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Report:

The long term project (LTP) HE1534 was intended to pursue our exploration of resonant Raman scattering (RRS) of soft x-rays and of its newest and most advanced applications. In particular we have been focussing on the use of RRS for studying the electronic states of magnetic and strongly correlated materials. Such an advanced research is thus twofold, technical and methodological. On one side we have been upgrading our instrumentation to make new experiments technically feasible, on the other we have been applying RRS both to prototypical samples and to advanced materials to test the actual capabilities of the methods under development.

The LTP had two main branches: integrated resonant Raman scattering (IRRS) and high resolution resonant inelastic x-ray scattering (RIXS). We present here a report for both after having used already $\frac{3}{4}$ of the beam time originally allocated. Rather than organising the report chronologically we will summarise the main results obtained on each of the two subjects, starting from the technical achievements.

IRRS

The integrated RRS spectroscopy is based on a partial x-ray emission detected at selected angles with respect to the incident photon beam and to the sample magnetisation and/or crystallographic orientation. The spectroscopic variable is the incident photon energy, so the IRRS spectra look somehow similar to x-ray

absorption spectra although their meaning is very different. Using IRRS we have extensively studied the magnetic circular dichroism in the perpendicular geometry of 3d metal magnetic systems: when the sample magnetisation is orthogonal to the incident beam no circular dichroism is measured in absorption at the $L_{2,3}$ edges of the 3d metal, but a sizable signal is measured when detecting at an angle the photons issued from the 3s-2p radiative decay of the 2p holes. The magnetic circular dichroism measured at the resonance is an effect genuinely coming from the second order nature of the excitation-deexcitation process. We have exploited the angular dependence of the dichroism to use the special sum rules applicable to RRS under the fast collision approximation and leading to the estimate of the quadrupolar, octupolar and hexadecapolar atomic moments of the scattering atom in its ground state¹. During the LTP this type of measurements have been further developed. In addition we have measured linear dichroism spectra in IRRS at the Ce $M_{4,5}$ edge by selecting the 4f-3d deexcitation channel and a 90° scattering geometry.

Technical development.

An IRRS apparatus exploiting filters to energy discriminate the scattered photons was developed during the HE1088 LTP, which allows to detect the IRRS signal along any emission direction over the whole 2p region outside the sample surface. The filter approach used for the previous measurements is extremely versatile as far as the angle dependence has to be explored, however it does not allow measuring samples where an energy resolution better than ~80 eV is needed. These are the cases of Fe or even worse of Mn in the ferrites, where the Oxygen fluorescence introduces strong artefacts in the measurements. To overcome this limitation, we developed a new apparatus where a multilayer mirror (ML) acts as a continuously tuneable energy selective device in the energy range between 400 and 1000 eV. The reflection at the ML also adds selectivity for the linear polarization of the emitted photons. This allows, for the first time, the realization of the so-called “complete” experiment in RRS, where the energy and the polarization are defined for both the exciting and emitted photon. FIGURE 1, left panel, shows the detailed characterization of the resolution and relative reflectivity of the ML with respect to the linear polarization (parallel or perpendicular to the mirror surface) of the photons. The intrinsic ML resolution varies between 10 eV at 400 eV (38° incidence) and 34 eV at 1000 eV (15°). This resolving power was decreased by tuning the sample-ML distance in order to get a band pass of ~50 eV needed to integrate over the whole energy range of the emission channel. The ratio of the reflectivity scales roughly with a $\cos^2(2\theta)$ law characteristic of the reflection from a single surface.

Magnetic Circular Dichroism (MCD) in perpendicular geometry.

The sum rule analysis of IRRS magnetic circular dichroism (MCD), which had already been applied in the test case of Co in Co ferrite (CoFe_2O_3)¹, was extended to Ni in the Ni ferrite (NiFe_2O_3) allowing a quantitative comparison with the theoretical predictions of the Hund’s rule and of a cluster model. The results are extensively described in reference² from where FIGURE 2 is reported. The ML was then exploited to measure the IRRS signal from Co and Fe in the metal and in the Co ferrite. FIGURE 1, right panel, shows the spectrum taken on Co metal extrapolated for full linear polarization selectivity of the analyser. The dichroism of the photons emitted with electric field parallel to the scattering plane³ has the same shape obtained with the filter approach in the previously published data¹, whereas nearly no dichroism is present when the photons have electric field perpendicular to the scattering plane. This behaviour comes from the polarisation of the core hole in the intermediate state and can be explained by a qualitative model taking into account the symmetry of the scattering process, as explained in a future work.

