



Measurement of Quadrupole Interactions in LaMO_3 ($M = \text{Cr, Fe, Co}$) Perovskites by TDPAC

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Abstract. The perturbed angular correlation (PAC) technique has been used to study the electric field gradient (EFG) in LaCoO_3 perovskite. The results are compared with those for LaCrO_3 , LaFeO_3 measured earlier. The PAC probe, $^{111}\text{In} \rightarrow ^{111}\text{Cd}$, was introduced in the oxide lattice by means of chemical reaction during sample preparation. In the present work, the temperature dependence of the electric quadrupole interaction parameters, for LaCoO_3 was investigated. The resulting systematics of EFG at ^{111}Cd , in $\text{La}(\text{Cr, Fe, Co})\text{O}_3$ perovskites, reveals a linear dependence with temperature.

Key words: quadrupole interaction, perovskite oxides, perturbed γ – γ angular correlation.

1. Introduction

Perovskite oxides of 3d transition metal of the type RMO_3 , where R is a rare-earth element, are found to exhibit a rich variety of unusual and interesting transport, magnetic and structural properties. In general, the structure of an ABO_3 type perovskite is characterized as a cubic closest-packed array of oxygen anions and large cations A with small cations B occupying the octahedral interstitial sites. The ideal cubic structure is distorted by cation size mismatch and becomes orthorhombic or rhombohedral. Goldschmidt [1] defined a tolerance factor $t = (A - O)/\sqrt{2}(B - O)$ to describe perovskite structures. The factor t is unity for an ideal cubic structure. For $t < 1$ the space group symmetry is lowered from cubic to tetragonal, rhombohedral, or orthorhombic. At room temperature LaCrO_3 and LaFeO_3 have an orthorhombically distorted perovskite structure of the type GdFeO_3 that changes to rhombohedral at high temperature (~ 500 K for LaCrO_3 and ~ 1200 K for LaFeO_3 perovskite). LaCrO_3 is a weak antiferromagnet below ~ 300 K [2] while LaFeO_3 is a canted antiferromagnet with high transition temperature of about 743 K [3]. LaCoO_3 crystallizes in a distorted rhombohedral structure and also shows interesting changes in the electronic and magnetic properties as a function of temperature. One of the important properties of LaCoO_3 is its unusual temperature dependent magnetic susceptibility, which increases with temperature and shows a maximum around 90 K and then becomes Curie–Weiss like.

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Although the structural as well as the magnetic phase-transition behavior of the LaCrO_3 , LaFeO_3 and LaCoO_3 perovskites has been confirmed by other techniques, only a few microscopic studies on atomic scale have been reported. Recent microscopic investigations of perovskites ABO_3 [3–7] were carried out through determination of the electric field gradient (EFG) and magnetic hyperfine field (MHF) with probes located at A and B sites by time differential perturbed angular correlation (TDPAC) technique and have shown the power of this method to follow changes such as bond distances, symmetry and defect trapping on microscopic scale. In the present work, TDPAC measurements were performed in the LaCoO_3 perovskite, at different temperatures, using $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ probe to obtain information about the phase transition and the temperature dependence of EFG at Co sites.

2. Experimental

Stoichiometric polycrystalline samples of LaCoO_3 were prepared from a mixture of lanthanum nitrate and cobalt nitrate solutions. Approximately 20–30 μCi of carrier free ^{111}In (as InCl_3) was added and the solution was slowly evaporated to dryness. The resulting powder was pressed into small pellets and sintered for 5 hours at 1300 K in air, ground to a powder and sintered again at temperatures between 1600 and 1700 K for 5 hours in air. The powder samples were analyzed by the X-ray-diffraction method.

The hyperfine interaction of the 245 keV, $5/2^+$ spin state of the ^{111}Cd probe nuclei in the polycrystalline samples has been measured by the TDPAC technique utilizing the 171–245 keV γ – γ cascade. TDPAC spectra were recorded at several temperatures using a standard set up with four conical BaF_2 detectors arranged in a planar 90–180° geometry, generating simultaneously 12 coincidence spectra. The detector system had a time resolution of ~ 600 ps. A small tube furnace was used for the measurements above room temperature and the temperature was controlled to within 2 K. For low temperature measurements the sample was attached to the cold finger of a closed-cycle-helium refrigerator with temperature controlled to better than 0.1 K. The perturbation function $R(t)$ was calculated from the coincidence spectra and fitted to $R(t) = A_{22} \sum_i f_i G_{22}^i(t)$ where A_{22} is the unperturbed angular correlation coefficient, f_i are the fractional site populations and $G_{22}^i(t)$ are the corresponding perturbation factors for the static quadrupole interaction in polycrystalline material. The perturbation factor $G_{22}(t)$ is given in terms of the primary frequencies ω_n and their amplitudes S_{2n} which are related to the hyperfine splitting of the intermediate nuclear level and depend on the spin-independent quadrupole frequency $\nu_Q = eQV_{zz}/h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{xx} , V_{yy} and V_{zz} are the elements of the EFG tensor in its principal axis system. Q is the nuclear electric quadrupole moment of the intermediate level. The known quadrupole moment of 0.83 b for $I = 5/2^+$ intermediate level of ^{111}Cd has been used to determine V_{zz} .

