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INTERMETALLIC PEROVSKITES Mn_3 MeX (Me=metal, X=N,C)

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ABSTRACT

We have measured the XANES (X-ray near edge structure) spectra on the manganese and metal K-edge of the intermetallic perovskites Mn_3MeX (X=N, Me=Mn, Cu, Zn, Ga, Sn; X=C, Me=Ga, Sn) to investigate the distribution of the partial density of the empty states.

The information of the local electronic structure at the two different sites, obtained from the spectra in the first 10 eV above the onset, are discussed in terms of one-electron band model. The relative shape change in the spectra between the differents compounds are explained by the different magnitude of hybridization between the electronic states of different atoms and/or the filling of the empty band by the electrons supplied by the substituted metal. Also, information about the local geometrical structure has been obtained from the 10 to 50 eV range of the spectra.

RIASSUNTO

La distribuzione della densità parziale degli stati vuoti sulle perovskiti intermetalliche Mn_3MeX (X=N, Me=Mn, Cu, Zn, Ga, Sn; X=C, Me=Ga, Sn) è stata studiata mediante spettroscopia XANES (X-ray Near Edge Structure) alle soglia K del Mn e del metallo X.
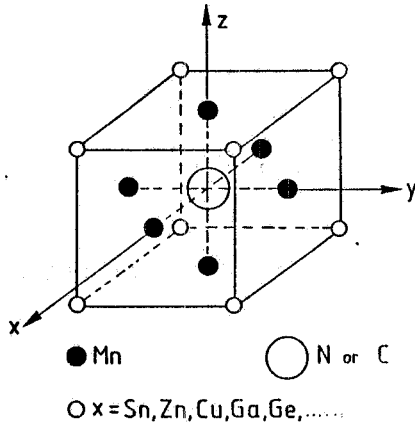
Le informazioni sulla struttura elettronica locale su entrambi i siti, ottenute dall'analisi dei primi 10 eV degli spettri XANES, sono discusse in termini di un modello a banda proposto. Il cambiamento relativo della forma negli spettri dei diversi composti è posto in relazione alla differente ibridizzazione tra stati di atomi diversi e/o dal riempimento degli stati della banda vuota con elettroni forniti dal metallo sostituente. Sono state anche ottenute informazioni sulla struttura geometrica locale analizzando gli spettri nel range da 10 a 50 eV.

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1. - INTRODUCTION

Intermetallic Mn_3MeN and Mn_3MeC compounds (Me=metallic atom) with the cubic perovskite structure, have been extensively studied in the last fifteen years by several experimental techniques, such as X-ray and neutron diffraction, magnetic and thermal measurements[1-10]. These compounds are magnetic conductors and they have attracted large interest because of the existence of magnetic phase transitions in which the magnetic ordering or reordering is normally associated to structural pand electronic changes.

This family of compounds are derived from the interstitial compounds Mn_4X, where N or C are situated in the octahedrial site in the fcc manganese lattice. Correspondingly, two types of Mn sites are present, at the cubic faces (Mn(I)), and cubic vertices (Mn(II)). The perovskites are formed by ordered substitution of the Mn(II) atoms at the corners by the metal (see Fig. 1). This substitution could be complete giving rise to the stoichiometric compounds. Moreover, solid solutions $Mn_3Me_xMe_{1-x}N$ or $Mn_3MeN_xC_{1-x}$ may be obtained by mixing of the parent compounds. The metal substitution permits to change the number of electrons in the conduction band, influencing the structural and magnetic properties of the compounds.

● Mn   ◯ N or C

◯ x = Sn, Zn, Cu, Ga, Ge, ...

FIG. 1 - Crystalline structure of Mn_3X Me perovskites.

