Proceedings of the IV Forum EMR–PL, June 27–29, 2016, Poznań, Poland

Microwave X-Band Resonances in Doped $Cd_2Nb_2O_7$ Monocrystals

S. Waplak, A. Ostrowski*, M. Wencka and W. Bednarski
Institute of Molecular Physics Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

Cadmium pyroniobiate (CNO) is the ferroic material with unusual diffuse phase diagram which includes both relaxor and nanocluster domains. We present the data for CNO crystals with several admixtures of paramagnetic ions studied on X and S microwave bands at zero-external magnetic field and classical EPR conditions. Our results lead to an assertion of a ferroelectric resonance effect due to "electronic ferroelectricity". The data fit well to the Falicov–Kimball theoretical model applicable to strongly-correlated-electron or mixed-valence systems.

DOI: 10.12693/APhysPolA.132.7
PACS/topics: 76.30.Fc, 77.22.Ch, 77.80.B–, 77.84.Ek

1. Introduction

Cadmium pyroniobiate $Cd_2Nb_2O_7$ (CNO) is a ferroic material with unusual diffuse phase transition (PT) despite the absence of compositional fluctuations, unlike the conventional relaxors $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), where a frequency-dependent broad dielectric peak is brought about by nanoscopic polar clusters, but macroscopic ferroelectric ordering does not appear [1,2].

We will present data strongly suggesting that both the ferroelectric/ferroelastic and local order do coexist in $Cd_2Nb_2O_7$ compounds and the interplay between them leads to a rich phase diagram and relaxation [3–5].

Recently, attention has been paid to the possibility of electronic ferroelectricity based on charge-ordering phenomena in complex oxides like perovskite structure manganites [6, 7]. An intriguing behavior of dielectric permittivity versus external electric field [8] stimulated us to look closely on this problem by means of EPR spectra of doped $Cd_2Nb_2O_7$.

Some EPR papers with the aim to study the molecular mechanism of the phase transitions in $Cd_2Nb_2O_7$ crystals have been published [9, 10]. Our papers [11, 12] concerned especially EPR of Cr^{3+} and Gd^{3+} ion dopants under the influence of temperature and/or external electric field. The EPR data on Gd^{3+} give us a clear evidence of various types of ferroic states in $Cd_2Nb_2O_7$. By using the $Gd^{3+}(S = 7/2)$ probe, one can study the temperature behavior of the order parameters η_1, η_2 and indexes γ, β estimated from the EPR line splitting: $\Delta B \sim \eta_1 \sim (T_s - T)^\gamma$ or $\Delta B \sim \eta_2 \sim (T_c - T)^\beta$, where T_s, T_c are the critical temperatures of the ferroelastic and ferroelectric phase transitions with $\gamma = 1$ and $\beta = 0.5$, respectively [11]. The intensity ratio of split lines characterizes thermally or DC electric-field induced changes in the domain pattern below T_s and T_c. Thus, two ferroic states of different nature (an improper ferroelastic-ferroelectric state, with the latter appearing below T_c) coexist in the ferroelectric phase.

The dielectric behaviour of cadmium pyroniobiate $Cd_2Nb_2O_7$ shows "unusual properties" around PT and strongly suggests the presence of polar clusters carrying additional polarization. However, no molecular origin of such a behavior has been yet elucidated [8, 13].

The most striking effects observed in current study represent anomalies in the microwave resonator quality parameter Q versus temperature in zero external magnetic field. In $Cd_2Nb_2O_7$, this effect appears only in the X-band (≈ 9.5 GHz) and is absent from the S-band (≈ 3.5 GHz). The details of the dependence $Q = Q(T)$ rely on the type and concentration of the doping (paramagnetic) ions Mn^{2+}, Cr^{3+}, Fe^{3+} introduced. In current paper, mainly electric (Q) data, complemented with the EPR ones in case of necessity, will be discussed.

2. Sample description and experimental setup

The cubic pyrochlore structure of $Cd_2Nb_2O_7$ is a three-dimensional framework consisting of corner-connected oxygen octahedra with Nb ions inside forming NbO_6 chains and parallel O–Cd–O zigzag chains [4]. The crystal exhibits as many as seven phase transitions and several dielectric relaxation features below 525 K, making it a very complex system. Obviously, the specific feature of $Cd_2Nb_2O_7$ consists in its crystal structure which is characterized by a rigid network of NbO_6 octahedra and a very flexible CdO subnetwork. Recently Paściak et al. [14] have determined a paraelectric phase of $Cd_2Nb_2O_7$ from X-ray diffuse scattering and found dynamic disorder of both sublattices and an anisotropy between longitudinal and transversal correlations of ionic displacements from average positions. This local distortion leads to a shift in the structure containing cations toward their nominal valences.