Linear Dichroism (LD) in 90° scattering.

The versatility provided by the multilayer was exploited to study the linear dichroism (LD) in the IRRS of Cerium compounds having different Kondo temperature, i.e. different hybridisation between 4f localized and 5d extended states. LD in the RIXS of Cerium systems measured with our emission spectrometer AXES had confirmed the theoretically predicted relation between LD and the 4f occupation⁴. Namely, LD is stronger for the $4f^0$ configuration of total angular momentum $J = 0$ than for the $4f^1$ configuration ($J = 5/2$) due to the rules imposed by J conservation. The dependence of LD upon the excitation energy was studied in the present experiment on polycrystalline samples of CeAl_2 , CeRh_2 , and of the solid solution $\text{CeSn}_{1-x}\text{In}_x$ (CeSn_3 , CeIn_3 , CeIn_2Sn , CeInSn_2). Spectra of 4f-3d valence emission were recorded at incident energy across the 3d edge, with vertically and horizontally polarized incident light. The scattering angle was 90°. FIGURE 3 shows results for the two most different systems: in CeRh_2 the occupation of the 4f states is ~0.8 due to the strong 4f-5d hybridization, CeAl_2 is less hybridized, with a 4f occupation close to 1. LD is observed in both compounds along the whole energy range. The most noteworthy feature is the presence of the spectral

structure at ~ 6 eV above the main peaks in CeAl_2 excited with vertical light. This structure is the signature of the $4f^0$ component in X-ray absorption. Accordingly, it is absent in the XAS of CeAl_2 and is pronounced in CeRh_2 . Its presence in the V spectrum of CeAl_2 indicates a strong selectivity of IRRS at 90° to the $4f^0$ ground state component. Finally, similar effects to those of FIGURE 3 were seen by collecting the Total Fluorescence emission from the sample, at 90° scattering angle without the energy analysis by the multilayer. This points to important anisotropy effects in the emission. The presented results are currently being analyzed.

RIXS

Technical development.

During the LTP we have further upgraded the instrumentation for high resolution RIXS in the soft x-rays. The dedicated monochromator (PoLIFEMo) has been working since March 2004 with a single new plane grating in place of the three spherical gratings previously installed. The new grating has higher groove density (1400 l/mm) and a variable groove density that allows us to cover the whole energy range with a single grating. The greater dispersion and the groove density law brought a gain in energy resolution at all energies, a widening of the available range down to 400 eV and a resolving power more homogeneous over the whole range. Together with an upgrade of the energy scanning mechanics and of the exit slits, the change of the grating led to a considerable improvement of the monochromator in terms of energy resolution (180 meV at 600 eV, 300 meV at 1000 eV, 400 meV at 1200 eV) and of ease of use (better reproducibility and stability of the absorption spectra). The $E/DE > 3000$ was obtained through a loss in efficiency going from 2 to 5 for the higher and lower energies respectively: nonetheless in most of the cases a high quality spectrum does not require more than 20 minutes of accumulation time. In FIGURE 4 a spectrum of MnO, measured in drain current with the new grating demonstrates the good performances of the monochromator (NB: PoLIFEMo cannot be used with a point per point I_0 re-normalisation due to its special lay out, where the exit slit is only a few mm before the sample).

Another important modification was the replacement, in the spectrometer AXES, of the CCD detector. A 25.4×6.4 mm² CCD has been working since November 2003: the smaller pixel size (13.5 μm instead of 20 μm) and the lower working temperature (-70°C instead of -55°C) gave a gain in spectral quality and eliminated completely the problems of dark current subtraction.

dd excitations of simple 3d metal oxides.

