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Temperature dependence of electric field gradient in $LaCoO_3$ perovskite investigated by perturbed angular correlation spectroscopy

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Abstract

The time differential perturbed angular correlation (TDPAC) technique was used to study the temperature dependence of electric field gradient (EFG) in $LaCoO_3$ perovskite using $^{111}In \rightarrow {}^{111}Cd$ and $^{181}Hf \rightarrow {}^{181}Ta$ nuclear probes. The radioactive parent nuclei ^{111}In and ^{181}Hf were introduced into the oxide lattice through a chemical process during sample preparation and were found to occupy only the Co sites in $LaCoO_3$. The PAC measurements with ^{111}Cd and ^{181}Ta probes were made in the temperature range of 4.2–1146 K and 4.2–1004 K, respectively. No long-range magnetic order was observed up to 4.2 K. The EFGs at ^{111}Cd and ^{181}Ta show very similar temperature dependences. They increase slowly between 4.2 and about 77 K and then decrease almost linearly with increasing temperature until about 500–600 K, where a broad peak-like structure is observed, followed by linear decrease at still higher temperatures. These discontinuities at about 77 K and 500–600 K have been interpreted as thermally activated spin state transitions from the low-spin ($t_{2g}^6e_g^0$) ground state configuration to the intermediate-spin ($t_{2g}^5e_g^1$) state and from the intermediate-spin to the high-spin ($t_{2g}^4e_g^2$) state of the Co^{3+} ion, confirming previous observation in other recent studies. An indication of a Jahn–Teller distortion, which stabilizes the intermediate-spin state with orbital ordering, is also pointed out.

1. Introduction

$LaCoO_3$ has attracted much attention in the past few decades because of the peculiar way its lattice, electronic and magnetic properties change with temperature [1–7] as well as due

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In the present work, in order to obtain microscopic information on its electronic properties, the temperature dependence of quadrupole interaction (QI) in the $LaCoO_3$ perovskite has been investigated using the time differential perturbed angular correlation (TDPAC) technique. PAC measurements offer the possibility to follow changes such as bond distances, local symmetry, trapping of defects etc, as a function of temperature [19, 20]. Sample preparation is therefore the most important aspect in perovskite materials as defects can be produced altering the characteristics of these materials. Recently, in order to attain homogeneity, stoichiometry and high density, several ceramic preparation techniques based on chemical routes such as the citrate gel process, co-precipitation and complex compound process have been employed. We adopted one of the chemical processes [20] to synthesize polycrystalline samples of $LaCoO_3$. This process offers a unique way to introduce the radioactive probe ions homogeneously in the sample and this homogeneity is retained even after sintering at high temperatures. PAC measurements were performed in $LaCoO_3$ at different temperatures using a $^{111}In \rightarrow {}^{111}Cd$ probe to obtain information about the temperature dependence of QI at cation sites. Additional measurements, using a $^{181}Hf \rightarrow {}^{181}Ta$ probe, were also carried out to observe the effect on QI of the substitution of host cations with impurity probes having different chemical properties. The preferences for the occupation of La^{3+} and Co^{3+} sites in $LaCoO_3$ are likely to be distinct for In^{3+} and Hf^{4+} ions.

2. Experimental procedure

Polycrystalline samples of $LaCoO_3$ were prepared from a mixture of lanthanum nitrate $La(NO_3)_3$ and cobalt nitrate $Co(NO_3)_3$ solutions. The $La(NO_3)_3$ was prepared by dissolving a known quantity of La_2O_3 (99.9%) in concentrated HNO_3. The required quantity of $Co(NO_3)_3$ solution obtained by dissolving metallic Co (99.99%) in concentrated HNO_3 was then added to the $La(NO_3)_3$ solution to obtain a homogeneous aqueous solution. Approximately 20–30 μCi of carrier free ^{111}In was added and the whole solution was slowly evaporated to dryness. The resulting powder was pressed into small pellets and sintered for 5 h at 1300 K in air. The pellets were ground to a powder and sintered again at about 1600 K for 5 h in air. The radioactive ^{181}Hf probe was introduced in the $LaCoO_3$ sample using a similar procedure. Approximately 1 mg of Hf metal (99.9%) was irradiated with thermal neutrons at the IEA-R1 research reactor at IPEN for about 30 h and then dissolved in a couple of drops of HF to obtain a dilute solution. About 20–30 μCi of this solution containing ^{181}Hf was added to the mixture of $La(NO_3)_3$ and $Co(NO_3)_3$ solutions which was dried and sintered as described above.