Although these compounds have been widely studied, very little is known experimentally on their electronic structure. A band model which qualitatively explains the complicated behaviour of these compounds has been proposed[11,12]. This model consists of a large conduction band formed by the s electrons of the Mn and the s-p electrons of the metal atom Me, overlapping a narrow band, which results from the strong hybridization between p-orbitals of C or N and some of d-orbitals of manganese. This p-d sub-band present sharp singularities in the density of states near the Fermi level. In the cubic and paramagnetic phase, such a singularity has six-fold degeneracy. Magnetic and structural instabilities appear in these compounds decreasing the temperature, and are explained by the removal of the degeneracy, which implies a change on the density of states at the Fermi energy. The electronic origin of the instabilities of these compounds is corroborated by heat capacity studies[8-10] which shows an anomalously high γ electronic constant and moreover, some phase transitions are characterized by a γ discontinuity across the transition temperature. In Table I, we summarize the principal properties of the studied compounds.

We have studied Mn_4N, Mn_3GaN, Mn_3ZnN, Mn_3CuN, Mn_3GaC, Mn_3SnN, Mn_3SnC and the solid solution $Mn_{3.2}Ga_{0.8}N$ by XANES (X-ray Absorption Near Edge Structure) to obtain both, the local and partial density of unoccupied states[13,14] and the geometrical atomic distribution around selected sites[15]. The experiments have been performed at room temperature at which all compounds are cubic (Pm3m). In this work Mn and Me (Me=Zn, Cu, Ga) K-XANES spectra at

TABLE I - Principal properties of the studied compounds. γ=heat capacity electronic coefficient, ϱ=resistivity, V=specific volume, μ=magnetic moment.

Mn_4N	Ferrimagnetic, Tc=756 K a(300K)=3.871 A.
Mn_3GaN	Antiferromagnetic tringular below T_A=278.5 K Paramagnetic at room temperature a=3.885 A First order phase transition at T_A, change in γ, ϱ,V.
Mn_3GaC	Antiferromagnetic collinear below T_A=171.7 K Ferromagnetic between T_A and T_B=243.1 K Paramagnetic at room temperature a=3.986 A First order transition at T_A, discontinuity in γ,ϱ, V,μ.
Mn_3ZnN	Antiferromagnetic quadratic below T_A=127.5 K Antiferromagnetic triangular between T_A and T_B=191.4 K. Paramagnetic at room temperature First order phase transition at T_A and T_B, discontinuity in γ, ϱ, V,μ.
Mn_3CuN	Ferrimagnetic below T_A=143 K. Paramagnetic at room temperature a=3.908 A. First order phase trans. at T_A, tetragonal distortion change in ϱ.
Mn_3SnC	Ferrimagnetic below T_A=284 K Paramagnetic at room temperature a=3.955 A First order phase transition at T_A.
Mn_3SnN	Ferrimagnetic below 273 K. Antiferromagnetic between 237 K and T=357 K, a=4.06 A. Tetragonal distortion at 273 K.
$Mn_{3.2}Ga_{0.8}$	Paramagnetic at room temperature a=3.091 A Ferrimagnetic between 260 K and 160.5 K Below 160 K spin-glass behaviour.

room temperature have been measured to study the two different sites. In this case, because of the matrix element and selection rule for dipole electronic transitions, we select the local and p-partial density of states around the absorbing atom. In particular, we have analyzed the effect of the metal or metalloid substitution in the electronic structure in relation to the p-d hybridization. Also, information on geometrical local atomic distribution has been extracted from the shape of absorption spectra in the multiple scattering region.

2. - EXPERIMENTAL

The samples were prepared at UA 1109, INP Grenoble and they have been characterized at the Laboratoire de Cristallographie, C.N.R.S. Grenoble by x-ray diffraction and thermomagnetic properties[16]. Some samples are the same used in previous heat capacity and susceptibility studies[8-10].

The experiments were performed at the Frascati National Laboratories using the storage ring ADONE operating at 1.5 GeV, and about 50 mA. The beam was monochromatized by a Si(111) channel cut single crystal monochromator and the energy resolution using a slit of 1 mm at 6.5

KeV was $\Delta E = 1.5$ eV. The absorption coefficient has been calculated from transmission data T using the formula $\alpha = -(1/d)\ln$ T, where d is the thickness of the sample. Samples were obtained by spreading power on a kapton tape.

