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X-RAY ABSORPTION MEASUREMENTS AT THE Ag L_3 EDGE ON SILVER BORATE GLASSES WITH SYNCHROTRON RADIATION

E. Bernieri[x], E. Burattini[*], G. Dalba,[o§] P. Fornasini,[o] F. Rocca[+]

[x]Dipartimento di Fisica de L'Aquila and INFN Napoli, Italy
[*]INFN -PWA group- Frascati, Università di Napoli, and CNR, Italy
[o]Dipartimento di Fisica dell'Università di Trento, 38050 Povo (Trento), Italy
[+]Istituto per la Ricerca Scientifica e Tecnologica, Trento, Italy

X-Ray absorption measurements have been performed for the first time at the Ag L_3 edge on glasses $Ag_2O \cdot nB_2O_3$ (n=1,2,3,4) and on crystalline Ag_2O. The L_3 edge exhibits a peak, which has been associated to a 2p → 5d dipole transition. A comparison of both the edge and EXAFS structures reveals that the first coordination shell around the silver ion is substantially insensible to variations in the Ag_2O content of the glass. Minor differences in the EXAFS signal are attribute to second shell effects suggesting a lower degree of order beyond the first shell in the glasses n=1,2 than in the glasses n=3,4.

1 - INTRODUCTION

Borate glasses have been widely studied for many years, in order to understand the microscopic structure of the glassy state, an particularly the consequences of the introduction of various oxides into the network of the glass-former B_2O_3. The interest has grown again recently[1,2], due to the possibility of obtaining "fast ion conductor" glasses exhibiting ionic conductivities of the order of $10^{-5} \div 10^{-2} \Omega^{-1} cm^{-1}$ at room temperature. For instance, the insertion of 20% (molar) AgI in the glassy matrix $Ag_2O \cdot nB_2O_3$ is sufficient to enhance the ionic conductivity two order of magnitude $(n=[B_2O_3]_{mol}/[Ag_2O]_{mol})$.

In order to clarify the dependence of the functional properties of the "fast ion conductor" glasses on their structural characteristics, a preliminary understanding of the microscopic structure of the binary matrix $Ag_2O \cdot nB_2O_3$ is desirable.

As a result of various measurements performed in the last years with different techniques[3,4,5], the insertion of Ag_2O or other analogous oxides (Li_2O, Na_2O,...) into the matrix of the glass former B_2O_3 has been shown to modify both the macroscopic properties (density, transition temperature, viscosity, etc.), the coordination of the boron atoms and the more complex structural groups which characterize the microscopic structure, according to the Krogh-Moe model.

It has however to be noted that the measurements so far performed give direct information mainly about the glass-former network; little is known, on the contrary, about the position and the surroundings of the silver ions. In order to better understand the electronic and geometrical structure around the silver ion, we began a series of X-ray spectroscopy measurements at the absorption edges of silver in binary glasses $Ag_2O \cdot nB_2O_3$, for various n values.

It is well known that the fine structures near the X-ray absorption limit ("edge structures"), due to transitions to empty bound electronic states, can give information about the chemical bond[7]. The fine structures beyond about 20 eV from the absorption limit (XANES and EXAFS), imputable to the autointerference of the photoelectron backscattered by the neighbouring atoms, directly give geometrical information[8,9].

In this work we show and discuss the fine structures at the Ag L_3 edge in the glasses $Ag_2O \cdot nB_2O_3$ (n=1,2,3,4)[10] and in crystalline Ag_2O, considered as a standard compound for the EXAFS analysis.

2 - EXPERIMENTAL DETAILS

The X-ray absorption measurements have been performed with synchrotron radiation at the Adone Wiggler Facility in Frascati[11] utilizing a Si(111) channel-cut crystal monochromator. The energy resolution of the monochromator was 0.6 eV at the Ag L_3 edge. The energy interval between two consecutive measurements was 0.3 eV.

The glasses, obtained by heating weighted amounts of silver nitrate and boron oxide[1], had

been powdered and deposited on filter paper by
means of a sonication technique, in order to
obtain an uniform thickness.

All measurements have been performed at
room temperature.

3 - RESULTS

The "edge structures" and the XANES are better
studied at the Ag L_3 edge than at the Ag K
edge: at the lower energies the resolving power
of the monochromator is higher and the lifetime
broadening of the core level becomes negligible.
The analysis of the EXAFS at the L_3 edge, on
the contrary, is troubled by the early onset of
the L_2 edge, which limits to about 100 eV the
useful energy range.