We assume that the valence instability may be crucial for the rich phase diagram as well as for the contradictory experimental data for $Cd_2Nb_2O_7$. Our long-term crystal investigation by EPR leads to a conclusion

*corresponding author; e-mail: ostrowski@ifmpan.poznan.pl

that producing really pure crystals of $Cd_2Nb_2O_7$, without paramagnetic impurities down to the purity of the order of 0.001%, is yet not accessible. This may be due to the high temperature of growing process.

In the Isupov [3] review paper it is pointed out that the colourless crystals and the weakly coloured ones were found to be most imperfect in contrast to the highly doped ones. It is supposed that the cadmium pyroniobiate formula can correspond to the $(Cd_2Nb_2O_8)_m^{-2}$ composition, or possibly rather to the $(Cd_2Nb_2O_{8-x}\square)_x^{-2(1-x)}$ one, with $x < 1$ and $\square$ denoting the oxygen vacancy. Thus, the introduced additionally ions like Zn, Ni, Cu, Fe, and Gd [5], most likely hindered the formation of structural units in CNO analogous to fluorite groups [3] in the corresponding cubic fluorite-type structure and thereby possibly changed the number of the oxygen vacancies.

We have performed an EPR experiment on crystals doped with paramagnetic ions with concentration in the range of 0.02–5 wt%. For example, introducing Fe^{3+} ions with concentration of 5 wt% cancels ferroelectricity indicated for the low ion concentration by EPR line splitting. This means that $Cd_2Nb_2O_7$ is transformed into the non-ferroelectric $CdNb_2O_6$ pyrochlore structure. Hence, we postulate the crystal formula in the form of $Cd_{2-x}Nb_2O_{7-x}\square_x$ in order to stress the essential role played by oxygen vacancies. For the data under consideration earlier and in the current work, the paramagnetic probes: Cr^{3+}, Mn^{2+}, Fe^{3+} were chosen. The question for this data is: how do the electric parameters of cadmium niobiate behave if the dopant ions introduced bear either the same charge as Cd^{2+} (Mn^{2+}) or an excess charge (Fe^{3+}). Both samples with Mn^{2+} and Fe^{3+} dopants have been grown with a procedure described in our earlier works [5, 11] and prepared in the form with dimensions of $2 \times 2 \times 1$ mm^3. Subsequently, the samples were investigated with EPR ELEXSYS E500 Bruker spectrometer operating on X (9.5 GHz) or S (3.5 GHz) microwave bands at temperatures in the range of 5–300 K. Both the EPR spectra and the resonator quality Q were measured. The resonator quality is defined as $Q = \Delta\nu/\nu$, where ν is the resonance frequency and $\Delta\nu$ is the width at the half height of the resonance line.

The Q measurements have been done at a low value of microwave power (2 mW) to avoid sample heating [15].

3. Experimental data

The EPR data indicate [10] that Mn^{2+} ion replaces Cd^{2+} ion in the $Cd_2Nb_2O_7$ crystal lattice. Both Cd^{2+} and Mn^{2+} ions have the same valence but different ionic radii ($R(Cd^{2+}) = 0.97$ Å, $R(Mn^{2+}) = 0.80$ Å). In cases of Fe^{3+} and Cd^{2+} the difference in ionic radii is 0.33 Å, although the 1+ excess charge of Fe^{3+} needs compensation.

The quality parameter Q values for Mn^{2+} sample is shown in Fig. 1 versus temperature for two runs: from the high temperature down to the low one and back. No essential temperature hysteresis was observed for $Cd_2Nb_2O_7$:Mn^{2+} and Fe^{3+} samples. In Table I, our earlier data obtained for the $Q = Q(T)$ dependence for $Cd_2Nb_2O_7$ crystals doped with Cr^{3+} ion are also shown. The temperatures of dielectric anomalies for the pure CNO crystal [3] are also added.

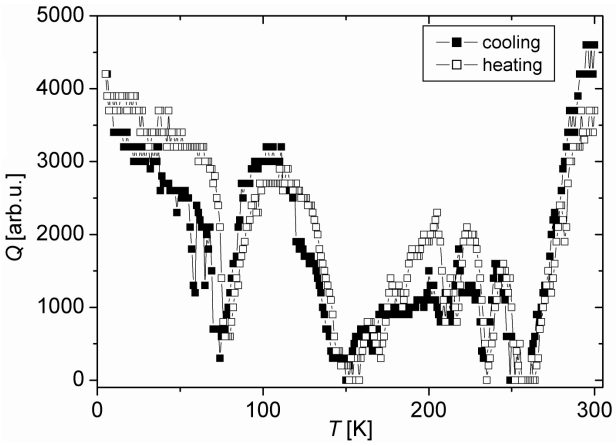

Fig. 1. The resonator quality parameter Q versus temperature for Mn^{2+}-ion doped CNO.