3. - RESULTS

We present in Fig. 2 the Mn K-edge X-ray absorption spectra of Mn_3MeX perovskites together with the spectra of manganese metal. The pre-edge background has been substracted in all spectra and the absorption coefficient has been normalized to the atomic absorption level above the absorption jump α_A, obtained in the range above 50 eV. All perovskite samples exhibit similar spectra because of the same crystalline structure but small important differences appear in the region of the Mn-threshold related to the unoccupied bands above the Fermi level. To point out these small differences we report in Fig. 3 the derivative of the absorption spectra of these manganese compounds. In these figures two principal structures (labeled A,B), which shift in energy and vary their intensties with the substitution of Me and/or X atoms, are present above the Fermi level at E_F.
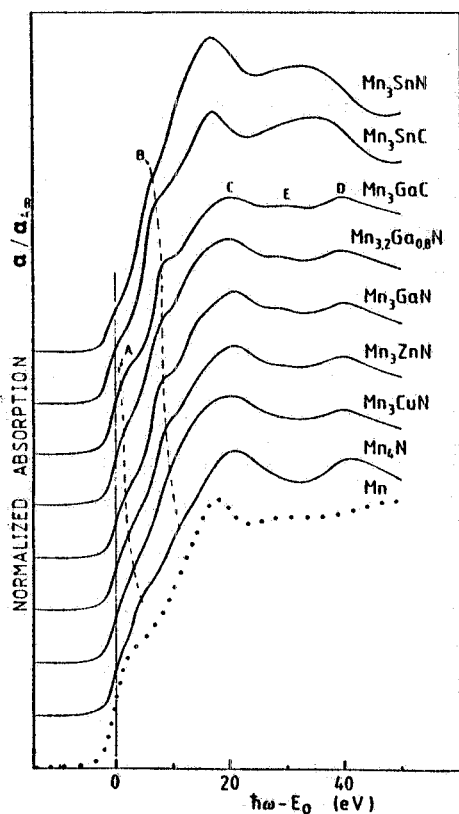

FIG. 2 - Mn K-XANES of $Mn_3MeN(C)$ perovskites. The zero of the energy scale is fixed at the Fermi level identified as the first derivative maximum. The energy E_0 is 6539 eV.
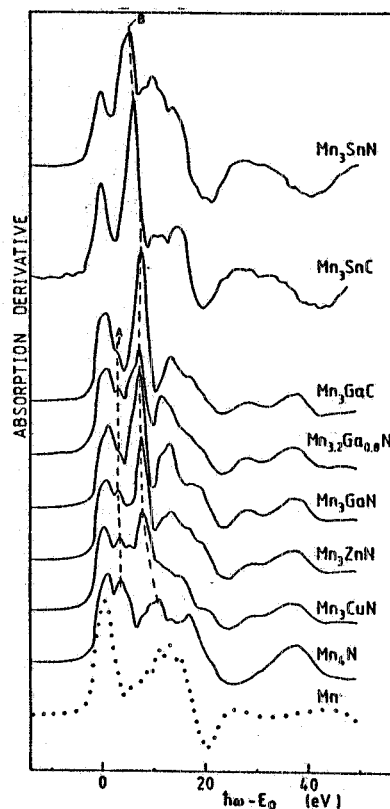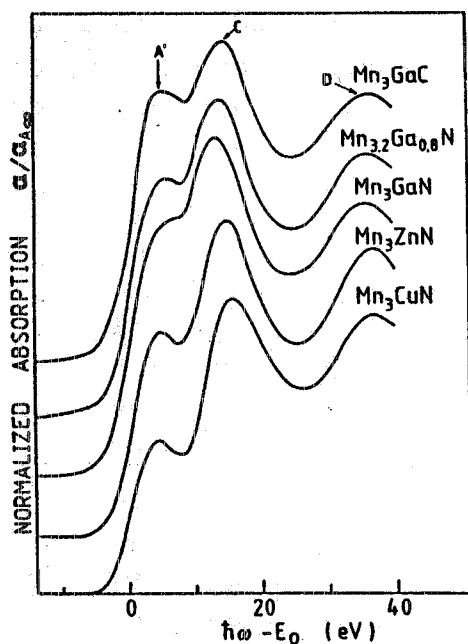
FIG. 3 - Derivative spectra of the absorption coefficient of the same samples and in the same energy range as in Fig. 2.