This is clearly shown in Fig. 1, where two
typical spectra at the Ag L_3 edge, in crystal-
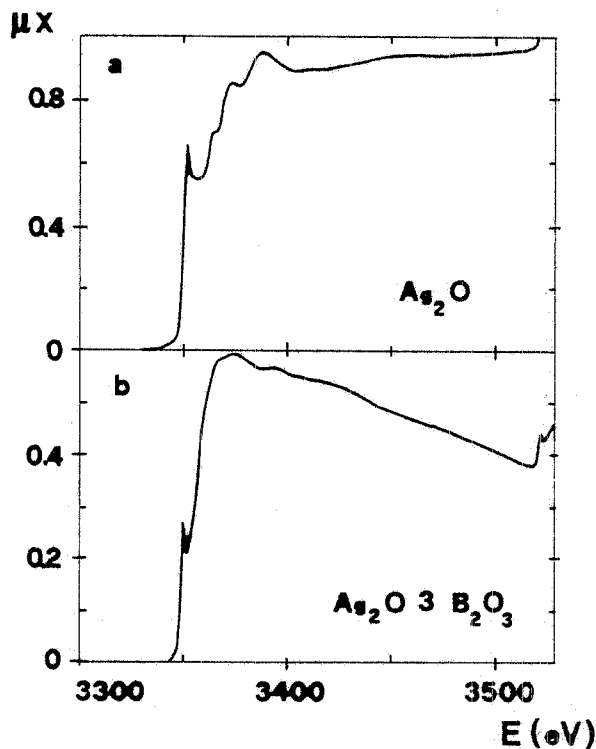line Ag_2O and in the glass $Ag_2O3B_2O_3$, are
compared.

Fig. 1. X-ray absorption spectra at the Ag L_3
edge for Ag_2O and for the glass Ag_2O $3B_2O_3$.
The onset of the L_2 edge is visible at about
3525 eV.

The Ag_2O spectrum is remarkably structured
within 50 eV from the edge. In the glassy com-
pound only the peak at about 3350 eV is notice-
able, the structures at higher energies being
very weak. This behaviour reflects the drastic
reduction of order beyond the first coordina-
tion shell taking place when one pass from a
crystalline to a glassy compound.

The EXAFS, besides being limited by the
L_2 edge, looks rather weak in both spectra.

In Ag_2O this is due to the low number of oxygen
nearest neighbours (N=2); in the glass the ef-
fect of static disorder prevails.

3.1 - Edge structures

The fine structures at the Ag L_3 edge for me-
tallic silver, silver oxide and the glasses
$Ag_2OnB_2O_3$, n=1,2,3,4, are shown in detail in
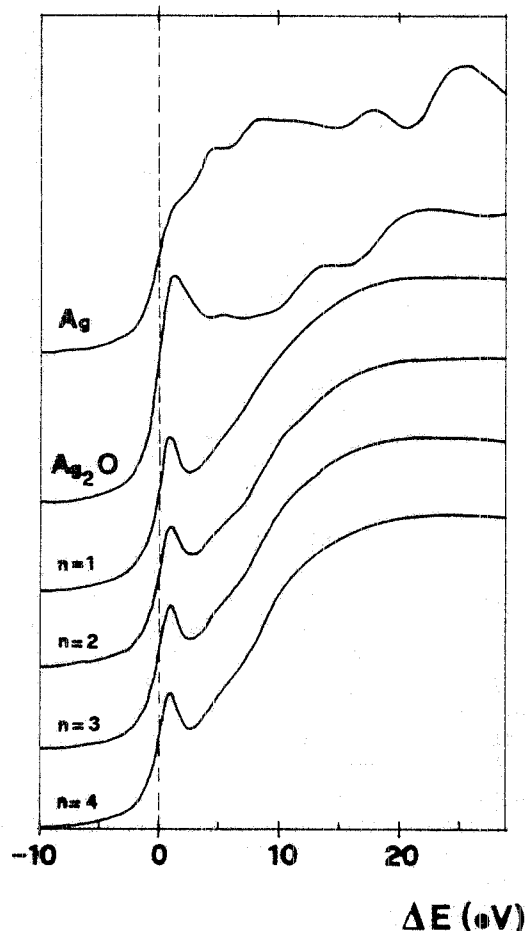Fig. 2; the energy values refer to the absorp-

Fig. 2. Fine structures at the Ag L_3 absorp-
tion edges in silver, silver oxide and in the
glasses Ag_2O nB_2O_3.

tion limit (first maximum of the derivative).
The energy position of the absorption limit was
the same for all the spectra, within the reso-
lution of the measurements.

