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MÖSSBAUER SPECTROSCOPY INVESTIGATIONS OF PHASE TRANSITIONS IN FERROELECTRICS

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Abstract. Due to the complexity of the problems regarding the mechanism of occurrence of ferroelectricity in various ferroelectrics, the interpretation of the Mössbauer spectra and the derivation of some correct information from them is a difficult task which has to take into account the peculiarities of the given ferroelectric. From this point of view, in this paper the results obtained by means of Mössbauer spectroscopy investigations in ferroelectrics are reviewed, underlying the derived information on the lattice dynamics and changes of the electric properties and crystalline structure of ferroelectrics passing through the critical points.

1. Introduction

After the early phenomenological explanations of ferroelectricity /1-3/, considerable progress was made taking into account the connection between ferroelectricity and dynamics of the crystalline lattice /4-5/. Among the experimental techniques able to measure "local" properties of the ferroelectrics, Mössbauer spectroscopy plays an important role. The data obtained by means of Mössbauer spectroscopy have been reported on different types of ferroelectrics (Table 1) using $^{57}$Fe, $^{119}$Sn, $^{40}$K, $^{176}$Hf and $^{121}$Sb isotopes.

<table>
<thead>
<tr>
<th>TABLE 1. Ferroelectric compounds investigated by means of Mössbauer spectroscopy:</th>
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</thead>
<tbody>
<tr>
<td>Perovskite oxides: BaTiO$_3$ /6-13/, BiFeO$_3$ /14-16/, PbZrO$_3$ /12,17-19/, PbTiO$_3$ /12,20,21/, ErFeO$_3$ /27/, KXO$_3$ /28/, Perovskite complexes Ba(Ti,Sn)$_3$O$_9$ /29-30/, Pb(Ti,Sn)$_3$O$_9$, Pb(ZrSn)$_3$O$_9$ (Ba,Pb)SnO$_3$, Sr(TaFe)$_3$O$_9$, Pb(NbFe)$_3$O$_9$, SrFeO$_3$, Ba$_2$FeO$_3$, Sr$_2$FeO$_3$, La$_2$FeO$_3$, La$_2$FeO$_3$, Bi$_4$Ti$_3$Fe$_2$O$_9$, (Mn,Fe)$_2$O$_3$, (La,Pr,Bi)Bi$_4$Ti$_3$Fe$_2$O$_9$, (A=Pb,Sr,Ba, Bi=Fe,Co,Ni,Mn,Mg,Ca,Li) /43/, Ba$_2$FeSbO$_6$, Ba$_3$Fe$_2$O$_3$ (B=Re, Te, W, Mo)</td>
</tr>
</tbody>
</table>

44. Solid solutions of perovskite type: BiFeO$_3$-BaTiO$_3$, BiFeO$_3$-SrSnO$_3$ /45-47/, BiFeO$_3$-PbTiO$_3$, BiFeO$_3$-PbZrO$_3$ /14,16,18,29/, BiFeO$_3$-Sr(Sn,Mn)O$_3$ /50/, BiFeO$_3$-PbTiO$_3$, PbZrO$_3$, PbTiO$_3$-PbZrO$_3$-PbO /51/, PbTiO$_3$-PbZrO$_3$-sNi /19/. Boracides: Fe$_3$B$_7$O$_{13}$X (X=C1, Br, I) /52-55/, Ni$_x$Fe$_{3-x}$B$_7$O$_{13}$X (X=C1, Br, I) /52,56-60/, Co$_3$B$_7$O$_{13}$Cl /55/. Chalcogenides: Sn(Se,Te,S) /61,62/. Pseudo-ilmenites: Li(Fe$_{1/2}$Ta$_{1/2}$)$_2$O$_4$, Li(Fe$_{1/2}$Ho$_{1/2}$)$_2$O$_4$ /87/, Alums: NH$_4$Fe(SO$_4$)$_2$, 12H$_2$O /63-67/, NH$_4$[Al,Fe(SO$_4$)$_2$, 12H$_2$O /68/. Other types: SbSBr, SbSI, SbSeBr /69/, SbTeI, SbS$_2$I /70/. KFe(CN)$_6$.3H$_2$O /66,67,79,81,82,86/.

The purpose of this paper is to discuss the interpretation of Mössbauer spectra in ferroelectrics in order to obtain information about lattice dynamics, crystalline structure and electrical properties.