The powder samples of $LaCoO_3$ were analysed by the x-ray diffraction method to verify the crystal structure and presence of any contaminating phase. The TDPAC technique was used to measure the quadrupole interaction in the polycrystalline sample of $LaCoO_3$ using ^{111}Cd and ^{181}Ta probe nuclei. The PAC method is based on the hyperfine interaction of nuclear moments with extra-nuclear magnetic fields or EFGs. A detailed description of this method can be found in [21]. γ–γ cascades of (171–245) keV and (133–482) keV, populated in the electron capture decay of ^{111}In and β^- decay of ^{181}Hf respectively, were used to measure the quadrupole interaction of the 245 keV ($5/2^+$) spin state of ^{111}Cd and the 482 keV ($5/2^+$) spin state of ^{181}Ta. TDPAC spectra were recorded at several temperatures using a standard set-up with four BaF_2 detectors [20].The PAC measurements were carried out in the temperature range of 4.2–1146 K for the sample containing $^{111}In \rightarrow {}^{111}Cd$ probe and 4.2–1004 K for the sample containing $^{181}Hf \rightarrow {}^{181}Ta$ probe. A small tubular furnace was used for heating the sample 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 measurements at 4.2 K were

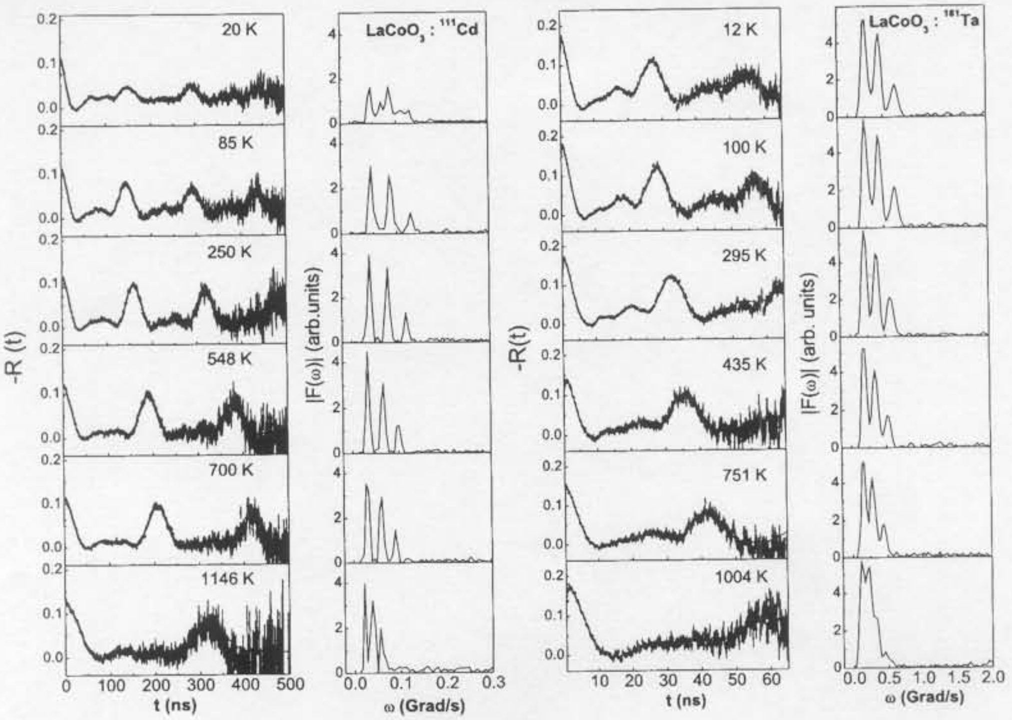

Figure 1. Perturbation functions with corresponding frequency spectra for ^{111}Cd and ^{181}Ta probe nuclei in $LaCoO_3$ perovskite at various temperatures. Solid lines are the least squares fit of the theoretical function to the experimental data.

made by immersing the sample in liquid helium. Details of PAC data acquisition and analysis of quadrupole interaction in a polycrystalline sample are described in [20].