The spectrum of metallic silver is mono-
tone within the first 5 eV above the absorption
limit. A peak at about 1 eV is on the contrary
present in the spectra of Ag_2O and of the
glasses.

The height of this peak has been calculated
with respect to the zero absorption level -- ob-
tained by extrapolation of the Victoreen-type
pre-edge fitting curve - and then normalized to
the mean absorption coefficient above the edge
extrapolated from the EXAFS region. The peak is
lower in the glasses than in Ag_2O by a factor

about 1.5. A slight variation in the height of the peak has been found as a function of the glass composition: the height decreases progressively (Fig. 4) at the decreasing of the molar fraction R=1/n of silver oxide from R=1 (n=1) to R=0.25 (n=4). It has been verified that these variations in the peak height do not depend on thickness effects, comparing measurements performed on samples of different thickness.

The structures at the L_3 edges are due to dipole transitions of 2p electrons to states of s or d symmetry, the transition to d states being by far more probable than to s states.

The absorption limit at the $\overline{Ag}$ L_3 edge has been related to transition 2p→5d in metallic silver and in Ag_2O[12]. The similarity between the L_3 edges of the glasses here considered and that of Ag_2O within 3 eV from the absorption limit allows to assume a · corresponding similarity in the band structure of partial symmetry d. The similarity between Ag_2O and the glasses lacks, on the contrary, for what concerns the empty states of p symmetry, as one can deduce by comparison of the L_1 edges in Ag_2O and in the glass n=1 (Fig. 3).
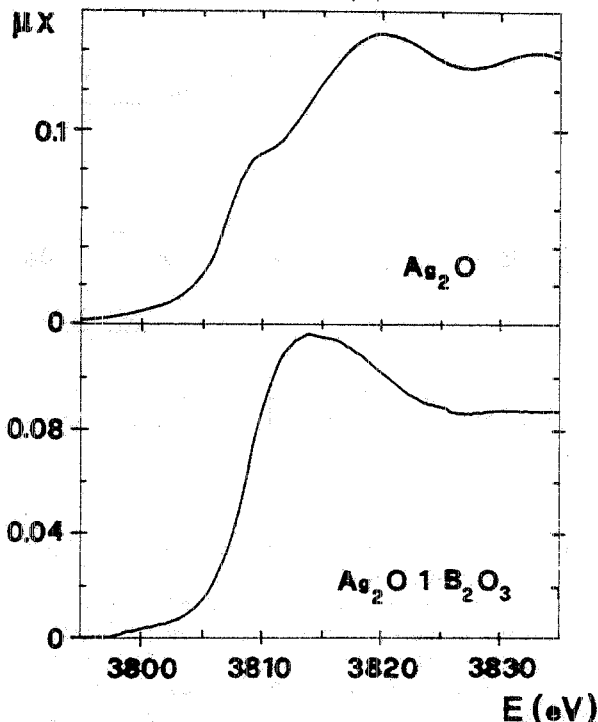
Beyond about 5 eV from the absorption

Fig. 3. Fine structures at the Ag L_1 absorption edges in silver oxide and in the glass Ag_2O B_2O_3.

limit the spectrum of Ag_2O presents strong structures (Fig. 2). The spectra of the glasses, on the contrary, are only weakly structured: one can only see a slight oscillation in the slope

of the edge between 6 and 7 eV, more pronounced for the glasses n≳2 than for the glass n=1. This structure is more clearly seen in the derivative of the spectrum (Fig. 5), where it is present as a local minimum.

3.2 - EXAFS

The range of the EXAFS oscillations at the Ag L_3 edge is too short to allow a reliable complete data analysis. It is nevertheless possible to obtain some information by a direct comparison of the EXAFS spectra of Ag_2O and of the glasses (Fig. 6).

Above about 4 Å^{-1} the signal $X(k)$ can be considered as due only to single scattering of the photoelectron, and can thus be analyzed as pure EXAFS. The main frequency and the amplitude of the signal above 4 Å^{-1} are very similar for all the glassy compounds. The frequency of the signal of Ag_2O is on the contrary remarkably lower than that of the glasses, denoting a shorter Ag-O distance in Ag_2O than in the glasses.

