Characterizing transition metal perovskites with PAC spectroscopy

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Among the several experimental techniques based on different principles available to investigate the materials, the microscopic techniques based on hyperfine interaction form a subclass that characterizes a material at the smallest possible atomic scale. After an introduction to the basic properties of the transition metal perovskites of type $ABO_3$, the hyperfine interactions along with hyperfine technique such as Perturbed Angular Correlation (PAC) have been briefly described in this paper. The characteristics of the materials analyzed have been expressed in terms of internal magnetic hyperfine fields, electric field gradients and the microscopic point symmetry at the probe site. In particular in this review, a special attention has been paid to the information that can be obtained from a PAC spectroscopy applied to perovskite materials, which may help to understand the microscopic nature of different physical environments around the probe nucleus.

While the fever of superconductivity is still not over, the transition metal oxides of type $ABO_3$ ($A$= mostly light rare earths and Ca, Ba, Sr, Bi, Pb, Li; $B$= transition metals) with perovskite structures again disturbed the whole scientific community with a new surprising and fascinating structural, magnetic and electronic properties (e.g. coupling of spins, charge ordering, metal-insulator transitions, low-spin to high-spin transitions, giant-magneto-resistance and Colossal-magneto-resistance). In particular, the perovskite oxides have been intensively investigated in the recent past because of their extensive use as material for inter-connector of solid oxide fuel cells, IR detector, piezoelectric transducers, electrodes for magneto-hydrodynamic power generators, refractory conducting materials, conducting leads for ZrO$_2$ based heating elements, ferro-electric memory devices and thin film multi-layer capacitors. So far, a definitive agreement does not exist on the mechanism that give rise to the origin of all these vast number of properties in the perovskites, the studies carried through until the moment relate many of these properties mainly to the variations of crystalline structures of these materials and, coupling between $B$(nd) and O(2p) orbitals.

Although the ideal perovskite structure is cubic with largest A cations located at the center of each unit cell, B cations occupying the eight vertices of the cell and the oxygen anions at the center of each edge of the unit cell forming two sublattices: A and BO$_6$ (see Fig. 1a), the archetypal cubic symmetry is rarely encountered. The ideal cubic structure is distorted by cation size mismatch and Jahn-Teller effect, whereby a distortion of oxygen octahedron surrounding the B cation splits the energy level of a ‘$d$’ ion into triply degenerate $t_{2g}(d_{xy}, d_{xz}, d_{yz})$ and doubly degenerate $e_g(d_{z^2}$ and $d_{x^2-y^2}$) levels, thus lowering the energy. The magnitude of distortion depends upon the ionic size and bond character of the mixed oxide. For the distorted perovskite systems of type $ABO_3$, a certain

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Thus, to understand deeply the mechanism that give received a distinguished recognition in solid state available. This technique using appropriate probes at A and B sites is material research, provides information on the local microscopic scale if some suitable microscopic leads to unusual magnetic and electronic properties. A changes the valence of transition metal ion and thus become necessary to disclose details on microscopic scale if some suitable microscopic technique using appropriate probes at A and B sites is available.

The hyperfine interaction studies, which have received a distinguished recognition in solid state material research, provides information on the local environment by observing magnetic and electric hyperfine interactions. The measurements like heat capacities, electric and magnetic susceptibilities, neutron and X-ray diffraction derived parameters in perovskite materials represent only gross averages over the atomic scale properties of these materials. It is the hyperfine spectroscopy, which probes the strength and symmetry of the local crystal fields at the microscopic scale. The basic principles of the technique involve interaction of the nuclear electromagnetic moments (electric-quadrupole moment \( Q \) and magnetic-dipole moment \( \mu \)) with the electromagnetic fields (electric field gradient EFG and magnetic hyperfine field MHF) arising from the extra-nuclear electronic charge and spin distributions in the crystal lattice. The hyperfine interaction measurements in solids directly give corresponding electromagnetic coupling energy of the nucleus, namely (i) electric quadrupole interaction, and (ii) magnetic hyperfine interaction.