3. Experimental results

The powder x-ray diffraction pattern of the $LaCoO_3$ sample measured at room temperature was analysed and refined using the Rietveld method. The results confirmed a single phase having rhombohedral structure. The measured crystallographic lattice parameters for hexagonal $LaCoO_3$, $a = 5.4399$ Å and $c = 13.0846$ Å, corresponding to the space group $R\bar{3}c$, show good agreement with earlier x-ray and neutron diffraction measurements [5, 22].

Some of the perturbation functions with respective fast Fourier transforms, measured at different temperatures using ^{111}Cd and ^{181}Ta probes, are shown in figure 1. The PAC spectra were least square fitted in both cases using an appropriate theoretical perturbation function [20]. Measurements carried out with the ^{111}Cd probe show a predominant fraction with well resolved quadrupole interaction at all temperatures. A second minor fraction was observed only at temperatures below ~300 K. We have associated the major interaction with ^{111}Cd nuclei substituting for Co sites in $LaCoO_3$. This assignment is essentially based on the results of a previous PAC measurement in $LaCrO_3$ and $LaFeO_3$ [20] where the $^{111}In \rightarrow {}^{111}Cd$ probe was introduced in the samples by the same chemical process as in the present case. In these perovskites the ^{111}Cd probe atoms were found to substitute both La as well as Cr(Fe) sites with characteristic quadrupole frequencies of about 140 and 30 MHz respectively at room temperature. The higher quadrupole frequency (~140 MHz) was assigned to the ^{111}Cd nuclei to the existence of a insulator to metal transition. The unusual behaviour of these properties, believed to be associated with the spin state transitions of cobalt ions, is not fully understood yet. $LaCoO_3$ is a charge transfer type nonmagnetic insulator at low temperature [8], crystallizing in a rhombohedrally distorted perovskite structure with space group $R\bar{3}c$ [3, 9, 5]. One of the important properties of $LaCoO_3$, which attracted the attention of many investigators, is the unusual temperature dependence of its magnetic susceptibility.

The main controversy has involved the interpretation of two broad transitions in the magnetic susceptibility observed near 90 and 600 K. Neutron diffraction studies of $LaCoO_3$ [10, 2] showed that no long-range magnetic ordering exists down to 4.2 K, indicating that in the ground state Co^{3+} ion has a low-spin nonmagnetic configuration $t_{2g}^6e_g^0$ with $S = 0$. The first explanation for the anomalous behaviour of the magnetic susceptibility was given by Goodenough [1], who described the system as undergoing a transition around 90 K from the low-spin (LS) state to a thermally activated high-spin (HS) state, $t_{2g}^4e_g^2$, with $S = 2$. The crystal field splitting [11] is almost equal to the intra-atomic exchange interaction energy and this causes the spin state transition in $LaCoO_3$ as a function of temperature. The concentration of thermally excited high-spin Co^{3+} configurations increases smoothly with temperature [6]. The second anomaly was later [3, 6] interpreted as an order–disorder transition with a symmetry change to $R\bar{3}$, where electrons are more itinerant and destroy the LS–HS state ordering. As this symmetry change was not experimentally confirmed, such a picture of the traditional ligand field model, where only two spin states are expected, was not sufficient to explain the two anomalies in the magnetic susceptibility.

In a work [12] where a related compound $SrCoO_3$ was investigated, it was proposed that an intermediate spin (IS) state, $t_{2g}^5e_g^1$, with $S = 1$ can be stabilized by hybridization between oxygen 2p orbitals and the Co 3d states. Based on the possible existence of such an IS state, the second anomaly in the susceptibility was then explained [13, 7] as a thermally activated transition between the IS and HS state in $LaCoO_3$. This description was also supported by calculations [14] based on the LDA + U approach of the electronic structure in $LaCoO_3$. The calculations indicated that the IS state is indeed stabilized by a strong hybridization between Co e_g and O 2p orbitals and found to be only slightly higher in energy than the LS state but much lower than the HS state. As the difference in energy was too high to explain the second transition, it was suggested that the degeneracy of the e_g levels is lifted in the IS state by a Jahn–Teller (JT) distortion of the structure at lower temperatures. Recent measurements [15] of magnetic susceptibility and thermal expansion indicated a lack of orbital degeneracy up to 500 K, attributed to a local JT distortion of the CoO_6 octahedra. Many structural investigations [3, 5, 16] carried out in a wide temperature range via neutron or x-ray diffraction have reported the rhombohedral $R\bar{3}c$ symmetry and have failed to detect structural transitions for $LaCoO_3$. Very recently, two independent experiments [17, 18] using high-resolution synchrotron x-ray absorption spectroscopy (XAS), however, reported a monoclinically distorted $I2/a$ symmetry for $LaCoO_3$ below 300 K, interpreted as a consequence of a cooperative JT effect.