A quantitative determination of the Ag-O distance has been attempted by Fourier filtering the EXAFS signal and analyzing its phase by the "R constant" method[13]. An Ag-O distance 1.95 Å has been obtained for Ag_2O; the agreement with the crystallographic value 2.04 Å can be considered satisfactory, in view of the limited k range, of the difficulty in background subtraction for a very short signal, of the inadequacy of the theoretical phase-shifts at low k values. The mean distance Ag-O in the glasses resulted to be about 0.5 Å larger than in Ag_2O.

The oscillations included between 2 and 4 Å^{-1} in the spectra of the glasses are due to a superposition of multiple scattering effects (prevailing at low k) and single scattering effects. They cannot thus be simply included in the EXAFS signal, yet they undoubtedly contain structural information. The shape of the structure at about 2.6 Å^{-1} is largely influenced by the procedure of background subtraction. A physical significance has instead to be attributed to the structure at about 3.5 Å^{-1}, very strong in the glasses n=3,4, scarcely visible in the glasses n=1,2.

4 - DISCUSSION AND CONCLUSIONS

The analysis of NMR spectra of boron atoms[14] has shown how the insertion of Ag_2O in the glass-former B_2O_3 modifies some of its BO_3 structural units into BO_4^- tetrahedra, whose faces can accommodate the Ag^+ ions. The fraction N_4 of four-coordinated boron atoms is a function of the molar fraction R. For R ≤ 0.4 one finds simply N_4 = R. When R ≳ 0.5, N_4 decreases slowly at the increasing of R. For R ≃ 1 evidence has been obtained of non-bridging oxygens.

I.R. and Raman measurements, on the other hand, show the consequences, on the structural

groups considered by the Krogh-Moe model, of the variations in the Ag_2O content[4]. For low R values the boroxol ring structure is preserved, and the BO_4^- units are contained mainly within triborate and pentaborate groups; at the increasing of R, triborate and pentaborate groups are progressively substituted by diborate groups[14].

The present X-ray spectroscopy measurements probe the surroundings of the Ag^+ ions, and can then give complementary information with respect to previously utilized techniques.

A striking similarity has been found in the EXAFS spectra of all the glasses here considered, for what concerns both frequency and amplitude above $k=4$ $\overset{\circ}{A}^{-1}$; this suggests that the first coordination shell of Ag^+ ions is substantially insensitive to variations in the glass composition, at least for what concerns the mean radial Ag-O distance and the coordination number.

This conclusion is confirmed by the close similarity in the peak structure near the L_3 absorption limit, which monitors the chemical bond of the Ag^+ ion.

The slight variations in the peak height (Fig. 4) could depend on minor variations in
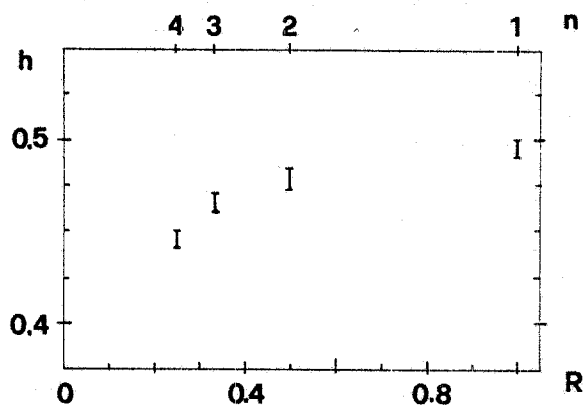

Fig. 5. First derivatives of the fine structures at the Ag L_3 edges in Ag_2O and in the glasses.

Fig. 4. Height h of the peak at 1 eV above the L_3 absorption limit of the glasses (Fig.2) as a function of the molar ratio

$$R = [Ag_2O]/[B_2O_3].$$

the first coordination shell. The variations in the edge slope (Fig. 5) are perhaps related to the presence of non-bridging oxygens for n=1; they could also be sensible to second shell effects.