FIG. 4 - Me(Me=Ga, Zn, Cu) K-XANES of the same perovskites compounds. The zero of the energy scale is fixed at the Fermi energy.

In order to investigate more deeply the distribution of the empty states, we have also measured the K-XANES of the substituted metal in the same compounds. In Fig. 4 we report the K-edge of Cu, Ga, Zn in the Mn_3GaN, Mn_3GaC, Mn_3ZnN, Mn_3CuN and $Mn_{3.2}Ga_{0.8}N$ normalized in the XANES region and aligned with the zero energy at the maximum of the first derivative of the absorption spectra. Also, in this case, the K-XANES are very similar except in the threshold region, but the density of states around the metal atom are less structured than in the manganese K-edge and only a decrease of the low energy structure is observed in the gallium to copper trend.

4. - DISCUSSION

We have analyzed separately two regions: The "threshold region" which extends nearly over 10. eV above the edge and the "multiple scatteringg region" in which the atomic distribution around the excited atom determines the main shape of the absorption spectrum.

Multiple scattering region

We discuss here the region which extends from 10 eV up to 60 eV above the onset. In this region the Mn K-spectra of Mn_4N (see Fig. 2) and the Me K-spectra (see Fig. 4) exhibit two main structures (labeled C and D) characteristics of a fcc geometrical arrangement around the absorbing atom[17,18]. This fact is in agreement with the crystalline structure, in which, except for the interstitial atom, the atomic distribution around the Mn atom in Mn_4N and the metal atom Me in the other samples is the same. On the other hand, the Mn K-spectra in the perovskites shows a third structure, labeled E, which clearly is due to the effect of the substituted metal (the second Mn shell is formed by 8 manganese atoms and 4 Me atoms). The difference between the Mn and Me atom scattering amplitudes and scattering phase determines the appearance of this feature which increses with the difference between the atomic number of Mn and Me atoms. This effect becomes dramatic in the case of Mn_3SnN and Mn_3SnC compounds because of the large difference between Sn and Mn atomic number. Another evidence of this effect is the increase of the E structure in the series $Mn_4N-Mn_{3.2}Ga_{0.8}N-Mn_3GaN$ which is in agreement with the degree of gallium substitution. These results show the selectivity to site II of the metal substitution in the Mn_4N lattice.

In relation to the metalloid effect, no qualitative differences have been observed in the Mn K-XANES spectra of the Mn_3SnN Mn_3SnC and Mn_3GaN - Mn_3GaN, and the Ga K-spectra of Mn_3GaN

- Mn_3GaC. Only a small difference in height of peak C, which is higher in nitride than in carbide compounds. The difference may be explained in terms of the different scattering strength of the nitrogen and the carbon atoms. Although this small difference on atomic number has no detectable effect in the oscillations at the EXAFS energy range[19], this can become significant at the main XANES resonance.

Threshold region

The shape of the K-edge in the first 10 eV (for metals) gives direct information about the unoccupied local density of states with p symmetry. In the case of d-metal, pure p-states are not present at the Fermi energy, therefore the absorption is due to excitations to the hybridized states by d-orbitals with s-p band[20]. In our case, near the Fermi level, hybridization is present, because N or C p-levels are mixed with some of d-Mn levels[11,12]. Also mixing between s-p band (formed by the s-p manganese levels and p states of substituted metal) and d-Mn levels can not be disregarded since the evolution of the structures observed are related to these two effects.