2. Information about the lattice dynamics.

The ferroelectric phase transitions are considered an apart class of structural transitions, when the structure changes are accompanied by the occurrence of the electric spontaneous polarization /71/.
In order to give an explanation of ferroelectricity, it has been suggested by Cochran and Anderson [4,72] that the para-ferroelectric phase transition may be considered as a consequence of the instability of a normal mode, named "soft mode" (ferroelectric model) as the temperature $T$ and the wave vector $\vec{q}$ approach their critical values $T_0$ and respectively $\vec{q}_0$.

The parameters of the Mössbauer spectra which may provide information regarding the lattice dynamics of a ferroelectric, are the area of the spectrum (which depends on the Mossbauer fraction $f$) and the second order Doppler shift, SOD, of the nucleus. These two parameters depend on the lattice dynamics through the displacement and momentum correlation functions at different moments of the Mossbauer nuclei, which include the Green function of the crystal [73].

We have to mention from the beginning that the obtaining of information on the lattice dynamics from Mössbauer spectra of ferroelectrics comes up against two major difficulties. The first is an experimental one, since the most ferroelectrics do not contain Mossbauer nuclei. For this reason the samples have to be dopped with Mössbauer atoms. This leads to a perturbation of the lattice dynamics. A second difficulty derives from the fact that the standard theory of the Mössbauer effect has been developed in terms of harmonic oscillation approximations whereas the occurrence of a ferroelectric mode is connected to important anharmonic effect of the lattice dynamics. In spite of these difficulties, in many cases, precious information about the lattice dynamics at the ferroelectric phase transitions have been obtained.

2.1. The Influence of the Soft Mode

The first theoretical attempt to find out the influence of the soft mode on the Mossbauer spectra belongs to Muzikar et al [74]. They showed that the branch of the ferroelectric mode might cause a decrease of $f$, i.e. of the area of the spectrum, as the temperature decreases to its critical value $T_0$. The first experimental evidence of the influence of the soft mode on the area of the spectrum at the Curie point has been brought by Fam Zui Hien et al [46] for solid solution BiFeO$_3$ - Sr$^{119}$SnO$_3$. At the molar concentration of 50% SrSnO$_3$, a drastic decrease (4,1/1) of the effect at 250 K has been observed. The authors have considered this decrease as a clear evidence of the influence of the soft mode on $f$. Later, analogous changes of area have been observed in other compounds [6-14, 16, 20-30, 29, 48, 61-67]. In 1966 Dvorak [89] suggested that in the antiferroelectric phase transition would be expected to appear a more pronounced decrease of the area compared to the case of the ferroelectric transition. The results reported by Canner [14, 19] seem to offer no support for this suggestion.

The existence of a soft mode responsible for the ferroelectric transition in ammonium sulphate has been already presumed [75]. In a previous paper [76] carrying out ESR measurements, has been confirmed the presence of a soft mode having its $\omega$...
and $T$ dependence given approximately by

$$\omega(Q,T) = \alpha(T_0 - T)^{\gamma} + B Q^{\delta}$$  \hfill (1)

where $T_0$ is the transition temperature, $\alpha$ and $\beta$ are material constants and $\gamma$ is the critical exponent. The influence of this mode on the hyperfine constant $A$ is given by the expression:

$$A(T) = A_0 - A_1 T + A_2 T \left[ \frac{|T - T_0|^{\gamma/2}}{\eta} \tan^{-1} \left( \frac{\eta}{|T - T_0|^{\gamma/2}} \right) \right]^{1/2}$$  \hfill (2)

where $\eta = (\beta/\alpha)^{1/2}$, $Q$ being the cut-off of the Brillouin zone. For the two positions occupied by $\text{Cd}^+$ ions substituting $\text{NH}_4^+$ groups, the experimental data have been fitted to the curve given by eq. (2); the agreement with the experimental points is very good (fig.1). Mössbauer measurements on ammonium sulphate doped with 1% Fe$_2$(SO$_4$)$_3$ have pointed out a change of about 16% of the area of the spectrum, which was attributed to the soft mode $/77/$.

One has to pay a special attention to all the sources which may contribute to the temperature dependence of the area of the Mössbauer spectrum, as the polarization effects $/78/$, the possible rotation of the E.F.G.$/66-68/$ and the vibrational anisotropy of Mössbauer isotopes $/52,53,57/$.