Several techniques [Mössbauer effect (ME), nuclear orientation (NO), nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), electron spin resonance (ESR) and perturbed angular correlation/distribution (PAC/PAD)], which partly compete and partly complement, have been utilized for the measurements of these hyperfine interactions. Because of several advantages (like temperature insensitive, smaller impurity-impurity interactions) of perturbed angular correlation technique over others, it is better suited to follow phenomena as a function of temperature (many perovskites show magnetic ordering and phase transition phenomena at high temperature). Moreover, the perturbed angular correlation technique has been successfully applied in the past decades to investigate electrically ordered and magnetically ordered perovskite materials. Basically, this technique is based on the correlation between emission directions of two successive radiations emitted during a nuclear decay cascade and thus, the method requires an introduction of radioactive probe nuclei into a specific site in the crystal lattice of interest and subsequently measuring the hyperfine interactions at those sites. For practical reasons (e.g. concerning radiochemistry, anisotropic \( \gamma-\gamma \) cascade population, the half-life of the intermediate level, nuclear electromagnetic moments of the intermediate state), the most favourable PAC probes at present are very few and are summarized in Table 1 along with their useful nuclear properties.
Table I—Properties of PAC probe nuclei. T1/2, I, T1/2, Q, μ, A22 respectively represent the half life of parent nuclei, intermediate spin, half life of intermediate spin level I, quadrupole moment intermediate level I, magnetic moment of intermediate level I and anisotropy of the γ-γ cascade under consideration.

| Probe                  | T1/2 (ns) | I   | T1/2 (ns) | γ-γ (keV) | Q (μN) | |A22| (%) | Production                  |
|------------------------|-----------|-----|-----------|-----------|--------|-----|------|----------------------------|
| 48Ti EC→ 48Sc          | 48        | y   | 1         | 153       | 78-68  | 0.18 | 0.344| 4.5 | 48Sc(p,2n)48Ti             |
| 99Mo EC→ 99Tc          | 67        | h   | 5/2       | 3.6       | 740-181| 0.23 | 0.384| 4.5 | 99Mo(n,γ)99Mo              |
| 99Rh EC→ 99Ru          | 16        | d   | 3/2       | 20.5      | 528-90 | 0.23 | 0.284| 22  | 99Ru(d,2n)99Rh             |
| 3.6 d 2+              | 2         | 215 | 84-75     | 0.076     | 4.324  | 16   | 103Rh(p,4n)106Pd           |
| 7.5 d 5/2+            | 84.5      | 95-247| 0.83    | 0.765     | 13    | 110Pd(n,γ)110Pd            |
| 2.8 d 5/2+            | 84.5      | 173-247| 0.83    | 0.765     | 18    | 109Ag(α,2n)111In           |
| 49 m 5/2+             | 84.5      | 95-247| 0.83    | 0.765     | 16    | 110Cd(n,γ)110Cd           |
| 8.3 m 3/2+            | 91-1095   | 2.87 | 0.65     | 172Yb(p,n)172Lu |
| 2.87 d 5/2+          | 10.8      | 133-482| 2.35    | 2.57     | 23    | 186W(n,γ)186W             |
| 2.9 h 9/2+           | 554       | 480-134 | 3.3    | 5.11     | 12    | 186W(n,γ)186W             |

A more detailed description of the PAC technique can be found elsewhere. A typical PAC set-up is shown in the Fig. 2. After the emission of first γ-ray, the nucleus starts to live in an intermediate state with spin direction I (t = 0) and during this time the nuclear electromagnetic moments (Q or μ) interact with the hyperfine fields (MHF or EFG) at the probe nucleus. This interaction causes the probe nucleus to reorient and to emit a second γ-ray in a direction different than if no hyperfine field is present at the probe nucleus and, the spin changes to direction Q (b) after time Δt through an angle Δθ. In a semi-classical picture, this effect is known as precession of the nuclear spin around the direction of the hyperfine field with precession frequency proportional to Δθ/Δt which results from the torque originated by hyperfine fields acting on the electromagnetic moments. This measurable effect...
perturbs the spatial angular correlation of the $\gamma$-rays and forms a basis for PAC spectroscopy.

In practice, PAC measurements are sensitive to both electric quadrupole interactions and magnetic hyperfine interactions. The static electric quadrupole interactions provide a measure of the strength and symmetry of the crystal field in the vicinity of the probe nucleus. In this case, since the vibrational motion of the atoms in the lattice is very rapid relative to the PAC timescale, the measured EFG appears to arise from the time-averaged positions of the atoms, and the sharpness of the spectral lines reflects the "motional narrowing" effect. In contrast to static interactions, time-varying interactions arise when the EFG fluctuates during the intermediate-state lifetime. These interactions provide information about defect and ionic transport. The effect of the fluctuating EFG is to destroy the orientation of the intermediate level which appears as attenuation of the angular correlation. On the other hand, the magnetic hyperfine interactions, which can be measured in ferromagnetic/antiferromagnetic and paramagnetic materials, are used to study the effects of defects and lattice distortions in materials that have cubic symmetry. The general approach is to measure the magnetic hyperfine interaction in a material with few defects. The cubic symmetry requires that the electric quadrupole interaction vanish. When either defects or distortions are produced, a quadrupole interaction attenuates the usually well-defined magnetic interactions, the analysis of which can provide information about the type of defect that produced the quadrupole interaction.