The Mn K-edge spectra of perovskites are diverse from that of Mn metal in where only one structure appears, since only hybridization between Mn (3d) and a large Mn s-p band is present. In the Mn_3MeX compounds two structures, A and B, in the range of energy of about 10 eV have been found. The similarity between the spectra confirms that a unique band model can explain the band structure, and the small differences between them are related to the metal/metalloid substitution.

The effect of atomic substitution in the Mn K-spectra can be summarized as follows: i) The K threshold at E_F for transitions to the Fermi level is unaffected by the metal substitution, except for Mn_3SnN compound. However, carbide compounds show a higher and sharper threshold than the nitride compounds. ii) Structure A is significant in Mn_4N but disappear in a continuous way when the atomic number of metal substitution grows and simultaneously moves toward the Fermi level. No significant effect is associated with carbon or nitrogen substitution. iii) Structure B depends on the metal substitution, (see Figs. 2, 3) the sharpness of this structure increases with the atomic number of the Me metal, (from Mn to Sn) and shows an energy shift similar to feature A. The effect of metalloid gives higher and sharper structure in carbide compounds than in nitride compounds.

The Me K-spectra (see Fig. 4) shows only one structure A' in the threshold region, related to the p-density of states at the metal site. This broad structure extends in an energy range of about 10 eV, consistent with a wide unoccupied conduction band. One observes that this structure grows in the trend Cu to Ga. This is due to a larger p character of the s-p empty band, as is expected from the difference of electronic configuration of these elements. On the other hand, the sharper A' structure, observed in Mn_3GaC respect to the homologous nitride, points towards a larger localization of p electrons in the carbide.

In Fig. 5 we report the comparison between the different metal edges in the same compound for Mn_3CuN and Mn_3GaN. The absorption K-spectra probe the states with p-symmetry in two different sites. The first unoccupied delocalized sp-band with contributions from the Cu or Ga metals clearly appears as the peak A'. At the Mn site this band shows a fine structure and the Fermi level threshold is well separated by the feature A.

The structures observed in the Mn K-edge shows that the electronic structure above the Fermi level is formed by two sub-bands with pd symmetry. This fact can be connected with the proposed band model[11,12]. According to this model the d-orbitals of Mn are completely separated by the crystal field in three sub-bands: $E_I(b_{1g}, b_{2g})$, $E_{II}(e_g)$ and $E_{III}(a_{1g})$.

FIG. 5 Comparison between the K-XANES of Cu and Mn for Mn3CuN, low panel, and of Ga and Mn for Mn3GaC, upper panel.
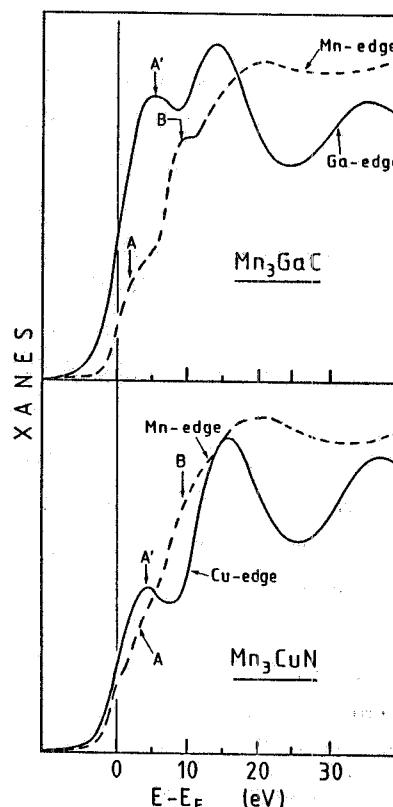
The main E_{II} band results from the hybridization between the p orbitals of N or C with the e_g doublet of the manganese nearest neighboors. When the collective model is considered, this E_{II} state develops into two bands, the π-bonding which also contains a localized d level and the π^*-antibonding sub-band. The Fermi level was assumed to lie in the π-band. A scheme of the band structure and the calculated density of states is presented in Fig. 6. The Fermi energy is not well determined in this model, because this work is pointed to the study of the instabilities originated by the neighborhood of the Fermi level in one of the singularities. If we assume that the position of the Fermi level is at the bonding π-band, two empty states with p-d symmetry can be reached. The energy difference between the experimental Fermi level and structures A and B is of the order of magnitude of the estimated separation between the Fermi level and the
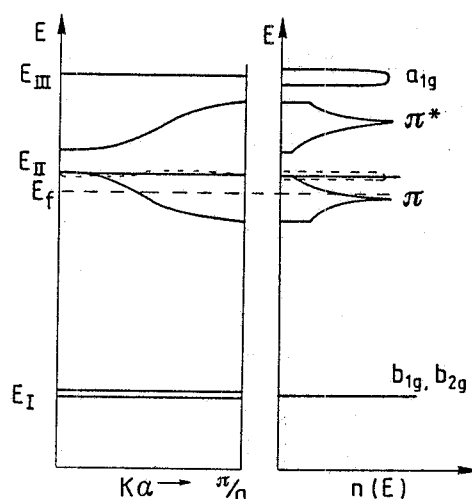

