable to clarify if rings of Se_8 are truly present in the bulk or if such a structure is simulated by chain distorsion.

The information one obtains is that, below and above the glass transition region, the atomic arrangement is in chains and eventually also rings, with a coordination number of two.

The surprising behaviour of the a-selenium in the T_g range becomes evident when one analyses the effects of the Debye-Waller factor as a function of the temperature. Owing to the action of the $\exp[-2\sigma^2 k^2]$ term one normally expects the whole $k\chi(k)$ is damped, particularly at the higher values of k, because of the k^2 dependence. The crude absorption data (see fig. 3) show EXAFS oscillations up to 600 eV above the absorption edge, thus indicating a weak action of the damping term; moreover, as can be seen from the whole set of the $k\chi(k)$ in fig. 1, the overall amplitude (the envelope amplitude) increases with T, revealing a contribution to it which compete with the damping effect of the $\exp[-2\sigma^2 k^2]$ term.
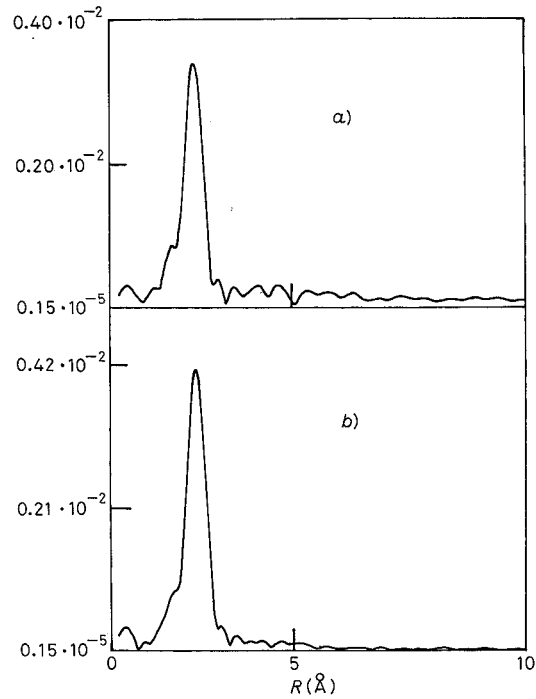
Fig. 2. – $P(r)$ for amorphous selenium at $-15\,°C$ (upper curve a)) and $Se_{80}Te_{20}$ alloy at $-15\,°C$ (b)).
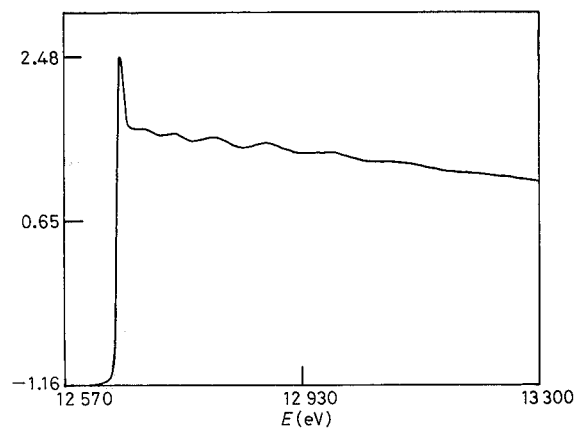

Fig. 3. – Absorption curve for a-Se ($T = 15\,°C$) vs. E, the energy of the incoming X-ray photons.

EXAFS answers, as those sketched by selenium in this work, are not completely unexpected; structural transformations could, in effect, occur as a function of the temperature, producing modifications in the population of a coordination shell, as can happen in aqueous solutions of electrolytes[7], where an explanation is made through the modified number of the nearest backscattering atoms. Mechanisms such as these do not seem to be reasonably presumed in the case of this work.