Since the hyperfine fields are dominated by contributions from electronic charges and spins within the first few atomic distances around the probe atom, the more distant charges and spins only contribute to inhomogeneous broadening of signals, the precession frequencies can be used to characterize the different local atomic environments around the probe atoms. Once such a frequency has been identified with an underlying environment, it can be utilized to study the following phenomena: (i) phase transformations: multiphase analysis, (ii) structural and magnetic phase transitions: critical behaviour and exponents, (iii) magnetism: spin dynamics, stability of atomic magnetic moments, (iv) surfaces and interfaces: nano-materials, and (v) point defects: their types, properties, interactions, radiation and implantation damage and hydrogen trapping at defect sites in metals.

It has been learned through past experience in different types of materials that (a) if the charge distribution around the probe nucleus has cubic symmetry, the EFG is zero, (b) if the charge distribution around the probe nucleus has axially symmetric environment (e.g. trigonal, hexagonal and tetragonal), the EFG is non-zero and asymmetry parameter is zero, (c) if probe nucleus has surroundings of lower symmetry (e.g. orthorhombic, monoclinic, triclinic), both EFG and asymmetry parameter are non-zero, and (d) besides, a probe nucleus symmetrically surrounded by neighbours with anti-ferromagnetically coupled magnetic moments will probably feel a zero or small hyperfine field, whereas ferromagnetically coupled surroundings will give considerably higher value.

Thus, the transition metal perovskites, which exhibit variety of structures, offer very good candidates to investigate these observations through PAC technique, which is highly sensitive to local structure variations.

**Experimental Procedure**

**PAC probe chemistry**

It is the probe atoms that play a very decisive role in the PAC experiments. The major problem in these experiments is that of sample preparation, that is mainly doping of host material with probe atoms, without changing the properties of the host metals. The PAC experiments can be performed with radioactive probe atoms at concentrations much lower than 1 ppm. To dope a material with the radioactive probe atoms, following procedures can be used: (i) implantation of accelerated radioactive ions into the sample, (ii) thermal treatment of the sample, so that the probe atoms are introduced via diffusion or melting, and (iii) through chemical reaction. The advantage of the first procedure is its applicability to all isotopes even in the case of low solubility of probes atoms into host, e.g., alkali metals in rare-earths or vice versa. With the help of sufficiently high implantation energies, the surface layers of the metal can be easily overcome. Second procedure leads to well-defined metallurgical state of the impurity in the respective metal. The third procedure is well suited to metal-oxides (e.g.
delafossite $\text{ABO}_x$, perovskite $\text{ABO}_3$, and ferrites $\text{AB}_2 \text{O}_4$, which can be prepared through chemical reaction (citrate gel process, co-precipitation and complex compound process) and during sample preparation, the required quantity of radioactive probe can be added. The radioactive material is detected at time $\tau$. The delafossite complex compound process and during sample coincidence counting rate when succeeding $\gamma$-ray is detected by the scintillation detectors coupled to photo-multiplier tubes, are fed to the time-to-amplitude converter (TAC). Before feeding start and stop signals to TAC, the signals are properly corrected with the help of electronic module, differential constant fraction discrimination (DCFD). Using DCFD, the contribution from noise signals, X-rays and unwanted gamma rays can be minimized. The multi-channel analyzer records the time intervals between start and stop gamma rays, known as time distribution of nuclear lifetimes. The recorded time distribution is a lifetime decay curve modulated by the spin precessions of the nucleus by the extranuclear fields known as internal fields (magnetic hyperfine fields or electric field gradient). Measuring these time distribution curves will provide information about the internal fields present in the sample. To keep the sample at desired temperature, a specially designed tubular furnace of diameter about 3-4 cm is installed at the center of the detectors geometry. Since the smaller detector-sample distance reduces the prompt time independent baseline shift (or hard core value) that takes into account the effects of $\gamma$-rays that are not in well-defined chemical environments. $G_{22} (t)$ are the corresponding perturbation factors given by:

$$G_{22}(t) = A_{22} \sum \delta_i \frac{|S_{22}(\eta_i)|^2}{2} \exp \left(-\frac{(\delta_i \omega_m t)^2}{2} \right) \exp \left(-\frac{(\tau_i \omega_m t)^2}{2} \right)$$