FIG. 6 - Schematic structure of d(Mn)-p(X) band in the $K\alpha$ direction (α=x,y,z) and calculated density of states.

unoccupied π^* and $E_I(a_{1g})$ bands[11]. The difference between E_0-A is $\sim$3 eV and between E_0 and B $\sim$ 7 eV. Therefore we assign the peak A to the unoccupied π^* band and peak B to the a_{1g} band.

The experimental results can be discussed in the context of this model. Hybridization between Mn and N or C is evident. Indeed, points i) and iii) show that the hybridization between Mn and C atoms is greater than that of Mn-N showing a more localized character in the cabride compounds as could be expected from the model. On the other side, comparison between the Me-K spectra shows that a mixing of p-orbitals of N/C with the Me atom is also important (see the difference between Mn_3GaC and Mn_3GaN). This effect had not been considered by the model.

The effect of metal substitution appears in two ways. First, our experiment shows that mixing of the s-p band of the Me metal with the Mn is relevant, in fact, resonance B is strongly dependent on metal B. Again, this is not considered in the simplified model. Second the trend Cu:Zn:Ga produces a decrease of energy of peak B with the simultaneous disappearance of the peak A. This effect is correlated with the increase of the electrons supplied by the substituted metal and consequently, may be explained by a filling of the hybrid d-band. Our analysis suggest that this effect is correlated also with the interpretation of Mn_4N where is necessary to take account of two different Mn sites.

The effect of electron filling of bands with the atomic substitution follows the evolution of the magnetic susceptibility measurements in these compounds[5,6]. The observed effect in susceptibility appear in the Curie-Weiss term, which decreases in the trend from Cu to Sn, and the same behaviour occurs in the N to C direction. Our experiment shows that the unoccupied band moves toward the Fermi level going from Cu to Sn perovskites, giving rise a larger delocalization and in consequence, a smaller Curie-Weiss term.

In tentative way we may say that the filling of the 3d-band is correlated with the electronic instability. In this sense, the transition temperature increases in the trend Mn_3CuN; Mn_3ZnN; Mn_3GaN, and the same effect can be seen, by comparison with the Sn compounds. In the case of isoelectronic compounds Mn_3GaC and Mn_3ZnN the effect of C or N hybridization is more important in the description the electronic structure, than the effect of total electronic population.

In conclusion, our experimental results agree with the proposed theoretical model, but important details not considered in this model have been found: i) There is a little mixing of the pstates of C or N with the states of the substituted metal Me. ii) The a_{1g} band is highly hybrydized with sp conduction band.

Finally, the effect of the atomic substitution in the Mn_3MeX lattice can be summarized as follows: the carbide are stronger hybridized than the nitride compounds. The effect of the metal Me manifests in a transference of electrons from the sp-band to the E_{II} band giving rise to a shift towards the Fermi energy of the π^* sub-band.

ACKNOWLEDGEMENTS

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