The different interpretations of the scenarios involving the spin state of the Co ion in $LaCoO_3$, mainly the existence itself and nature of the IS state, must be unambiguously determined. It is expected that a change in the spin state of cobalt would result in a corresponding change in the octahedral Co–O bond length. A detailed study of $LaCoO_3$ as a function of temperature therefore becomes necessary with some suitable microscopic technique using an appropriate probe at the cobalt ion site. In particular, techniques based on hyperfine interaction, like perturbed gamma–gamma angular correlation for instance, would be helpful in this case because it can measure the local electric field gradient, which is very sensitive to slight structural changes around the probe.

occupying the La site and the smaller frequency (~30 MHz) to the probe atoms occupying Cr(Fe) sites (see [20] and references therein for details). Since we observed a well defined quadrupole interaction in $LaCoO_3$ characterized by a frequency of ~40 MHz, quite close to that observed for Cr(Fe) sites in $LaCr(Fe)O_3$ perovskites, we believe that the observed interaction in $LaCoO_3$ also results from the ^{111}Cd nuclei occupying the Co atom sites. The second quadrupole interaction felt by a minor fraction of nuclei appears only at temperatures below ~300 K. Here we rule out the possibility of this interaction originating from ^{111}Cd nuclei occupying the La site as the observed quadrupole frequency is much smaller than the corresponding values reported for $LaCr(Fe)O_3$ perovskites [20]. At present, we do not know the exact origin of this fraction. We believe that this interaction is probably due to some impurity or defect in the crystal structure or corresponds to a minor structural phase change not detected by normal x-ray measurements. PAC data, however, indicate that for these sites the distortion of the CoO_6 octahedra is larger than the normal Co sites. While we shall focus our attention on the major interaction, a possible explanation of this minor fraction will be presented briefly later.

It is somewhat surprising that the ^{111}Cd nuclei substitute only Co atoms in $LaCoO_3$ while both La and Cr(Fe) sites are substituted in the analogous perovskites $LaCr(Fe)O_3$. However, the effect of sintering temperature on the relative site occupation probability investigated in detail in a previous study [20] has shown that the relative fraction of ^{111}Cd nuclei occupying Cr(Fe) or the La atom site is quite sensitive to the temperature at which the oxide is sintered. It is therefore quite possible that the thermal treatment received by the $LaCoO_3$ sample eventually determined the observed site preference.

As in the previous case a well defined major quadrupole interaction was observed for the measurements with ^{181}Ta probe. A second minor interaction was also observed in this case for temperatures below ~300 K. The major interaction with a room-temperature quadrupole frequency (ν_Q) of 200 MHz was assigned to the ^{181}Ta probe nuclei occupying Co sites. For this assignment we have used the conclusions of a recent PAC study of $LaMnO_3$ using the ^{140}Ce probe [23]. It was shown, by comparing the measured hyperfine field of ^{140}Ce at La (see [23] for details) with the ^{181}Ta field obtained in an earlier PAC work on $LaMnO_3$ [24], that the assignment of the ^{181}Ta probe to the Mn site suggested by Rasera *et al* is not consistent with the experimental results. In fact all the available experimental evidence [20, 25], as well as a recent theoretical calculation of mhf at Mn in $LaMnO_3$ [26], clearly indicates that ^{181}Ta occupies the La site and not the Mn site in $LaMnO_3$. Since the observed quadrupole frequency of the order of 1000 MHz for the ^{181}Ta probe in $LaMnO_3$ is [24, 27] much higher than the value of 200 MHz determined for $LaCoO_3$ in the present study, we conclude that in $LaCoO_3$ the ^{181}Ta substitutes Co atoms rather than La.