After the first measurements on cuprates that gave the first evidence of the excellent performances of PoLIFEMo+AXES (already reported on HE1435 and in reference [5]) we have explored with L_3 RIXS the electronic excitations of some paradigmatic 3d metal mono-oxides: CuO, NiO, CoO, MnO. The data quality is excellent and demonstrates that at present the energy resolution of our RIXS spectra is much better than in any other published data. In particular we measured a combined FWHM of 620 meV, 550 meV, 440 meV and 320 meV at Cu (930 eV), Ni (850 eV), Co (780 eV) and Mn (640 eV) respectively. Some spectra of NiO and MnO are presented in FIGURE 5, where the effects of the change in the incident photon linear polarisation are also clearly visible. These spectra can be effectively used to refine the parameters in various models of the electronic structure: crystal field, cluster model, Anderson impurity model. The analysis and interpretation work is being made for NiO and MnO, also in collaboration with the group of A. Kotani for the theoretical and computational aspects⁶.

Crystal field effects in manganites.

In order to exploit the sensitivity of L_3 RIXS to the local coordination and nearest neighbour distances (*dd* excitation energies are directly determined by those local properties) we have measured two series of manganite samples with similar stoichiometry but different crystalline parameters. In one case we chose $\text{La}_{0.7}\text{X}_{0.3}\text{MnO}_3$, where X = Ca, Sr, Ba. The different size of the divalent X cations leads to different average cubic cell size (chemical pressure) clearly detectable in x-ray diffraction. The samples were thin films grown by pulsed laser deposition at the university of Roma Tor Vergata by the group of G. Balestrino. Despite the difficulties in recognising the character of the *dd* excited states in those doped compounds where Mn^{3+} and Mn^{4+} are both present a clear trend in the crystal field cubic parameter $10Dq$ can be seen: going from Ca (smallest ion) to Ba (biggest ion) the effective $10Dq$ gets reduced. A careful analysis of the Mn L_3 RIXS spectra (some of them are shown in FIGURE 6) is being done within a single configuration atomic model with crystal field⁷. Similarly we measured Mn L_3 RIXS on a series of samples with identical composition ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) but grown on different substrates in order to induce different biaxial strains. The samples

were prepared by molecular beam epitaxy at the University of Salerno by the Group of L. Maritato. The RIXS spectra are very different from those of the other samples and the interpretation of their shape is still not completed.

¹ L. Braicovich, A. Tagliaferri, G. van der Laan, G. Ghiringhelli, and N. B. Brookes., PRL **90**, 117401 (2003).

² G. van der Laan, G. Ghiringhelli, A. Tagliaferri, N. B. Brookes, and L. Braicovich, Phys. Rev. B **69**, 104427 (2004).

³ L. Braicovich, G. Ghiringhelli, A. Tagliaferri, G. van der Laan, E. Annese, and N.B. Brookes, submitted to Phys. Rev. Lett.