The coordination number of the amorphous selenium has been measured in a large temperature range[8], up to the liquid phase, and a good agreement exists on $N = 2$ in the whole temperature range, in which the glass transition region is also defined. Such previous measurements are not detailed around T_g, but it seems unreasonable to suppose that the coordination number and, therefore, the structure of the a-selenium will change at T_g becoming chainlike again at higher temperatures.

A quantitative treatment can be carried out by comparing the $k\chi(k)$ at each temperature with respect to its analogue, taken as a reference, at the lowest investigated one. Being

$$(2)\qquad k\chi(k)_{T_0} = A(k)_{T_0} \sin(kR + \phi(k)) \exp[-2\sigma_{T_0^2}] k^2 \exp[-2R/L]$$

for the shell of interest (the only first shell in this case) the modulated part of the absorption at $T_0 = -15\,°C$ and

$$k\chi(k)_T = A(k)_T \sin(kR + \phi(k))_T \exp[-2\sigma_{T^2} k^2] \exp[-2R/L]$$

the analogue at the higher T's, one obtains

$$\ln\frac{\chi(k)_{T_0}}{\chi(k)_T} = 2(\sigma_{T^2} - \sigma_{T_0^2}) k^2 + \ln\frac{A(k)_T}{A(k)_{T_0}}$$

from which, plotting $\ln(\chi(k)_{T_0}/\chi(k)_T)$ vs. k_2, it is possible to evaluate each $\Delta\sigma^2 = \sigma_{T^2} - \sigma_{T_0^2}$ from the slope and $\ln(A(k)_T/A(k)_{T_0})$ from the intercept.

Such a procedure has been successfully used by various authors[9] to distinguish small variations in the EXAFS Debye-Waller factor in crystalline materials and had proved to be more sensitive than the normal fitting procedure.

Using the data between $k^2 = 35$ and $120\ A^{-2}$ it is possible to obtain the whole

[7] G. GALLI, G. MAISANO, G. MIGLIARDO, C. VASI, F. WANDERLINGH and M. P. FONTANA: Solid State Commun., 42, 213 (1982).
[8] R. BELLISSENT and G. TOURAND: J. Non-Cryst. Solids, 35 & 36, 1221 (1980).
[9] E. A. STERN, D. E. SAYERS and F. W. LYTLE: Phys. Rev. B, 11, 4836 (1975); W. BOHMER and P. RABE: J. Phys. C, 12, 2465 (1979); R. B. GREEGOR and F. W. LYTLE: Phys. Rev. B, 20, 4902 (1978).

TABLE I. - *Table of values calculated from* $\ln(\chi(k)_{T_0}/\chi(k)_T)$ *vs.* k^2 *(see the text). Asterisk refers to results statistically not feasible for* $T = -5\,°C$ *too near to the reference temperature* $T = -15\,°C$*. The almost explicit 0 relative to* $T = 37\,°C$ *of selenium, is because of the indistinguibility of* $\chi(k)_{37\,°C}$ *from* $\chi(k)_{-15\,°C}$*.*

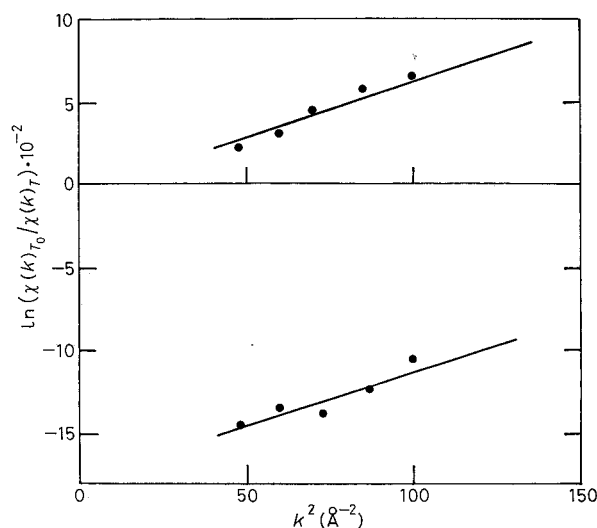|		$-5\,°C$	$5\,°C$	$15\,°C$	$25\,°C$	$37\,°C$
Se	$\ln(A(T_0)/A(T))$	*	-0.134	-0.169	-0.178	0
	$2\,\Delta\sigma^2$	*	0.0002	0.001	0.001	0
Se-Te	$\ln(A(T_0)/A(T))$	*	0.001	0.002	-0.004	-0.006
	$2\,\Delta\sigma^2$	*	0.0002	0.0003	0.001	0.001