TABLE I

Temperatures of dielectric anomalies for pure and quality parameter Q (EPR) for different ion-doped CNO crystals.

Ion	$T(Q_{\min})$ [K]
pure CNO [3]	18, 45, 85, 150, 188, 201, 205
Cr^{3+}	99, 149, 174, 207, 258, 275, 314
Mn^{2+}	73, 150, 165, 212, 233, 257
Fe^{3+}	92, 132, 149, 180, 195, 224, 229

We have applied the Falicov–Kimball-like model (FK) [6] to our data description. This model is proposed to describe the transition from the integer-valence ground state into the inhomogeneous intermediate-valence ground state. The FK model has been used extensively [16] for mixed-valent compounds, heavy fermion systems and associated metal–insulator transitions. In the mixed-valent compounds the built-in polarization breaks the inversion symmetry leading to electronic ferroelectricity. This model presents the conditions for ferroelectric resonance effect. The energy gap of several meV observed in the mixed-valence ferroelectrics is due to the electron–hole pairing. In the mixed-valent system, the response to AC electromagnetic field in the presence of DC bias field leads to ferroelectric response frequency [16]:

$$\omega_0 = 2(\alpha\mu_z E_z)^{1/2}, \quad \alpha = \frac{\Delta E_f}{U} \tag{1}$$

where ω_0 is the frequency of the AC field, E_z is the internal electric bias field, Δ is the gap of the localized-extended $(d-f)$ single electron states in the FK model or ion–hole gap in our case, U is the Coulomb repulsion

energy, μ_z is the electric dipole moment and E_f is the value of f-level energy.

Our discussion of $Cd_2Nb_2O_7$ data finds experimental support in the electronic ferroelectricity data of dielectric permittivity obtained by Ang et al. [8] who have observed a significant suppression of the dielectric permittivity by application of DC field of the order of 3–4 kV/cm in the temperature range of 160–220 K. As a result, they suggested the presence of the "polar clusters" with the size of 11–15 nm in $Cd_2Nb_2O_7$, carrying polarization of the order of 0.5–2.5 mC/m^2. Internal bias field E_z determines the size of the polar clusters.

According to Blinc [2], the condition for polar clusters stability is valid for

$$\mu_z E_z \approx kT. \tag{2}$$

In our case

$$\mu_z E_z = \frac{kT}{\sqrt{n}}, \tag{3}$$

where $n = 1, 2, 3\ldots$, and the value $n = 1$ is assigned to the lowest temperature at a minimum value of Q. The value $n = 1$ corresponds to a charge localized on the ions and our final equation of the FK type has the form

$$\frac{\omega^2}{4} = \alpha \frac{kT}{\sqrt{n}}. \tag{4}$$

The constant values of α as shown for the $Cd_2Nb_2O_7$ formally described crystal with low doping by Fe^{3+}, Cr^{3+} and Mn^{2+} ions are equal to $(4.7; 3.9; 4.1) \times 10^{-5}$ meV, respectively. These values are not clearly corrected with ionic radii of doped ions nor with their valences. As mentioned above, ferroelectric $Cd_{2-x}Nb_2O_{7-x}$ tends to be nonferroelectric as x tends to 1. Our EPR preliminary results for samples with Fe^{3+}, Cu^{2+} ions concentrations higher by a factor of ten (approximately) than before revealed that the number of $Q_{\min}$ are reduced in comparison with that having lower dopant concentration.

In the FK model simulation of the number steps of valence transition it has been shown that the staircase structure (like the number of $Q_{\min}$ in our case) is reduced with growing of U-Coulomb repulsive energy between the $d-f$ levels [17].

On the basis of our data we suggest that the effect of ferroelectric resonance is a characteristic feature of the pyrochlore structure of the $Cd_{2-x}Nb_2O_{7-x}$ type.

We have also measured the EPR spectra at temperatures at which the Q value was low, but still high enough to record the EPR spectra. In Fig. 2, the EPR lines for $5/2 \rightarrow 3/2$ electron spin transitions of Mn^{2+} at 300 K ($Q = 4500$) and at 70 K ($Q = 650$) are presented and at 70 K may be conceived as a sum of the first derivative (paramagnetic) and absorption (ferroelectric) lines.

