

Magnetic and Ferroelectric Properties of New Potential Magnetic Multiferroic $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoCl}_2\text{Br}_2$

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Received: 20.09.2021 & Accepted: 08.11.2021

Doi: [10.12693/APhysPolA.140.450](https://doi.org/10.12693/APhysPolA.140.450)

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The paper is devoted to study of the magnetic and ferroelectric properties of $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoCl}_2\text{Br}_2$ (TEACCB-2) solid solution. Investigations of the temperature dependence of the spontaneous polarization confirmed existence of the improper ferroelectric phase in this crystal. The anomalies corresponding to the ferroelectric phase transition were also observed in the temperature dependences of the inverse magnetic susceptibility — respectively at 227.7 K and 226.4 K, depending on the orientation of the magnetic field. These anomalies confirm both ferromagnetic interactions in a very small temperature range around this point and the spontaneous magnetoelectric effect arising in the phase, which simultaneously is improper ferroelectric and paramagnetic. Observation of such an effect testifies that the ferroelectric ordering is closely connected with magnetic interactions between Co^{2+} ions. The analyzed $\text{Co}(\text{II})$ complexes are monomeric and are characterized by antiferromagnetic interaction ($\theta < 0$ K) around the central ion.

topics: multiferroic, magnetic properties, ferroelectric, magnetoelectric effect

1. Introduction

Multifunctional materials, where magnetic and electric orders coexist at the same phase present high research interest due to the potential to drive exotic cross-functionalities in these materials. Such functionalities can include the electric field controlled magnetization or magnetic field controlled polarization [1]. For the technical applications it is important that these materials would possess not only large magnetoelectric coupling but also large magnetization and electric polarization values [1].

Often such materials meet preparation difficulties related to the fact that majority of magnetic materials are not good insulators and therefore cannot sustain electric polarization. The search for such materials is recently branching out to include also organometallic systems [2], where improper electric polarization can appear due to thermodynamically induced structural transformation. However, these materials are predominantly paramagnetic due to prevailing organic content. In that respect, the introduction of strong magnetic interactions to these materials and maintain electric polarization at the same time is a very challenging issue.

Here we report that coexistence of electric polarization and magnetic interactions could also be found within the rich family of the crystalline ferroics with an alkylammonium cation. The crystalline ferroics of such a type possess series of interesting properties and are actively studied using different experimental methods. First of all, they are characterized by the complex sequences of phases that are accompanied by different kinds of structural transformations connected with dynamics of organic cations and inorganic anions [3–8]. In the previous paper [4] we reported the data concerning the magnetic and electric properties of $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoClBr}_3$ (TEACCB-3) solid solution. This paper is devoted to another related potential multiferroic from the same family of solid solutions — TEACCB-2.

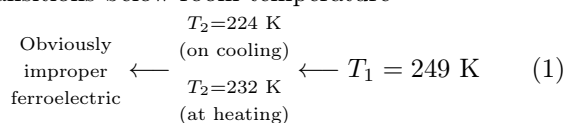
Previous investigations of the initial $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{MeCl}_4$ ($\text{Me} = \text{Co}, \text{Zn}, \text{Mn}$) single crystals by NMR and dielectric methods showed that these compounds undergo a phase transition around 225 K (in a heating run $T_1 = 225$ K for $\text{Me} = \text{Co}$, $T_1 = 226.2$ K for $\text{Me} = \text{Mn}$, and $T_1 = 227$ K when $\text{Me} = \text{Zn}$) [5]. At room temperature $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoCl}_4$ belongs to the $P4_2/nmc$

space group [6]. The phase transition obviously into the rhombic phase is connected with ordering of the organic cations.

Contrary to the compounds of $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{MeCl}_4$ group, $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{MeBr}_4$ crystals are characterized by availability of the first order phase transition at higher temperatures ($T_2 = 280$ K for $\text{Me} = \text{Co}$ and $T_2 = 266$ K for $\text{Me} = \text{Mn}$) [7, 8].

The initial crystals — $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoCl}_4$ and $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoBr}_4$ — do not look very attractive from the practical point of view since they do not show clear ferroelectric properties.

However, the solid solution TEACCB-2 is much more interesting since it obviously possesses the ferroelectric phase. According to [9] the bulk TEACCB-2 crystal undergoes two structural phase transitions below room temperature



One can conclude that considered solid solutions undergo phase transitions characteristic for both the corresponding pure chloride and bromide crystals but at the “intermediate” temperatures. The dielectric parameters of TEACCB-2 showed the sharp peaks at $T_2 = 224$ K in a cooling run (232 K at heating), whereas more slight anomalies were observed at $T_1 = 249$ K. On the basis of the shape and values of the anomalies of the real and imaginary part of dielectric permittivity the transition at T_2 was supposed to be improper ferroelectric. Moreover, it has been found that this phase transition manifests a considerable temperature hysteresis. Besides, above this transition the clear dielectric dispersion characteristic of the Debye type relaxation was observed [9]. Meanwhile, as it was deduced from the Cole–Cole diagrams, the relaxation is characterized by a certain distribution of relaxation time due to interaction between the dipoles [10]. It was suggested that observed dielectric dispersion as well as the phase transitions are connected with the cooperative motion of complex anions and cations [10]. The low temperature transition strongly affects mobility both of cations and anions leading to disappearance of the dielectric dispersion at low temperatures.