PAC set-up and data acquisition

The typical three detectors PAC set-up is shown in Fig. 2, where the crystalline sample containing radioactive probe nuclei is placed at the center of the detectors assembly. The start and stop gamma rays, are detected by the scintillation detectors coupled to photo-multiplier tubes, are fed to the time-to-amplitude converter (TAC). Before feeding start and stop signals to TAC, the signals are properly corrected with the help of electronic module, differential constant fraction discrimination (DCFD). Using DCFD, the contribution from noise signals, $\gamma$-rays and unwanted gamma rays can be minimized. The multi-channel analyzer records the time intervals between start and stop gamma rays, known as time distribution of nuclear lifetimes. The recorded time distribution is a lifetime decay curve modulated by the spin precessions of the nucleus by the extranuclear fields known as internal fields (magnetic hyperfine fields or electric field gradient). Measuring these time distribution curves will provide information about the internal fields present in the sample. To keep the sample at desired temperature, a specially designed tubular furnace of diameter about 3-4 cm is installed at the center of the detectors geometry. Since the smaller detector-sample distance reduces the prompt time independent baseline shift (or hard core value) that takes into account the effects of $\gamma$-rays that are not in well-defined chemical environments. $G_{22} (t)$ are the corresponding perturbation factors given by:

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PAC measurements and analysis

Experimentally, the primary quantity measured in the PAC experiment is the time distribution $W(\theta, t)$ of $\gamma$-rays in the $\gamma-\gamma$ cascade populating intermediate level $I$ and can be obtained by recording the coincidence counting rate when succeeding $\gamma$-ray is detected at time $t$ after the first $\gamma$-ray detection at an angle $\theta$. The coincidences are generally recorded at desired temperatures using a standard set-up of BaF$_2$/NaI(Tl) detectors arranged in a planar 90°-180° geometry which has a time resolution of 0.6 ns/1.0 ns corresponding to 511 keV annihilation gamma rays of $^{22}$Na radioactive source. For polycrystalline samples, the time distribution function $W(\theta, t)$ can be written as an expansion of Legendre polynomial $P_n(\cos \theta)$.

$$W(\theta, t) = \exp(-t/\tau) \left[ 1 + A_{22} G_{22}(t) P_2(\cos \theta) + A_{44} G_{44}(t) P_4(\cos \theta) \right]$$

where time independent terms $A_{kl}$ ($k=2,4$) denote the anisotropy coefficients which contain the spatial correlation information of the $\gamma-\gamma$ cascade involved. The time dependent functions $G_{22}(t)$ and $G_{44}(t)$ depend on the nature of the extranuclear fields and contain all the desired information about the hyperfine interaction of the probe ion with its environment. In most of the cases, as $A_{44} >> A_{22}$, the higher order terms in above expression are neglected. The exponential decay factor takes into account the radioactive decay of the intermediate level having lifetime $\tau$. The numerical reduction of these distributions removes the effects of exponential decay and provides the desired experimental quantity known as spin rotation or perturbation function $R(t)$ that shows the effects of modulation and is given by:

$$R(t) = \frac{[C(180°, t) - C(90°, t)]}{[C(180°, t) + 2C(90°, t)]},$$

where $C(\theta, t)$ are the geometric mean of the coincidences taken from the spectra recorded at angles 180° and 90° respectively. In the paramagnetic phase of the material, the measured perturbation function $R(t)$ are fitted with the suitable model for the static nuclear electric quadrupole interaction:

$$R(t) = A_{22} G_{22}(t) = A_{22} \sum \delta_i f_i G_{22}(t) + C$$

here $f_i$ are the fractional site populations and $C$ is the time-independent baseline shift (or hard core value) that takes into account the effects of $\gamma$-rays that are absorbed by the sample en-route to the detectors and the effects of probe nuclei that are not in well-defined chemical environments. $G_{22}(t)$ are the corresponding perturbation factors given by:

$$G_{22}(t) = \sum_n S_{22}(\eta_n) \cos(\omega_m t) \delta_i f_i G_{22}(t) + C$$

$$x \exp \left(-\frac{(\delta_i \omega_m t)^2}{2} \right) \exp \left(-\frac{(\tau_i \omega_m t)^2}{2} \right)$$