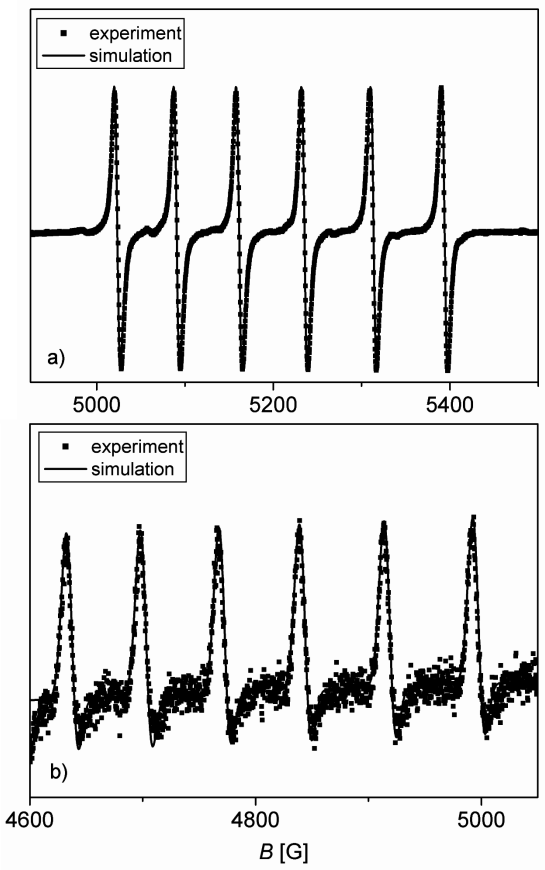

Fig. 2. EPR line for electron spin transition $5/2 \rightarrow 3/2$ (nuclear spin $I = 5/2$) of Mn^{2+} ion at (a) 300 K ($Q = 4500$) and (b) 70 K ($Q = 650$). Solid lines indicate simulations and symbols represent experimental data. The line asymmetry (b) has been obtained as sum of first derivative (paramagnetic) and absorption (ferroelectrics) lines with ratio 26 to 74.

4. Discussion

Our EPR data [11] revealed the coexistence of two ferroic states of different nature in the ferroelectric phase, which indicates the presence of an at least two-component order parameter. The pyrochlore structure of $Cd_2Nb_2O_7$ is described as consisting of two interpenetrating networks [4]. The rigid part of CNO is composed of $(NbO_6)^{2-}$ coordination polyhedra sharing their corners around hexagonal vacancies. The vacancies are occupied by the O(7)–Cd–O(7) dipole chains constituting the second network. It has been shown [14] that the dynamic disorder is significantly larger in the sublattice of Cd ions than in that of Nb ions. Within the octahedral NbO_6 groups and in the zigzag Cd–O chains, the longitudinal ion displacements are strongly correlated, but only weakly so for the transverse component. Local distortions lead to a shift in the valence bond sums for cations. Oxygen octahedra are deformed in a way that allows the bond valence sum of Nb atoms to decrease with simultaneous increase in the otherwise underbonded atoms. In the paraelectric phase, the valence bond sums amount to 1.6745 for Cd and 5.1982 for Nb [14]. The observed dynamic disorder leads to the fluctuation of valences: for Nb it is lowered to 5.02 and for Cd it is raised to 1.75.

According to the susceptibility data [5], in the pyrochlore family dielectric, ferroelectric and antiferroelec-