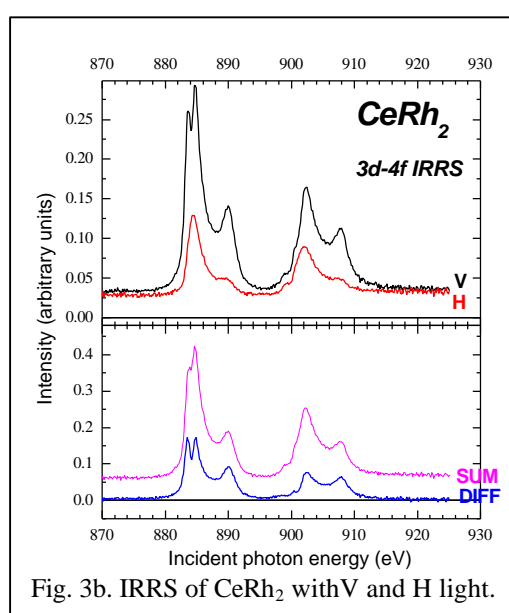
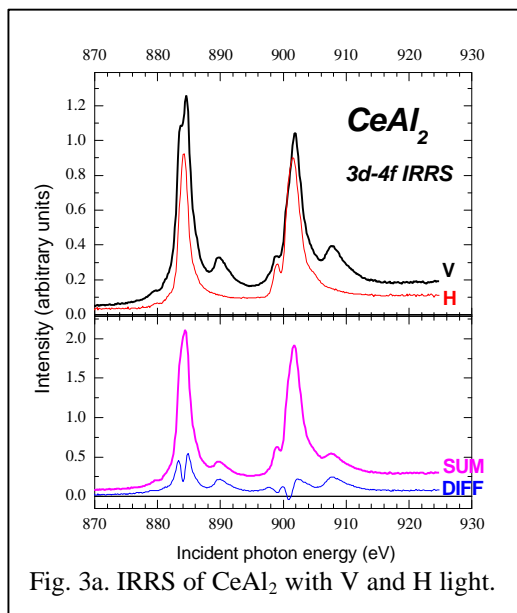
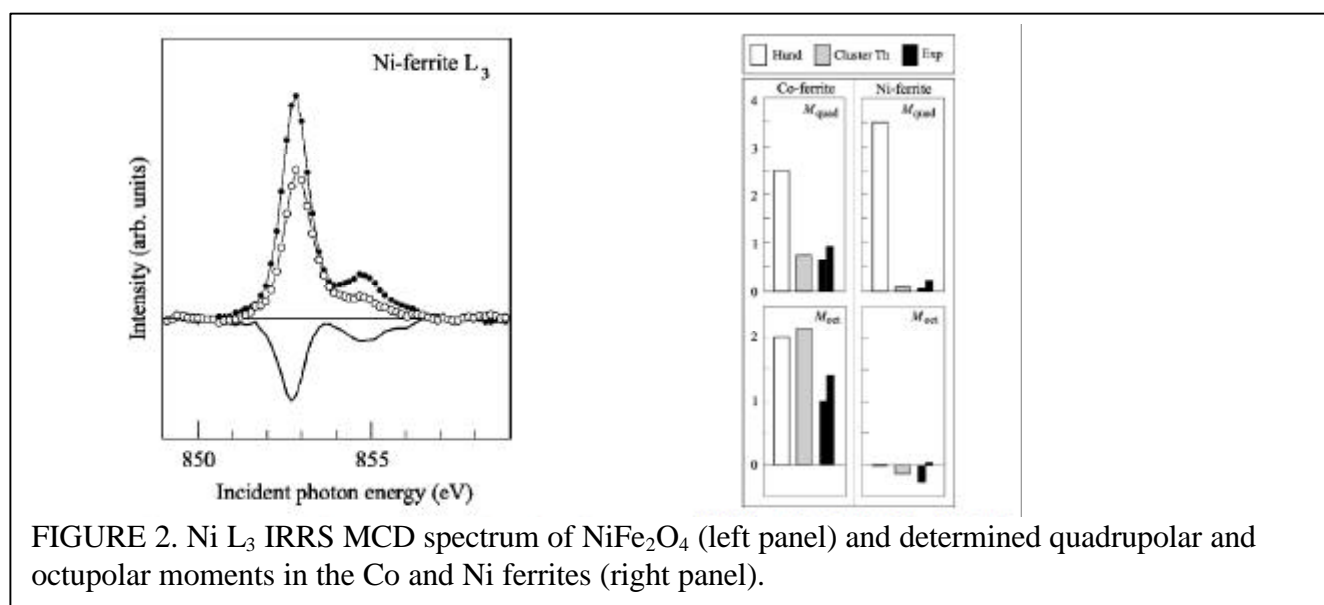
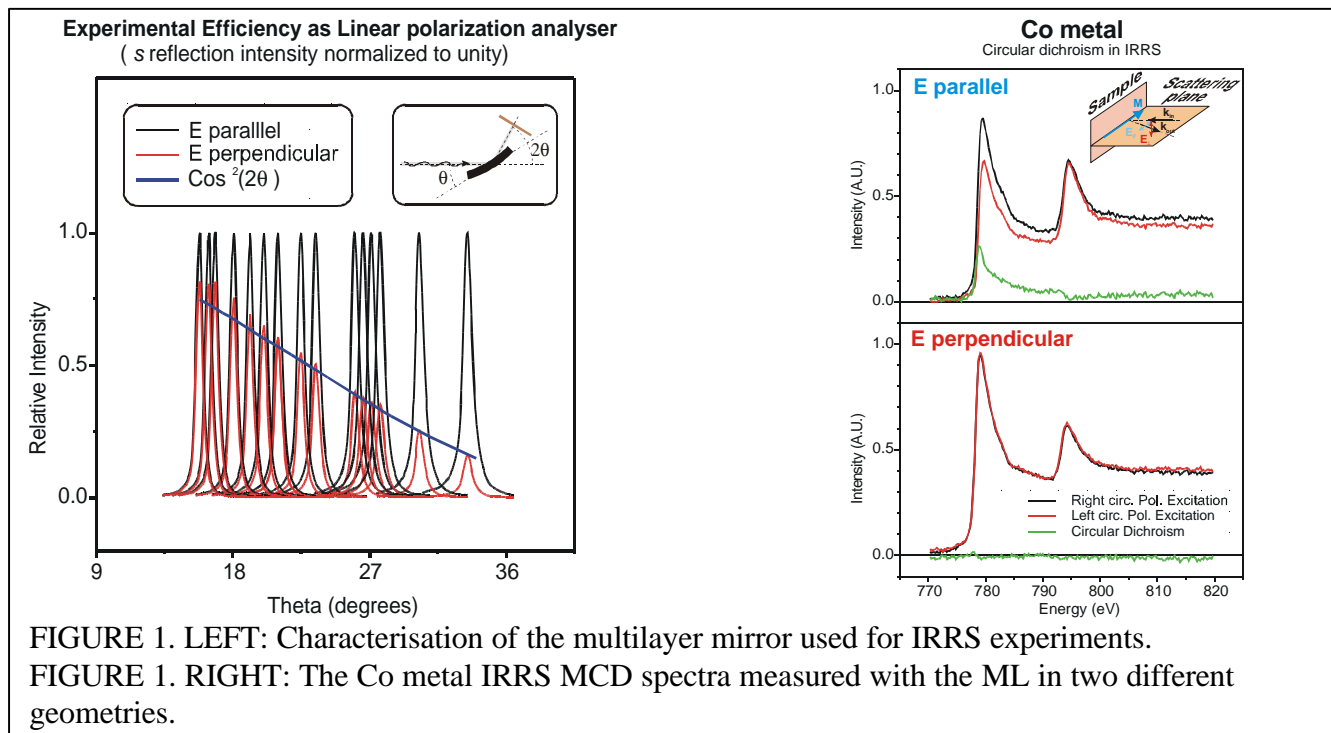
⁴ C. Dallera, M. Marcon, G. Ghiringhelli, A. Tagliaferri, N.B. Brookes, G. Olcese, A. Palenzona, L. Braicovich., "Study of bulk ground state properties of Cerium intermetallics by linear dichroism in 4f Resonant Inelastic X-ray Scattering", *Solid State Communication*, 121, 635-640 (2002). C. Dallera, M. Grioni, A. Palenzona, M. Taguchi, E. Annese, G. Ghiringhelli, A. Tagliaferri, N.B. Brookes, Th. Neisius, L. Braicovich, " α - γ transition in metallic Ce studied by resonant x-ray spectroscopies", Phys. Rev. B **70**, 085112 (2004).