... (3)
where the primary frequencies $\omega_n$ and their amplitudes $S_{2n}$ are related to the hyperfine splitting of the intermediate nuclear level and depend on the nuclear quadrupole frequency $\omega_Q$ and the electric field gradient tensor $V_{ij}$ ($i, j = x, y, z$), with $V$ as the electrostatic potential at the nuclear site. In the principal axis system of the EFG tensor, only the diagonal components are non-zero and $V_{xx} + V_{yy} + V_{zz} = 0$, the EFG is usually expressed in terms of largest component $V_{zz}$. The non-vanishing component of electric field gradient $V_{zz}$ is related to the quadrupole frequency $\omega_Q$ by $\omega_Q = eQV_{zz}/4I(2I-1)\hbar$ and is measured in terms of spin independent quadrupole frequency $v_Q = eQV_{zz}/\hbar$ where $Q$ is the nuclear electric quadrupole moment. The quadrupole frequency $v_Q$ is known as coupling constant that contains the information about the strength of the interaction. The deviation of the EFG from the axial symmetry is given by the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ with $0 \leq \eta \leq 1$. For $\eta = 0$, the perturbation function is harmonic and periodic, and for non-zero value of $\eta$, the oscillations in the perturbation function are periodic and non-harmonic.

The detector system should have sufficient time resolution in order to distinguish the different contributions towards observed spin rotation function. The effects of finite time resolution $\tau_R$ of detectors and the distribution of EFG with a width $\delta$ ($p=1$ and $p=2$ respectively represent Lorentzian and Gaussian type distribution) are properly taken into account in Eq. (3). In order to fit the perturbation functions measured in magnetic phase region, a known function for the combined electric and magnetic interaction in a polycrystalline sample can be used from which the quadrupole frequency $v_Q$ as well as the Larmor frequency $\omega_B = g \mu_N B_{hf}/\hbar$ can be deduced, where $g$ is the nuclear $g$-factor and $B_{hf}$ is the magnetic hyperfine field.

**Results and Discussion**

In the following, we will discuss the important informations that can be drawn from the PAC measurements in transition metal perovskites.

**Site allocations**

Since the spin rotation function $R(t)$ is characteristic of a particular surroundings around the probe nucleus, therefore if chemically different surroundings are present in a particular system the measured perturbation function will reflect an abundance of each contribution. Analysis of the observed perturbation function can make possible to separate these different contributions in the system and thus to assign these contributions to a specific positions in the system which will enable to know different occupation of the probe nuclei. The perturbation functions for LaFeO$_3$ and LaCoO$_3$ samples with $^{111}$In/$^{111}$Cd probe along with their respective Fourier transforms are shown in Fig. 3, that clearly indicating a superposition of signals from two local environments of the probe nuclei in LaFeO$_3$ and single interaction frequency in LaCoO$_3$ perovskites. The PAC spectra were least square fitted with up to two/three probe sites using theoretical perturbation function given by Eq. (2). It was observed in LaCrO$_3$ and LaFeO$_3$ compounds that the $^{111}$Cd probe nuclei prefer to substitute both at La as well as Cr(Fe) sites; the higher quadrupole frequency ($\sim$140 MHz) was assigned to La site and lower quadrupole frequency ($\sim$40 MHz) to Cr(Fe) sites. The observed quadrupole frequency at 295 K ($v_Q \sim 40.4(1)$ MHz) in LaCoO$_3$ perovskite is almost identical to those obtained at Cr(Fe) sites in LaCr(Fe)O$_3$ perovskites and therefore, we assign this to the $^{111}$Cd probe nuclei substituting the C atomic sites.