tric materials can be encountered. As to polar regions, a long-range ordering of polarization and a random orientation of local polarization can occur simultaneously. Below $T \approx 185$ K the polar clusters carry [8] polarization $P \approx 0.5{-}2.5$ mC/m^2 and the cluster size is $L \approx 11{-}15$ nm. It is a question, which type of polar clusters does exist in this compound? The mixed valence model can help answer this question. Inside the clusters, the additional dipole moments built due to the electron–hole pairs are stabilized by internal electric bias field. As we have shown years ago, the internal bias field is due to the uncompensated volume of charge around the "blocked" dipoles [18]. According to [7, 17], there are several mechanisms for electronic ferroelectricity like: mixed valence transitions (FK model) or charge ordering phenomena (including charge density waves). In our EPR (Q-data) experiments, we have found that paramagnetic ions with concentration of the order of 5 wt% cancel ferroelectricity in $Cd_{2-x}Nb_2O_{7-x}$, similarly as in the $CdNb_2O_6$ columbite structure. On the other hand, low concentration of paramagnetic ions with different charge and ionic radii leads to some differences in temperatures at $Q_{\min}$ (see Table I). Nevertheless, the parameter α in Eq. (4) lies in the narrow range of $(3.9{-}4.7)\times10^{-5}$ meV. This is probably due to the overwhelming effect of the electronic ferroelectricity of the pure bulk as compared to that of the doped regions occupying a few percent of the total volume only. The subtle differences in EPR spectra of different paramagnetic ions will be discussed in a separate paper in more detail. Herein, we can only state that most probably the so-called "incommensurability" at the lowest temperature in $Cd_{2-x}Nb_2O_{7-x}$ was observed in particular works due to the subtle differences in volumes of samples doped with foreign ions and those of samples free of such ions. The second feature worth mentioning is the fact that the step-like effect of the cluster dynamics behaves with temperature as $n^{-1/2}$ like in FK model with mixed valence transitions [17]. The existence of such peculiar patterns is related to the combination of ferroelectric and relaxor properties due to nanostructures embedded into ordinary ferroelectric domains. In such a situation, the variation in the commensurability ratio with varying physical parameters forms a devil's staircase [19].

After application of electric field of the order of 4–5 kV, similarly as in dielectric experiments [8, 20], the Q anomaly is shifted towards higher temperatures due to the breaking of the resonance condition according to Eq. (4). Finally, our data strongly support the occurrence of the ferroelectric resonance effect in CNO as special state of matter characterized by a resonance between the energy states of intermediate valence.

5. Conclusion

Our microwave X, S-bands data as well as direct current DC electric-field ε data [8] strongly support the existence of the polar nanoregions (PNR) in CNO. PNR are due to composition- or frustration-induced charge disorder leading to random fields. PNR exist in ferroelectric (highly polarised) CNO in the form of islands. The valence instability (frustration) is well established, even in pure CNO. There is no doubt that the strong microwave X-band absorption in CNO occurs in the internal bias field E_z and fits very well the FK-like equation. Also, resonance transitions ($Q_{\min}$) plotted versus temperature reveal a devil's staircase structure [17, 19].

References

[1] L.E. Cross, *Ferroelectrics* **76**, 241 (1987).

[2] R. Blinc, *Advanced Ferroelectricity*, Oxford University Press, New York 2011.

[3] V.A. Isupov, *Phys. Solid State* **47**, 2119 (2005).

[4] M. Tachibana, H. Kawaji, T. Atake, *Phys. Rev. B* **70**, 064103 (2004).

[5] N.N. Kolpakova, I.L. Shulpina, M.P. Shcheglov, S. Waplak, W. Bednarski, W. Nawrocik, M. Wisner, *Ferroelectrics* **240**, 1531 (2000).

[6] M. Falicov, J.C. Kimball, *Phys. Rev. Lett.* **22**, 997 (1969).

[7] N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, H. Kito, *Nature* **436**, 1136 (2005).

[8] C. Ang, L.E. Cross, R. Guo, A. Bhalla, *Appl. Phys. Lett.* **77**, 732 (2000).

[9] I.N. Geifman, G.W. Sirotkin, E.S. Sher, *Fiz. Tverd. Tela* **25**, 3606 (1983).

[10] I.N. Geifman, *Fiz. Tverd. Tela* **21**, 2250 (1979).

[11] N.N. Kolpakova, S. Waplak, W. Bednarski, *J. Phys. Condens. Matter* **10**, 9309 (1998).

[12] S. Waplak, N.N. Kolpakova, *Phys. Status Solidi A* **117**, 461 (1990).

[13] R. Pirc, R. Blinc, Z. Kutniak, *Ferroelectrics* **267**, 139 (2002).

[14] M. Paściak, M. Wołczyrz, A. Pietraszko, S. Leoni, *Phys. Rev. B* **81**, 014107 (2010).

[15] J. Minge, S. Waplak, N.N. Kolpakova, *Mater. Sci.* **XVII**, 41 (1991).

[16] T. Portengen, Th. Őstreich, L.J. Sham, *Phys. Rev. B* **54**, 17452 (1996).

[17] P. Farkasovsky, *Phys. Rev. B* **51**, 1507 (1995).

[18] S. Waplak, J. Stankowski, *Acta Phys. Pol. A* **54**, 465 (1978).

[19] S. Aubry, *J. Phys. (France)* **44**, 147 (1983).

[20] N.N. Kolpakova, E.S. Sher, S. Waplak, *Ferroelectrics* **111**, 257 (1990).