Fig. 4. – Plots, as an example, of $\ln(\chi(k)_{T_0}/\chi(k)_T)$ for a-Se (lower curve) and $Se_{80}Te_{20}$ (upper curve) at $T = 25\,°C$ and $T_0 = -15\,°C$.

set of parameters as a function of the temperature, as is shown in table I. Plots of $\ln(\chi(k)_{T_0}/\chi(k)_T)$ vs. k^2 are shown in fig. 4 as an example.

It is seen from the plot ($T = 25\,°C$, curve a)) and table I that the selenium-tellurium alloy behaves «normally» up to $15\,°C$, i.e. all the straight lines increase their slopes with the temperature thus revealing a corresponding increase of the Debye-Waller factor. The intercepts with the vertical axes converge here to the common value of zero indicating no changes in the term $A(k)$ of the EXAFS formula (eq. (2)). The same behaviour does not appear in the amorphous selenium case, where one notices a small variation of the Debye-Waller factor but also, as expected from the amplitude behaviour of the $k\chi(k)$, an intercept value that shows an increase, with the temperature up to $15\,°C$, of the $A(k)$ values. Now $A(k) = NF(k)/R^2$ and its increase must be connected to the one of N

(as normally happens) or $F(k)$ or to the corresponding reduction of the interatomic distance R. Fitting the experimental $k\chi(k)$ the interatomic distance R is strongly determined by the term $\sin(kR + \phi(k))$ and the eventual change of R must result in a corresponding change of the «frequency» in the $k\chi(k)$ vs. k plot. Similarly eventual variations of the phase factor $\phi(k)$ would result in a phase shift of each $k\chi(k)$ with respect to the one taken as a reference. In effect no «frequency» shifts are revealed between the various $k\chi(k)$ of the amorphous selenium, and the same between the correspondent of the selenium-tellurium alloy, the various plots of each set being completely superimposable, for both frequency and phase. The coordination number N could be varied by temperature if phase transformations are allowed in the system, but it does not seem to be the case of pure amorphous selenium. It has been previously pointed out that the coordination number of the a-Se results to be temperature independent and equal to two [8] in the whole range of the solid and liquid phases. In other words the chain (and, eventually, ring) structure is preserved along the temperature and physical-state excursion. It does not appear reasonable, at this point, to attribute to the coordination number N the overall increase of the EXAFS spectra in the limited (up to 15 °C) temperature range of the glass transition. Such a possibility would reflect two phase transitions: the first to an atomic arrangement with increased N below T_g and the other, above T_g, to come back to a chain structure. Even if it has not yet been revealed by EXAFS experiments, as far as we know, the last possibility could lie in the temperature dependence of the backscattering amplitude $F(k)$ term of $A(k)$.

To follow this line means admitting that the electronic structure of each selenium atom proves to be modified by thermal excursion through T_g, or suggesting the presence of a great number of defects, released, probably, as charged defects by the structurally frozen matrix, to which the responsibility of an overall modification of the $F(k)$ could be attributed.

The problem now arises as to why all of this happens in the case of pure selenium and not for the selenium-tellurium alloy where, since the atomic percentage of tellurium in the alloy is 13%, on the average one tellurium atom will substitute a selenium in the same percentage in the chain.

The EXAFS spectrum tuned on the selenium k-edge of a-SeTe is mainly driven by a first shell of selenium atoms while the expected second shell of tellurium is masked owing to almost the same distance between Se-Se and Se-Te in the chain (see fig. 2b)).