The remarkable variations in the structure at about 3.5 $\overset{\circ}{A}^{-1}$ in the $X(k)$ spectrum (Fig.6), which clearly differentiates the glasses n=1,2 from the glasses n=3,4, can be attributed to variations in the coordination beyond the first shell. This implies a lower degree of disorder in the second shell of glasses n=3,4 with respect to n=1,2, which can be related to a
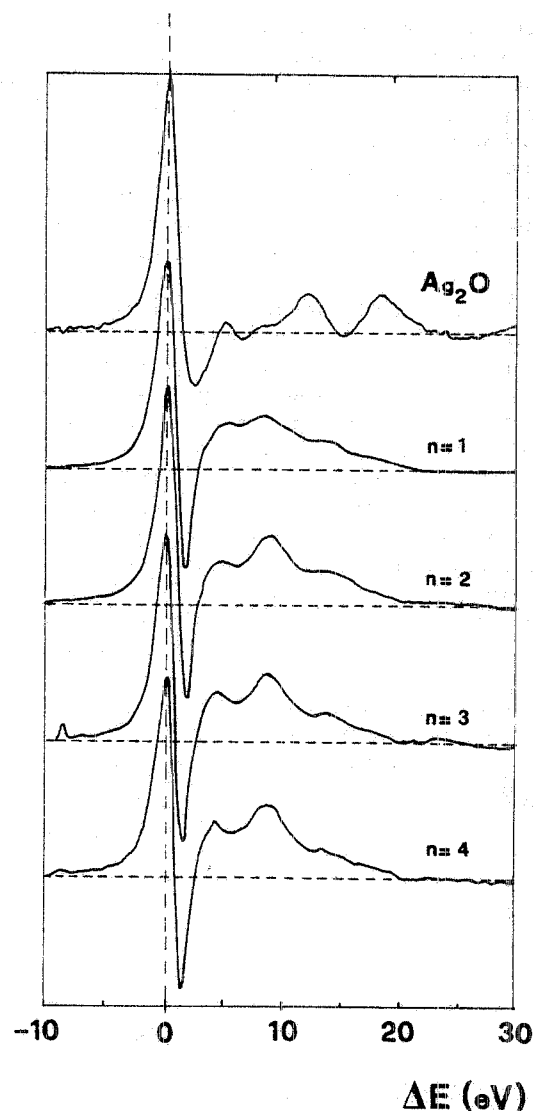
smaller variety of Krogh-Moe structural groups in the glasses n=3,4.

The short k range of the EXAFS signal prevents a deeper structural understanding; it is believed that the study of the EXAFS at the Ag K edge will allow to obtain quantitative information about radial distances and coordination numbers, and to better discriminate second shell effects.

Moreover, a theoretical interpretation of the L_3 and L_1 edge structures could clarify the peculiarities of the chemical bond Ag-O.
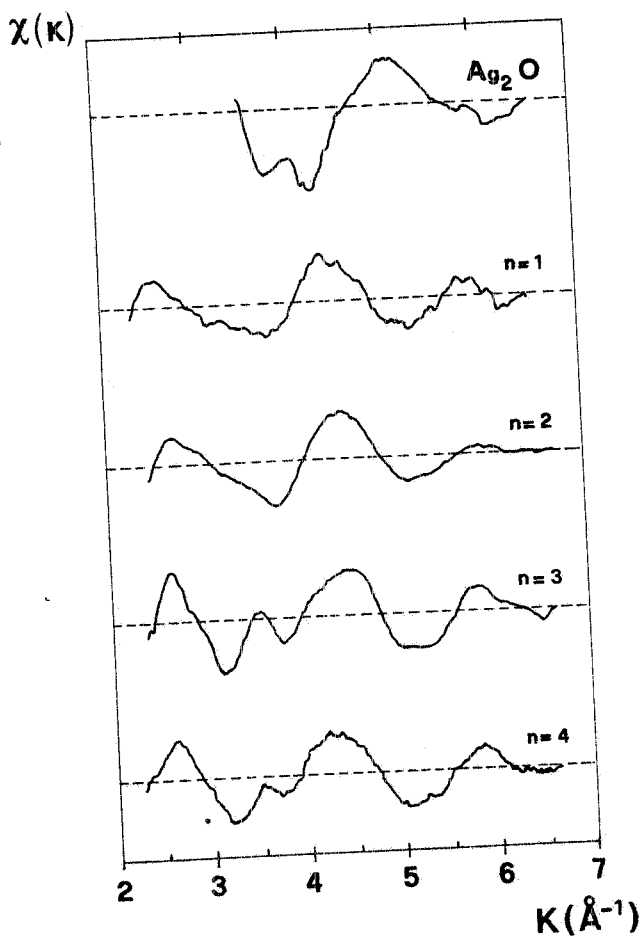
Fig. 6. X(k) oscillations for silver oxide and for the glasses. The vertical scales are the same for all the spectra.

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