An other parameter of the Mössbauer spectrum essentially depending on the lattice dynamics is SOD. The real measured parameter is the center shift (CS) which contains not only SOD, but also the isomer shift. In 1965 Bhide et al $/6/$ observed a jump of the CS at the ferroelectric phase transition of BaTiO$_3$ $/57/Fe$, considering it as a contribution of the soft mode at SOD. Later, Samuel $/21/$ has shown that the optical soft mode does not lead to any observable change of SOD at the transition point.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Temperature dependence of the $\text{Cd}^+$ hyperfine interaction constant in ammonium sulphate $\text{Cd}^+$ in a position, $\text{Cd}^+$ in $\beta$ position. At the top the change of the area of Mossbauer spectrum around the critical temperature is shown.}
\end{figure}

A careful analysis of the influence of the ferroelectric mode on SOD for $^{57/Fe}$ PbTiO$_3$ was carried out by Bhide et al $/20/$. Considering that in the high temperature region the isomer shift has a linear temperature dependence, and taking into account the temperature dependence of SOD they got the relation

$$\frac{\delta E_{\text{tot}}}{E} + \frac{3K_B}{2MC^2} - \frac{3}{2} = \frac{\delta E_{\text{is}}(0)}{E} - \frac{3K_B \delta D}{40MC^2}$$  \hfill (3)

At the critical temperature, the left hand side of eq.(3) against $1/T$ shows a jump of about 0.075 mm/s.

The authors have considered that the only sources responsible for this jump could be either an anomaly due to a mixture of
acoustical and optical modes for $a + o$ or a temperature dependence of the ferroelectric mode $\omega_{an}(T)$. Samuel et al. /21/ have shown that the last reason could explain the experimental data. Some cases have been reported when no any change of $\delta E_{tot}$ at $T_o$ was observed. Different reasons were attributed to this behaviour (change of linewidth at $T_o$/63,77/), opposite change of $\delta E_{is}$ in respect to SOD/52-60/). In other cases the jump of $\delta E_{tot}$ could be attributed either to a change of geometry of the vicinity of $^{57}$Fe /14,19,48/ or to a change of the resonance intensities of the quadrupole splitting caused by the reorientation of the EFG axes /66-67,79/.

2.1. Valuation of some lattice dynamics parameters

Since the lattice dynamics is involved in the temperature dependence of some parameters of Mossbauer spectra, it becomes possible to use them in order to get some information about the lattice dynamics of ferroelectrics passing through the critical points.

In order to find out the lattice dynamics parameters from the temperature dependence of the area of Mossbauer spectra of PbTiO$_3$: $^{57}$Co Shide et al /20/ have divided $f$ into two factors. The first one depends on the soft mode through $\alpha$, $\epsilon^2_{an}$ and the temperatures $T_c$ and $T_o$

$$f_{an}(T) = \exp \left[ \frac{(\hbar \omega_{an})^2}{2\hbar \omega_{an}} \left( \frac{2}{\hbar \omega_{an}} + 1 \right) \right]$$

(4)

where

$$\epsilon^2_{an} = \alpha \left[ (T - T_c) + (T_c - T_o) \right]$$

(5)

has a minimum value for a first order transition ($T_c \neq T_o$) and, respectively zero for a second order transition ($T_c = T_o$). The second factor depends on $\theta_D$ through the Debye distribution of the frequencies of the normal modes. Using the experimental values of $T_c$ and $T_o$, assuming the same value of $\epsilon^2_{an}$ in the two phases and using the value of $\theta_D$ from paraelectric phase reported by Shirane /85/, the authors have estimated the quantities $\alpha$ and $\theta_D$, from the fitting of the experimental and theoretical curves of $f$ (fig.2). Samuel et al /21/ have improved the fitting, assuming a linear temperature dependence of $\theta_D$ in the ferroelectric phase.

![Fig.2. Calculated curves $f(T, \theta_D)$ (solid lines) and the experimental one around $T_c$ for $^{57}$Co: PbTiO$_3$ /34/.