The temperature dependences of the quadrupole frequencies, determined with $^{111}In \rightarrow {}^{111}Cd$ and $^{181}Hf \rightarrow {}^{181}Ta$ nuclear probes, are shown in figures 2 and 3, respectively. The temperature dependences are quite similar for the two probes. The quadrupole frequencies (ν_Q) are quite sharp and slowly increase between 4.2 and ~50–75 K (see inset (a) in figures 2 and 3) and then gradually decrease with temperature. The asymmetry parameter and the frequency distribution are small and do not change much with temperature. Typical values for both probes are $\eta \sim 0.2$ and $\delta \leqslant 5\%$, respectively. The average value of the asymmetry parameter for ^{181}Ta is however slightly larger than the value for the ^{111}Cd probe. The quadrupole interaction with minor fraction, observed below 300 K in both cases, shows wider frequency distribution. Below 100 K, the fractional site population as well as the frequency distribution increased with decreasing temperature.

The low-temperature PAC measurements down to 4.2 K did not show any evidence of a combined magnetic and quadrupole interaction in either case. We therefore conclude

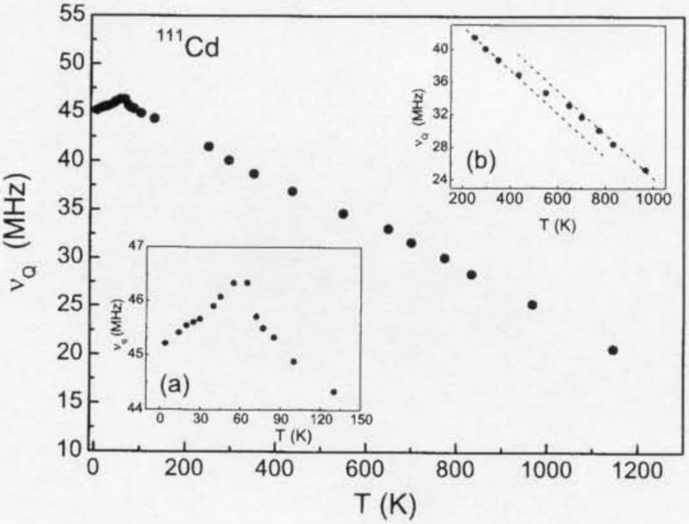

Figure 2. Temperature dependence of the fitted quadrupole frequency corresponding to the major fraction for ^{111}Cd probes at the Co site in LaCoO$_3$ perovskite.

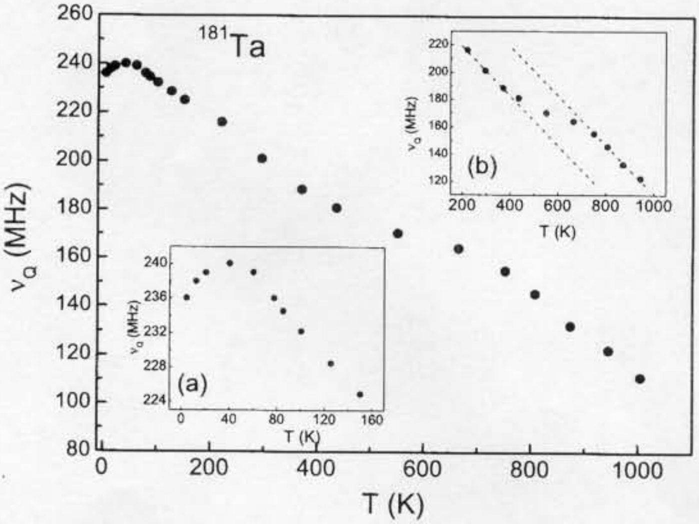

Figure 3. Temperature dependence of the fitted quadrupole frequency corresponding to the major fraction for ^{181}Ta probes at the Co site in LaCoO$_3$ perovskite.

in agreement with the previous findings [2, 10] that at low temperature the LaCoO$_3$ is nonmagnetic. The temperature dependence of the quadrupole frequency gives an indication of a slight discontinuity around 600 K (see inset (b) in figures 2 and 3). This and the other discontinuity observed around 60–70 K will be discussed later. While the basic features of the temperature dependence of the hyperfine parameters are similar for ^{111}Cd and ^{181}Ta probes, there is a noticeable difference. The discontinuity in the temperature dependence of the quadrupole frequency around 600 K is more pronounced for ^{181}Ta. This difference may be attributed to distinct chemical characteristics of the probe impurities Ta^{5+} and Cd^{2+} used to investigate the local charge distribution, which apparently show different sensitivities to their local environment in $LaCoO_3$.