**EFG and their distributions**

In a defect free crystal where each probe nuclei in the crystal lattice interact with an identical EFG, the measurement of static probe site EFG should yield a sharp spectral lines, i.e., $\delta$ should be very small (see Fig. 3). On the other hand, measurements yield broadened lines (i.e. $\delta$ is large) when small intrinsic defects (such as point defects, disordered structure or impurities) lie in the neighbourhood of probe ion as each probe nuclei in the lattice interact with somewhat randomly varying EFG. Therefore, this large distribution in EFGs will cause a damping of the amplitudes of spin rotation pattern with increasing time. Fig. 4 shows the damped PAC spectra for La$_{1-x}$Sr$_x$CoO$_3$ perovskite using $^{181}$Hf/$^{181}$Ta probe at room temperature. In view of the large number of possible microscopic La-Sr combinations, one should expect a broad distribution in spin rotation pattern of electric quadrupole interaction leading to a strong damping. Thus, the analysis of electric quadrupole interaction in disordered materials will give hyperfine parameters that would mask the actual values.
Magnetic hyperfine field

Fig. 5a represents the spin rotation pattern for antiferromagnetically ordered perovskite LaFeO$_3$ using $^{111}$In→$^{111}$Cd PAC probe where magnetic hyperfine field for $^{111}$Cd nucleus at Fe site is observed along with electric quadrupole interaction. The observed magnetic hyperfine field at $^{111}$Cd probe nuclei is coming from the transfer of spin density from paramagnetic Fe$^{3+}$ ions to the diamagnetic Cd$^{2+}$ ion through Fe$^{3+}$-O$^2$-Cd$^{2+}$ bonds. The transfer occurs through the spin polarization of the closed Cd$^{2+}$ s-shells by magnetic neighbours as well as through the overlap of the oxygen p-orbital transferring unpaired spin density into the outermost Cd 5s-orbital. Although LaCoO$_3$ perovskite is non-magnetic even at very low temperature, doped sample (La$_{0.7}$Sr$_{0.3}$CoO$_3$; 0.1<x<1) possesses localized itinerant ferromagnetism. Fig. 5b shows the PAC pattern obtained with $^{140}$La→$^{140}$Ce probe at 8 K in La$_{0.7}$Sr$_{0.3}$CoO$_3$, showing a very slow interaction frequency. Since the quadrupole moment of the 2083 keV 4$^+_1$ state of $^{140}$Ce is known to be very small, we expect the observed interaction is only due to pure magnetic dipole interaction at the La site. The observed magnetic hyperfine field at La site in La$_{0.7}$Sr$_{0.3}$CoO$_3$ compound is small ~1.8(2)T, as relatively small spin density is likely to be transferred to Ce ion at La site from the nearest Co$^{3+}$ ions. This is due to the fact that the Co$^{3+}$-O$^2$-La$^{3+}$ exchange bond angle is approximately 90° and produces a very small overlap of oxygen orbitals with orbitals of cerium.

Local point symmetry and phase transitions

Since the PAC spectroscopy usually involves impurity atoms, which generally differ in size or charge from the atoms of the host material, the measured hyperfine parameters may differ from the one measured using identical probe-host atom combination. That is why Mössbauer and PAC measurements give quite different results for the same material studied. But at the same time these size and charge differences are important when PAC technique is applied to characterize point defects in the materials, as probe atoms can trap vacancies and...
interstitials. The presence of these point defects in the neighbourhood of the probe breaks the local point symmetry of the crystal lattice, which in turn generates an EFG at the probe site and this EFG differs in magnitude and symmetry from the probe site EFG generated by perfect crystal lattice. Analysis of the temperature dependence of the hyperfine parameters can provide useful information concerning defects trapping, their diffusion and formation energies. Moreover, the EFG sensed by PAC probe nuclei represent the local point symmetry about the probe and not necessarily the overall symmetry of the crystal. Consequently, PAC can be used to follow the changes on the microscopic scale, when new microsurroundings at the probe site will start appearing such as change of bond distances, change of symmetry and trapping of defects, causing changes in the EFG value. An example of phase transition mechanism studied by PAC technique in perovskite materials is shown in Fig. 6, yielded information about the orthorhombic-to-rhombohedral phase transition in LaCrO$_3$, where co-existence of two different type of grains has been observed$^{11}$. The observed decrease in the asymmetry parameter $\eta$ to nearly zero and an increase in the EFG values for the $^{111}$Cd probe nuclei at La and Cr sites near structural phase transition temperature provide the microscopic evidence that the local point symmetry of the crystal has changed. A similar trend of hyperfine parameters has also been observed in LaFeO$_3$$^{11}$ and LaMnO$_3$$^{12}$ perovskites with $^{111}$Cd and $^{181}$Ta probe nuclei respectively. Furthermore, a linear temperature dependence of coupling constant $v_0$ at Co site in LaCoO$_3$ perovskite with $^{111}$In$\rightarrow$ $^{111}$Cd and $^{181}$Hf$\rightarrow$ $^{181}$Ta probes (see Fig. 7) has ruled out the possibility of symmetry change around temperature 600 K, in contrast to the observed one with other techniques. It is, therefore, apparent that the PAC technique can be used as a powerful tool (phase detector) for establishing crystallographic phase transitions in the materials. Moreover, a linear temperature dependence of EFG at transition metal site with $^{111}$Cd probe in rhombohedrally distorted perovskites LaBO$_3$ (B=Cr,Fe,Co) has been observed, indicating the strong dependence of the EFG on local oxygen coordination$^{14,15}$. This linear temperature dependence of EFG seems to indicate microscopic evidence for slight positional changes of the ions in the crystal lattice with temperature. Not only this, the observed temperature dependence of EFG in LaCoO$_3$ perovskite has also shown the thermally induced spin transition of Co$^{3+}$ ion from low-spin $t^6_2g_e^0$ ground state configuration to high-spin $t^4_2g_e^2$ state$^{13}$. 