3. Results and discussion

The powder X-ray diffraction pattern for LaCoO_3 measured at room temperature was analyzed using Rietveld method and confirmed a single phase. The result showed a rhombohedral structure for LaCoO_3 with no contaminating phases. The measured crystallographic lattice constants for hexagonal LaCoO_3 are $a = 5.4399 \text{ \AA}$, $c = 13.0846 \text{ \AA}$ corresponding to the space group $R\bar{3}c$. The X-ray pattern was refined with the La-cations at $6a$ (0, 0, 1/4), Co-cations at $6b$ (0, 0, 0) and oxygen anions at $18e$ (0.45136, 0, 1/4). With respect to the cubic symmetry, the O anions are twisted around the crystallographic direction [111] making the symmetry trigonal D_{3d}^6 . The CoO_6 octahedron is slightly compressed along the hexagonal c -axis. Whenever the tolerance factor t is only slightly less than unity in ABO_3 perovskites, a cooperative rotation of the corner shared BO_6 octahedra about [111] reduces the symmetry from cubic to rhombohedral. The tolerance factor for LaCoO_3 is 0.971.

Figure 1 shows the perturbation function for LaCoO_3 measured at 725 K with ^{111}Cd probe along with respective Fourier transform. Similar results for LaFeO_3 and LaCrO_3 samples measured at 1324 K and 295 K respectively are included in this figure for comparison. Below respective Néel temperatures, TDPAC spectra for LaCrO_3 and LaFeO_3 samples showed combined magnetic and electric hyperfine interactions [7]. No long-range magnetic order was observed for LaCoO_3 up to 13 K.

The measurements for LaCoO_3 cover the temperature range from 13–987 K. Where as two distinct electric quadrupole interactions were observed in

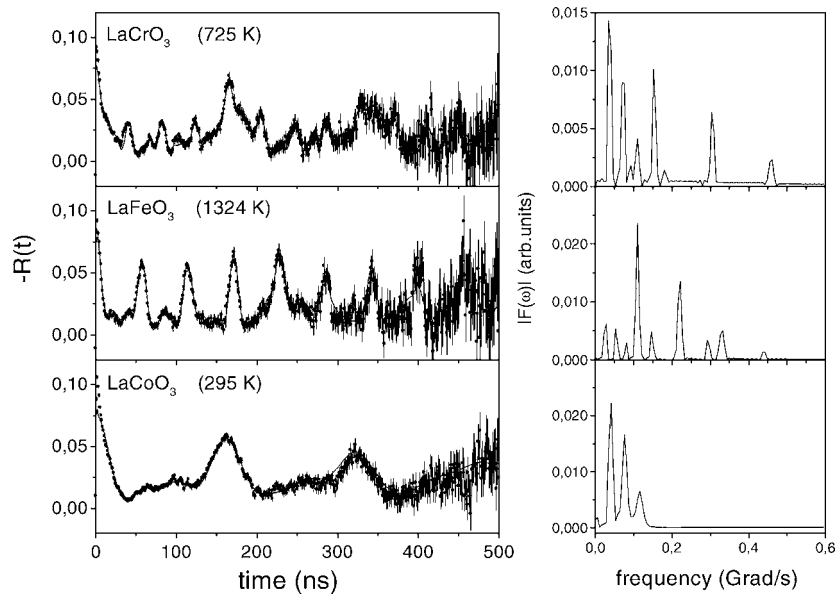


Figure 1. TDPAC spectra and their respective Fourier transforms for perovskite samples in rhombohedral phase measured at temperatures indicated in each case.