3. Information on some electrical properties and crystalline structure

Besides the valuation of the critical temperatures, the temperature dependence of some parameters of Mossbauer spectrum may provide useful information about the order of the phase transition, on some peculiarities of the ferroelectrics and also on the crystalline symmetry. Thus from $\Delta E_0(T)$ of the Mossbauer spectrum of PbTiO$_3$: $^{57}$Co/20/ it was concluded that one,
has to deal with a first order phase transition. Analogous conclusions were drawn for many perovskites, boracides etc. We would like to remark that by means of Mössbauer spectroscopy on Pr$_2$Bi$_4$Ti$_3$Fe$_2$O$_{18}$ and La$_2$Bi$_4$Ti$_3$Fe$_2$O$_{18}$, the coexistence of the polar and nonpolar phases in the critical region of diffuse phase transition was shown /41/. On the other hand, the almost linear temperature dependence of $\Delta E_q$ was considered a normal behaviour of the improper ferroelectrics /52-59/.

In order to perform a correct analysis of the polarization contribution to $\Delta E_q(T)$, one has to extract from $\Delta E_q(T)$, the ionic and electron valence contributions. An typical example is provided by the carefully computation of Bell/32,80/, of the ionic contribution to $\Delta E_q$ for the tetragonal nonpolar distortion and polar one in ABO$_3$ type perovskites. From this calculus it results an ionic contribution to $\Delta E_q$ smaller than 0.012 mm/s. At the same time they have estimated the electric dipole contribution as being

$$V_{zz} = \frac{1}{4\pi \varepsilon_0} (0.008\nu_{Pq} + 0.17\nu_{QII} + 0.20\nu_{QIII})$$

(6)

Using the Slater's model of cubic perovskites it follows that the polarization contribution to $\Delta E_q$ is about 0.34 mm/s at $T_c$ in BaTiO$_3$. This value is in good agreement with the experimental one of the jump of $\Delta E_q$ of about 0.40 mm/s, determined by Bhide/37/in BaTiO$_3$:57Fe at the critical point.

A quantitative valuation of the ionic polarizability, $\alpha$, from Mössbauer spectra was performed for Pb(Nb$_{1/2}$Fe$_{1/2}$)$_3$O$_3$ and Sr(Ta$_{1/2}$Fe$_{1/2}$)$_3$O$_3$/32,33/ from the ratio of $\Delta E_q$ ionic contribution to the electrical spontaneous polarization one.

Since the ratio of the inequivalent sites of the Mössbauer isotopes in respect to the polar axis varies at the change of crystalline symmetry, it is expected to point out easily the structural transitions. A typical example of structural changes in the ferroelectric phase is provided by the boracides, where the ratio of inequivalent sites relative to the polar axis changes from 1/2 to 1/52, at the orthorhombic-trigonal phase transition. By means of Mössbauer spectroscopy it was possible to point out, in the orthorhombic-trigonal transition region, an anomalous behaviour of $\Delta E_q(T)$ and of the ratio of inequivalent sites for Fe$_3$-In$_x$Fe$_3-x$-I$_x$Co$_3$-Cl boracides /52,55,59/. Assuming that the electrical spontaneous polarization contains two terms of different order in phase transition parameter (having different temperature dependence), it was concluded that in this transition region we have to deal with a monoclinic symmetry /59/. This is in agreement with the X-ray measurements on Fe$_3$-I boracide. Knowing the crystalline symmetry in the orthorhombic-trigonal transition region and using the space group theory have been estimated the displacement of iron and halogen ions in the structural phase transition. In this way it was possible to explain the anomalous temperature dependence of the ratio of the iron inequivalent sites.

We have to mention that in the solid solution the structural changes may be hardly observed due to the great number of
the inequivalent sites. In order to perform a correct valuation of the symmetry changes one has to take into account the distribution law of the inequivalent sites and their contribution to $\Delta E_Q$. An example is given by the understanding of complex Mössbauer spectra of Pb(Nb$_{1/2}$Fe$_{1/2}$)$_3$O$_3$, Sr(Fe$_{1/2}$Fe$_{1/2}$)$_3$O$_3$/32,33/and boracides Ni$_x$Fe$_{3-x}$-I/59/.

From Mössbauer spectra of some ferroelectrics may be found out the crystalline field parameters. As an example may be mentioned Mössbauer investigations on the quadrupole and magnetic splittings in Fe$_3$-X (X=Cl,Br,I)/54/and Ni$_x$Fe$_{3-x}$-I boracides/89/.

Conclusions

Mössbauer technique affords an useful tool in the investigation of the relationship between the lattice dynamics and ferroelectricity and in obtaining information about some macroscopic parameters of the ferroelectrics. One expected new successes as the theory of the Mössbauer effect will be improved by taking into account the anharmonic effects.

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