![Fig. 6—Temperature dependence of fitted hyperfine parameters for $^{111}$Cd at La and Cr sites in LaCrO$_3$ (The dotted lines in the figure show the region of the coexistence of both orthorhombic and rhombohedral phases$^{11}$)](image)

![Fig. 7—Temperature dependence of measured coupling constant $v_0$ at Co site in LaCoO$_3$ perovskite with $^{111}$Cd and $^{181}$Ta probes (from ref. 11) (The solid lines in the figure represent a least square fit of a function $v_0(T) = v_0(0)(1-CT)$ to the data points, with constants $C(Cd)=4.95(5)x10^4$ MHz/K and $C(Ta)=5.19(5)x10^4$ MHz/K)](image)
The hyperfine fields at the site of interest in solids arise from the electrons (the bonding electrons, the conduction electrons and local electronic shells of the probe ion) near the nucleus. The rest of the charges in the material produce the electrostatic potential at the nuclear site that determines the electron densities. It is, therefore, evident that for calculating components of electric field gradients, we must know the total electron wave functions. The charges outside the probe nuclei generate an electric field gradient which make polarization of the local electronic shells with contribution \((1-\gamma_w)V_{zz}^{\text{lat}}\), where \(\gamma_w\) is known as Sternheimer antiscreening factor with \(10 \leq -\gamma_w \leq 80\).

For atoms with unfilled, non-spherical electronic shells (e.g. rare earths ions) an additional local electric field gradient \(V_{zz}^{\text{loc}}\) is created and modified by a factor \(R\) \((-0.2 \leq R \leq 0.2\), therefore, total EFG at the site of interest is \(V_{zz} = (1-\gamma_w)V_{zz}^{\text{lat}} + (1-R)V_{zz}^{\text{loc}}\).

This model, generally known as Point Charge Model (PCM), offers a very good approximation in many ionic crystals and some insulators, it will thus be interesting to see whether this will work equally in the perovskites also and can be used to conclude about the ionic nature of the crystal.

The PCM calculations of \(V_{zz}\) and \(\eta\) were performed for both cation sites in these transition metal perovskites. Formal charges of +3 and -2 were assigned to La, Cr, Mn, Fe, Co and oxygen ions respectively. The lattice sum was performed numerically to within a sphere of radius of 100 Å with probe atom at the origin. The lattice parameters and the atomic positions were taken from the Rietveld analysis of the samples. The resulting value of \(V_{zz}^{\text{lat}}\) was then multiplied by \((1-\gamma_w)\) to obtain the value of EFG at the nuclear site, \(V_{zz}^{\text{PCM}} = (1-\gamma_w)V_{zz}^{\text{lat}}\). The results of the PCM calculation of \(V_{zz}\) and \(\eta\) are summarized in Table 2 for La and Cr/Mn/Fe/Co sites in LaBO₃ (B=Cr, Mn, Fe, Co) perovskites. The experimental results are included in this table for comparison purpose. While the agreement between the experimental and calculated values of asymmetry parameters \(\eta\) is reasonable only for the La sites, the agreement for \(V_{zz}\) is quite poor. The discrepancy between the experimental and PCM values can be associated with the incomplete description of the EFG involved in PCM calculations, where the local contribution to EFG, arising from electronic characteristics of the probe, has not been taken into consideration. In a previous compilation of EFG’s for \(^{111}\text{Cd}\) probe nuclei at cation sites for different types of oxides, a better agreement between the experimental \(V_{zz}\) and \(V_{zz}^{\text{PCM}}\) was obtained for cases where the cation-O²⁻ bond distances were greater than 2.1 Å. In the transition metal perovskites, the La-O²⁻ and B-O²⁻ bond distances range from 2.50 to 2.72 Å and 1.92 to 1.98 Å, respectively. Although the disagreement between experimental and calculated EFG values larger in this work, we can conclude that basically a similar behaviour is followed by these compounds. These results imply the strong covalent contribution to EFG at transition metal site in LaBO₃ perovskites. Recently, first-principle calculations based upon full-potential-linearized-augmented-plane-wave\(^{15}\) (FP-LAPW) have been applied successfully to see the influence of Cd impurity in delafossite oxides\(^{16}\) of type ABO₃, and these