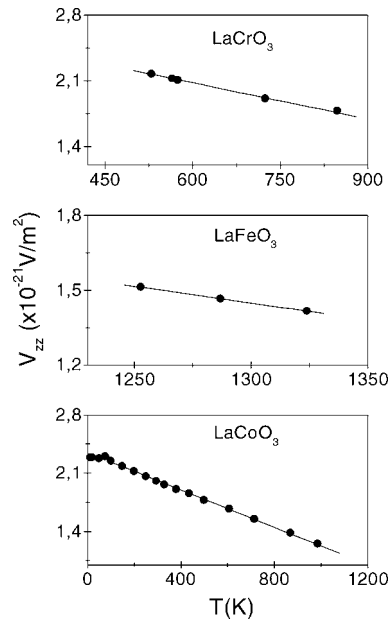


Figure 2. Temperature dependence of EFG for ^{111}Cd probe nuclei at Cr, Fe and Co sites in perovskite samples. Solid lines represent a least square fit of a function $V_{zz}(T) = V_{zz}(0)(1 + CT)$ to the data points.

$\text{La}(\text{Cr,Fe})\text{O}_3$ compounds, corresponding to the ^{111}Cd probes occupying Cr(Fe) atom and La atom sites respectively [7], the spectra for LaCoO_3 show only one major fraction with a sharp frequency and a highly distributed minor component. This fact may be related to the effect of sintering temperature on the fractional site occupation. In the previous study of $\text{La}(\text{Cr,Fe})\text{O}_3$ perovskites [7], it was observed that the fraction of ^{111}Cd nuclei occupying Cr(Fe) site relative to the La site changes with sintering temperature used in the preparation of the sample. Preliminary results of a PAC study of LaMnO_3 perovskite, carried out with the ^{111}Cd probe, in our laboratory has shown that in this compound also the probe nuclei occupy Mn atom site predominantly.

We have associated the observed quadrupole frequency ν_Q (295 K) ~ 40 MHz to the ^{111}Cd probe substituting Co atoms in LaCoO_3 . This assignment is essentially based on the results of earlier PAC measurements in $\text{La}(\text{Cr,Fe})\text{O}_3$ perovskites [3, 7] where the observed higher quadrupole frequency (~ 140 MHz) was associated with La site while smaller frequency (~ 30 MHz) was assigned to Cr(Fe) sites. Since the observed quadrupole frequency in LaCoO_3 at 295 K is very close to those obtained for Cr(Fe) in $\text{La}(\text{Cr,Fe})\text{O}_3$ perovskites, we assigned it to ^{111}Cd probe at Co site. The origin of the highly distributed minor component is unknown.

Figure 2 shows the temperature dependence of EFG for ^{111}Cd nuclei at Cr(Fe,Co) sites in LaCrO_3 , LaFeO_3 and LaCoO_3 , respectively. The EFG values in the case of LaCrO_3 and LaFeO_3 refer to the distorted rhombohedral phases, which

are stable in these compounds above 530 K and 1253 K, respectively, [7]. The temperature dependence of EFG for ^{111}Cd at Co site observed in LaCoO_3 follows closely the trends observed in LaCr(Fe)O_3 . In all the perovskites, the temperature dependence of EFG could be fitted with a linear relationship $V_{zz}(T) = V_{zz}(0)(1 + CT)$, with coefficient C determined as $-4.5(1) \times 10^{-4} \text{ K}^{-1}$, $-4.2(1) \times 10^{-4} \text{ K}^{-1}$ and $-4.8(1) \times 10^{-4} \text{ K}^{-1}$, for LaCr(Fe,Co)O_3 samples, respectively. We conclude from these results that the distortion of the transition metal octahedra (CrO_6 , FeO_6 and CoO_6) as a function of temperature is similar and shows strong dependence of the EFG on local oxygen coordination. This observation further indicates that the ^{111}Cd probe substituting the transition metal atoms on the center of the MO_6 octahedra does not distort the ionic array in the surroundings. The temperature dependence of the EFG for the LaCoO_3 did not show any symmetry related structural changes around temperature of 600 K within the measured temperature range as has been speculated in some earlier studies.

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References

1. Goldschmidt, V., *Geochemistry* Clarendon Press, Oxford, 1958.
2. Tezuka, K., Hinatsu, Y., Nikamura, A., Inami, T., Shimojo, Y. and Morii, Y., *J. Solid State Chem.* **141** (1998), 404.
3. Rearick, T. M., Catchen, G. L. and Adams, J. M., *Phys. Rev. B* **48** (1993), 224.
4. Rasea, R. L. and Catchen, G. L., *Phys. Rev. B* **58** (1998), 3218.
5. Roth, J., Uhrmacher, de la Pressa, P., Ziegeler, L. and Lieb, K. P., *Z. Naturforsch* **55a** (2000), 242 and references therein.
6. Catchen, G. L., Evenson, W. E. and Allred, D., *Phys. Rev. B* **54** (1996), R3679.
7. Dogra, R., Junqueira, A. C., Saxena, R. N., Carbonari, A. W., Mestnik, J. and Morales, M., *Phys. Rev. B* **63** (2001), 224 104.