⁵ G. Ghiringhelli, N. Brookes, E. Annese, H. Berger, C. Dallera, M. Grioni, L. Perfetti, A. Tagliaferri, and L. Braicovich, Phys. Rev. Lett. **92**, 117406 (2004).

⁶ G. Ghiringhelli, L. Braicovich, N.B. Brookes, C. Dallera, F. Fracassi, R. Gusmeroli, A. Kotani, M. Matsubara, Ogasawara, A. Tagliaferri, to be submitted to J. Phys. Cond. Mat.

⁷ G. Ghiringhelli, C. Aruta, G. Balestrino, L. Braicovich, N.B. Brookes, C. Dallera, A. Piazzalunga, A. Tagliaferri, A. Tebano, unpublished.

FIGURES



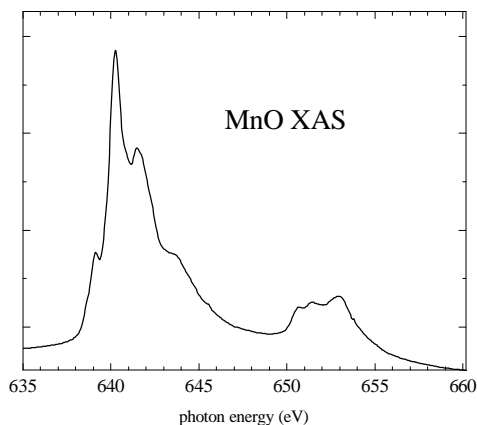


FIGURE 4: Example of $L_{2,3}$ XAS spectrum measured with PoLIFEMo after the change of the grating.