The crystallographic structure of $LaCoO_3$ is rhombohedral with a threefold symmetry axis at the Co site. An axially symmetric EFG is therefore expected. The observed EFG at ^{111}Cd and ^{181}Hf probe nuclei substituting regular Co ions comes mainly from six surrounding oxygen ions as first nearest neighbours. Small but non-zero values of the asymmetry parameter at all temperatures suggest that the EFG principal axis at the Co site is not exactly aligned with the crystallographic axis and the CoO_6 octahedra suffer a slight distortion resulting from the introduction of probe atoms. PAC measurements in similar perovskites $LaCrO_3$ and $LaFeO_3$ have also shown such effects [20, 25]. Small line broadening indicates that most of the probe nuclei occupy substitutional Co sites in the host lattice. The possibility of some impurities and defects, however, cannot be completely ruled out. The observed line broadening is therefore not unusual.

4. Discussion

The temperature dependence of the quadrupole frequency (ν_Q) is similar for ^{111}Cd and ^{181}Ta probes. The results show a wide peak-like structure in the region from 30 to 80 K, as seen in insets (a) in figures 2 and 3. A second discontinuity is seen at about 500–600 K, which is barely visible in the case of ^{111}Cd (inset (b) in figure 2) but clearly observed for the data taken with the ^{181}Ta probe (inset (b) in figure 3). Discontinuities at these temperatures were observed earlier in the magnetic susceptibility data [15]. These discontinuities were attributed to a thermally induced spin state transition in Co atoms from a low-spin (LS) nonmagnetic state ($t_{2g}^6e_g^0$) at around 50–75 K to an intermediate-spin (IS) state ($t_{2g}^5e_g^1$) and then from the intermediate-spin (IS) state to the high-spin (HS) state ($t_{2g}^4e_g^2$) at around 500–600 K [15, 16].

Except for a small increase in the value at around 500–600 K, the quadrupole frequencies decrease almost linearly, above ~100 K, with increasing temperature (see figures 2 and 3). The slope of the curves for the linear decrease is almost the same before and after the discontinuity around 500–600 K, as shown in inset (b) in figures 2 and 3. This behaviour is similar to one observed for the crystal structure data obtained through neutron diffraction measurements [5, 16]. The structural parameters as well as the volume per formula unit increase monotonically with increasing temperature, except around 500–600 K, where the increase is somewhat more pronounced. Since the electric quadrupole interaction at the probes substituting Co sites results mainly from the six surrounding O^{2-} ions forming an octahedron, a general increase in all the bond lengths resulting from thermal expansion of the crystal lattice is expected to reduce the quadrupole frequencies. However, at around 50–75 K and 500–600 K, where the LS–IS and IS–HS transitions take place, one can observe a sudden increase in the quadrupole frequencies. In this temperature region the spin-state transitions provoke a sudden increase in the Co ionic radius, which results in an increase in the Co–O bond length. As a consequence, the O atoms are pushed towards the probe atoms. Reduced O–probe distance produces an increase in the quadrupole frequency.

Magnetic susceptibility [15] as well as neutron scattering studies [16] have revealed an anomalous behaviour in the temperature dependence of the thermal expansion of $LaCoO_3$. The lattice constant exhibits a steep increase with increasing temperature above about 50 K in addition to the normal thermal expansion expected for a solid [7]. The anomalous thermal expansion in $LaCoO_3$ has been explained in terms of thermally induced spin transition from the LS nonmagnetic ground state to the mostly IS state of Co^{3+} ions. This anomaly in the thermal expansion is followed by TDPAC measurements in both probes.