The eventual increase of the selenium $F(k)$ would mean a corresponding increase, with T, of the $\chi(k)$ of the selenium-tellurium alloy. Such a circumstance clearly does not occur, thus suggesting the presence of competitive phenomena.

In effect the intrachain covalent strength of the selenium-tellurium is weaker than the corresponding selenium-selenium, reasonably allowing the thermal disorder to be more effective and then the Debye-Waller factor to play a more active role in damping the whole $k\chi(k)$.

In conclusion, the most important feature that emerges from the analysis of the experimental EXAFS data is the nonmonotonic behaviour of the $k\chi(k)$ envelope of the amorphous selenium vs. T. It can be seen from fig. 1 that the $k\chi(k)$ obtained at $T = 37\,°C$ shows the same amplitude and shape as at $T = -15\,°C$, and also the same calculated value of σ ($\Delta\sigma^2 = 0$). Such a circumstance could normally be interpreted as a consequence of a structural transition, the increasing of the Debye-Waller factor being connected to the intramolecular «disorder» due to the temperature effects in the first phase, followed by a second one characterized by a structurally less «disordered» arrangement (lower value of σ). Since the structural arrangement in chains of both a-Se and selenium-tellurium alloy is preserved, this does not seem to be the present case. It is possible that other mechanisms act on the structure (more probably on the electronic structure) in the temperature range of the glass transition, and the behaviour sketched by EXAFS experiments on such semiconducting samples need more detailed study to be clearly understood. Such a possibility could be improved by the availability of reasonable models for the $F(k)$ dependence from the temperature, that is for the electronic structure modification with T or by suitable defects theories.

* * *

[10] M. ABKOWITZ and D. M. PAI: Phys. Rev. B, 18, 1741 (1978).

● RIASSUNTO

Il selenio amorfo e lega $Se_{80}Te_{20}$ sono stati studiati con tecnica EXAFS nell'intervallo delle temperature noto come regione della transizione vetrosa T_g (da -15 a $37\,°C$). Il selenio amorfo mostra un comportamento inaspettato per effetto dell'aumento, con la temperatura sotto T_g, della parte modulata dell'assorbimento dei raggi X, in contrasto con quanto ci si aspetterebbe per l'effetto di smorzamento del fattore di Debye-Waller. Un comportamento analogo non si riscontra invece nella lega $Se_{80}Te_{20}$ dove, probabilmente, il legame covalente intracatena Se-Te, più debole del corrispondente Se-Se, rende più efficace l'azione di smorzamento del fattore di Debye-Waller, smascherando altri effetti. In assenza di modelli adeguati che descrivono la dipendenza dalla temperatura dei processi microscopici nei materiali vetrosi nella regione della transizione vetrosa, si ipotizza che il comportamento «anomalo» del selenio sia attribuibile ad una dipendenza dalla temperatura della funzione ampiezza di backscattering $F(k)$.

Исследование переходной области стекла в аморфном селене с помощью EXAFS.

Резюме (*). — Анализируются спектры EXAFS аморфного объемного селена и сплава $Se_{80}Te_{20}$ в области температур переходной области стекла (от 15° до 37 °C). a-Se обнаруживает неожиданное поведение, потому что модулированная часть X поглощения увеличивается с температурой, независимо от действия фактора Дебая-Уоллера EXAFS, который предполагает противоположное поведение. Аналогичные особенности не возникают в сплаве $Se_{80}Te_{20}$, так как сила межмолекулярной ковалентной связи Se-Te, по-видимому, слабее, чем соответствующвя связь Se-Se. В отсутствии соответствующих моделей для температурной зависимости микроскопических процессов, происходящих в стеклах вблизи $T_{g,a}$, предлагается предварительное объяснение в терминах температурной зависимости функции $F(k)$ амплитуды обратного рассеяния.

(*) *Переведено редакцией.*