| Sample | Crystal Structure | PAC Probe Utilized | Probe Nuclei at Sites | \(\eta\) \((10^2\text{V/m}^2)\) | \(V_{zz}\) \((10^2\text{V/m}^2)\) | \(\eta_{\text{PCM}}\) \((10^2\text{V/m}^2)\) | \(|V_{zz}^{\text{PCM}}|\) \((10^2\text{V/m}^2)\) | Remarks |
|--------|------------------|-------------------|------------------------|-----------------|------------------|-----------------|-----------------|-----------|
| LaCrO₃ | Orthorhombic     | \(^{111}\text{In} \rightarrow ^{111}\text{Cd}\) | La                    | 0.47(3)         | 7.0(9)            | 0.53             | 2.5             | Ref. [9] |
| LaCrO₃ | Orthorhombic     | \(^{111}\text{In} \rightarrow ^{111}\text{Cd}\) | Cr                    | 0.66(9)         | 1.5(2)            | 0.92             | 23.5            |          |
| LaMnO₃ | Orthorhombic     | \(^{111}\text{In} \rightarrow ^{111}\text{Cd}\) | La                    | 0.56(2)         | 7.4(1)            | 0.44             | 3.46            | Present work |
| LaMnO₃ | Orthorhombic     | \(^{111}\text{In} \rightarrow ^{111}\text{Cd}\) | Mn                    | 0.49(2)         | 3.2(1)            | 0.42             | 14.2            |          |
| LaFeO₃ | Orthorhombic     | \(^{111}\text{In} \rightarrow ^{111}\text{Cd}\) | Fe                    | 0.43(2)         | 7.3(9)            | 0.45             | 4.2             | Ref. [9] |
| LaCoO₃ | Rhombohedral     | \(^{111}\text{In} \rightarrow ^{111}\text{Cd}\) | Co                    | -              | 2.0(3)            | 0                | 2.21            | Present work |
calculations have reproduced the experimental results. Thus, such electronic structure calculations may also be required to describe correctly the effects of covalent bonding in perovskites of type ABO₃.

Conclusions

To perform all these measurements in transition metal perovskites, we used crystal chemistry to introduce an appropriate probe into the sites of interest. The following conclusions have been drawn from the PAC measurements: (i) the PAC measurements have shown that ¹¹¹In/¹¹¹Cd probe nuclei prefer to substitute both La and Cr/Mn/Fe sites in La(Cr/Mn/Fe)O₃ perovskites while in LaCoO₃ compound it substitute only for Co sites, (ii) in the doped sample LaₓSr₁₋ₓCoO₃, the static electric quadrupole interactions have shown the line broadening of spectral lines due to different microscopic combinations of La and Sr ions in the lattice, (iii) temperature dependence of hyperfine parameters in these perovskites has shown that the PAC technique can be effectively used for local crystal structure transitions, (iv) the PAC measurements in perovskites can be utilized to measure the supertransferred magnetic hyperfine field. Besides, the PCM calculations of Vₓ and asymmetry parameter η for ¹¹¹Cd nuclei substituting the La as well as Cr, Mn, Fe and Co sites were carried out for LaBO₃ (B=Cr, Mn, Fe, Co) compounds and prediction has been made about the covalent nature of B-O bond in ABO₃. We hope that the present work (as PAC measurements are very sensitive to electronic structure) in these transition metal perovskites will stimulate further interest among theoreticians to develop a better understanding to correlate effects of 3d-band occupation with the observed electric field gradients and magnetic hyperfine field. Furthermore, the PAC measurements in dimensionally confined thin films of these compounds are in progress that will provide information about the stability of novel structure in thin layers of perovskites.

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