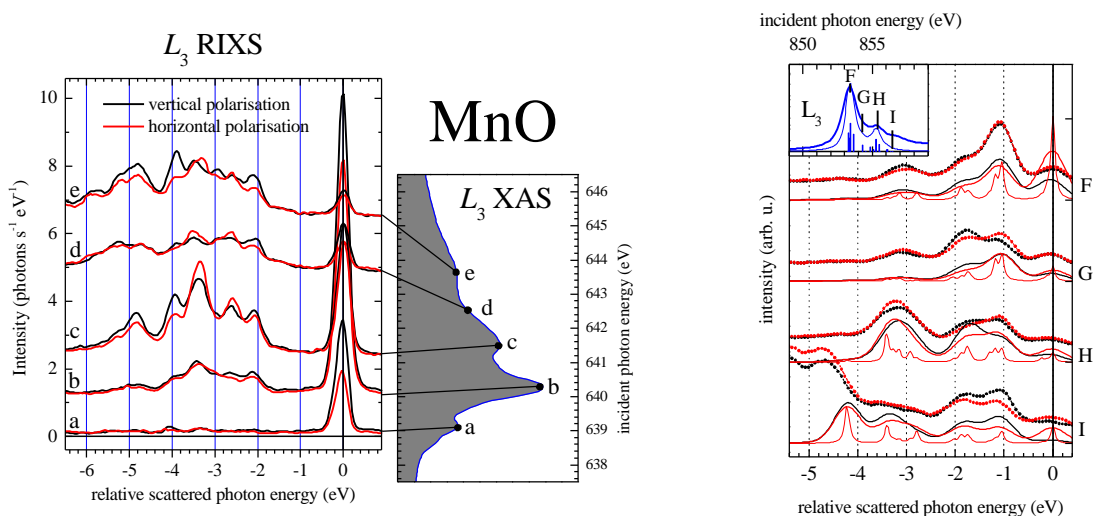


FIGURE 5. LEFT: The measured RIXS spectra measured at four different excitation energies across the Mn L_3 edge using vertical and horizontal linearly polarised incident photons.

RIGHT: Comparison of experimental and calculated (crystal field model) Ni L_3 RIXS spectra of NiO.

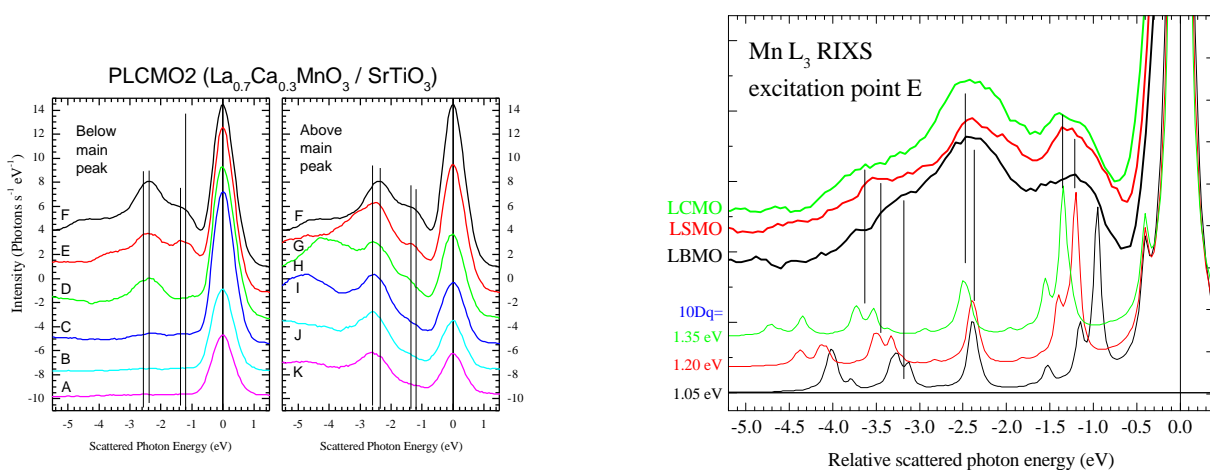


FIGURE 6. Mn L_3 RIXS spectra measured on $\text{La}_{0.7}\text{X}_{0.3}\text{MnO}_3$, where $\text{X} = \text{Ca}, \text{Sr}, \text{Ba}$ and some tentative calculations made in crystal field model for a Mn^{3+} ion.