As mentioned previously, the PAC results with both probes showed a second minor fraction at temperatures below 300 K. This fraction with slightly higher quadrupole frequency showed much broader frequency distribution compared to the main fraction. The site fraction as well as the frequency distribution were found to increase below 100 K. We believe that this interaction is due to ^{111}Cd and ^{181}Ta nuclei probing a neighbourhood which is somewhat different from that of the major fraction. High-resolution x-ray diffraction measurements [17] have recently reported that $LaCoO_3$ exhibits a monoclinic distortion in structure in the temperature range of 20–300 K. This distortion is caused by a cooperative Jahn–Teller effect that induces the long-range ordering of e_g orbitals. We suggest that the observed minor fraction represents a mixture of LS and IS states of Co^{3+} ion in the neighbourhood of nuclear probes as a consequence of the Jahn–Teller distortion in the structure. This mixture is also responsible for the observed broader frequency distribution. As the temperature goes down below 300 K the probability of mixed states increases, resulting in the growth of the second fraction. A mixture of LS and IS states was also suggested by the result of recent x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) using synchrotron radiation [18]. Above 300 K, our results show a single fraction with very small distribution for both probes. From this result we conclude that, whereas a small fraction of mixed LS–IS states appears below 300 K, after the LS–IS transition the system stabilizes in a pure JT distorted IS state. Around 600 K the thermal expansion also induces a second transition to a pure HS state.

It is known that $LaCoO_3$ is a nonmagnetic insulator at low temperature, usually referred to as a low-spin state with atomic configuration ($t_{2g}^6e_g^0$) of Co^{3+} ions. The intra-atomic exchange interaction and the octahedral crystal field splitting are comparable and the energy difference E_{LS}–E_{IS} between the low-spin Co^{III} ($t_{2g}^6e_g^0$) state and intermediate-spin Co^{3+} ($t_{2g}^5e_g^1$) state is small. Hence, an LS–IS transition is likely to take place with increasing temperature due to the thermal excitation. The change of the spin state with increasing temperature results in the formation of more and more IS Co^{3+} ions where electrons are promoted from t_{2g} to e_g orbitals. As a consequence, a Jahn–Teller distortion occurs inducing a change in the symmetry from $R\bar{3}c$ to $I2/a$, leaving the system as a mixture of LS and IS states for a broad temperature range of around 20–300 K. As e_g orbitals (d_z^2 and $d_{x^2-y^2}$) concentrate electron density along the octahedral Co–O bonds, an increase in the electron density in these orbitals causes repulsive electrostatic interaction between these electrons and O^{2-} anions resulting in longer Co–O bonds. As increasing numbers of electrons are promoted to the IS state with increasing temperature, the Co–O bond distance increases rather smoothly with temperature. The JT distortion stabilizes the IS state as the e_g orbitals are no longer degenerate and they are spatially ordered. The lifting of the degeneracy of e_g orbitals promotes the second transition to a metallic high-spin Co^{3+} ($t_{2g}^4e_g^2$) state. Increasing bond distances with increasing temperature, as described above, should naturally lead to decreasing EFG at ^{111}Cd and ^{181}Ta probes at the Co site, in agreement with the present observation.

5. Conclusion

Extensive PAC measurements were performed in order to microscopically investigate the electronic and structural properties of $LaCoO_3$ perovskite using ^{111}In → ^{111}Cd and ^{181}Hf → ^{181}Ta probes. The present measurements have shown that the parent probe nuclei ^{111}In as well as ^{181}Hf substitute only cobalt atom sites in $LaCoO_3$. While it is well known that ^{181}Hf replaces only transition metal atom sites in similar perovskites, the result for ^{111}In contrasts with that obtained for $LaCr(Fe)O_3$ perovskites, where this probe was observed to substitute for La as well as Cr(Fe) sites. The preference for only Co sites in $LaCoO_3$ has been attributed to a different thermal treatment received by the samples. The PAC measurements were performed in the temperature range from 4.2 to 1146 K using the ^{111}Cd probe and from 4.2 to 1004 K using the ^{181}Ta probe, and in both cases the principal quadrupole interaction was assigned to the probe nuclei occupying substitutional Co atom sites. The temperature dependence of the hyperfine parameters is found to be very similar for the two probes in the entire range and clearly shows two transitions at around 50–75 K and 500–600 K, which were identified as transitions from the LS state to the IS state and from the IS state to the HS state, respectively. A highly distributed second interaction is observed in both cases below 300 K. Although the origin of this component is not well understood at present, we rule out the possibility of this being assigned to the probe nuclei substituting the La site. We suggest that this minor fraction observed only at lower temperatures is due to mixed spin states of cobalt ions induced by a JT distortion in the local structure. PAC measurements carried out up to 4.2 K did not show magnetic interaction, indicating the absence of long-range magnetic order in $LaCoO_3$.

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