As it follows from the data of the spectroscopic study [11], the structure of TEACCB-2 contains $[\text{CoCl}_2\text{Br}_2]^{2-}$ groups carrying the dipole moment but not the separated $[\text{CoCl}_4]^{2-}$ and $[\text{CoBr}_4]^{2-}$ anions. The distortion of the metal–halogen complexes in the solid solution explains possible appearance of the ferroelectric properties in TEACCB-2 solid solution contrary to the case of the initial $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoX}_4$ ($\text{X} = \text{Cl}, \text{Br}$) crystals. Nevertheless, the ferroelectric nature of the phase lying below T_2 still demands confirmation using the direct methods of measurements of the spontaneous polarization.

The technical application of the considered crystals and solid solutions is restrained because of their hygroscopicity, brittleness, and damaging caused by overheating above 100°C . Nevertheless, it was shown [9, 12] that incorporation of the nanocrystals of TEACCB-2 into a polymer matrix may open a new opportunity for their practical application since such unfavourable properties in this case would be overcome. Moreover, our preliminary dielectric study of the TEACCB-2 nanocrystals incorporated into a polymer matrix revealed the resonant type dielectric dispersion at comparatively high frequency of the measuring field (around 1.2 GHz) [12] that might find the effective technological application in the principally new type of piezotransducers.

Taking into account all mentioned above one can conclude that study of the magnetic and ferroelectric properties of TEACCB-2 solid solution would be very interesting both for the fundamental science and for the practical applications.

2. Experimental

The system of interest, the TEACCB-2 compound, was grown in a single-crystal form at room temperature by slow evaporation of an aqueous solution of CoCl_2 , CoBr_2 , $\text{N}(\text{C}_2\text{H}_5)_4\text{Cl}$ and $\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$ salts taken in the stoichiometric ratio. The obtained single crystals were of deep blue colour. X-ray powder diffraction studies have revealed that at room temperature TEACCB-2 is isomorphous with TEA-CoX_4 ($\text{X} = \text{Cl}, \text{Br}$) compounds and belongs to the $P4_2/nmc$ group of symmetry [12]. The unit cell parameters were found to be $a = b = 9.028(1)$ Å and $c = 15.404(2)$ Å [12].

Polarization was calculated on the basis of the pyrocurrent measured with a Keithley 6517A electrometer. Silver paste was used to make electrical contacts to the sample. Measurement of the polarization was performed in direction coinciding with a axis of the single crystal.

Magnetic susceptibility of the single crystals of TEACCB-2 were investigated within the temperature range of 16–300 K. The measurements were made at a magnetic field strength of 9.9 kOe using Quantum Design SQUID–VSM magnetometer. The superconducting agent was generally operated at a field strength ranging from 0 to 7 T. Field dependences of magnetization were measured at room temperature and 50 K in an applied field up to 5 T. The SQUID magnetometer was calibrated with the palladium rod sample.

The magnetic field was applied in direction of c axis and in the perpendicular direction.

Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal’s constants [13]. The effective magnetic moment values were calculated as

$$\mu_{\text{eff}} = 2.83(\chi_M T)^{1/2}, \quad (2)$$

where μ_{eff} is the effective magnetic moment, χ_M — the magnetic susceptibility per molecule, and T — the absolute temperature.

3. Results and discussion

In order to confirm a ferroelectric nature of the phase lying below T_2 we investigated the spontaneous polarization in vicinity of this temperature point in regime of heating (see Fig. 1).

The temperature dependence of the spontaneous polarization confirms existence of the ferroelectric phase below T_2 . Its maximal value is considerably lower (practically, two orders of magnitude) than in TEACCB-3, which was related to the proper ferroelectrics [4]. These data confirm the supposition made in [9] concerning the improper character of the hypothetic ferroelectric phase in TEACCB-2. Similarly to the case of TEACCB-3 appearance of the spontaneous polarization also should be connected with ordering of the distorted anions. This conclusion fairly well correlates with the data of [9] concerning the change of the dielectric relaxation process in the point of the phase transition at T_2 . The organic cations also would be involved into this process. According to the data of previous study [9] no other anomalies of the dielectric parameters were observed down to 78 K. Therefore, the improper ferroelectric phase would exist at least down to this temperature.

The magnetic susceptibilities of TEACCB-2 were investigated for knowing whether the nature of atomic magnetic interaction changed at low temperatures.

From the obtained results it appears that the magnetic susceptibility for two different orientations of magnetic field obeys the Curie–Weiss law showing the paramagnetic character of their complex central ions (see Fig. 2). The dependences of the magnetic susceptibility reciprocal values and also of $\chi_M^{\text{corr}}T$ worth's as a function of temperature for Co(II) complexes are presented in Fig. 3.

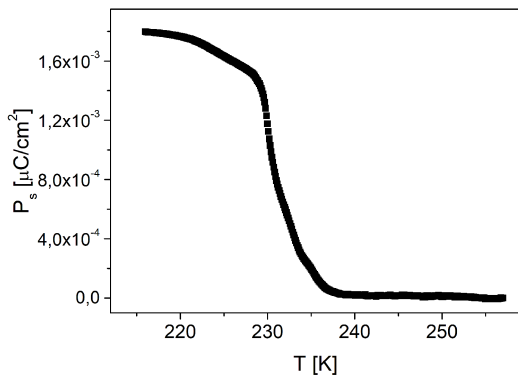


Fig. 1. Temperature dependence of the spontaneous polarization measured at heating.

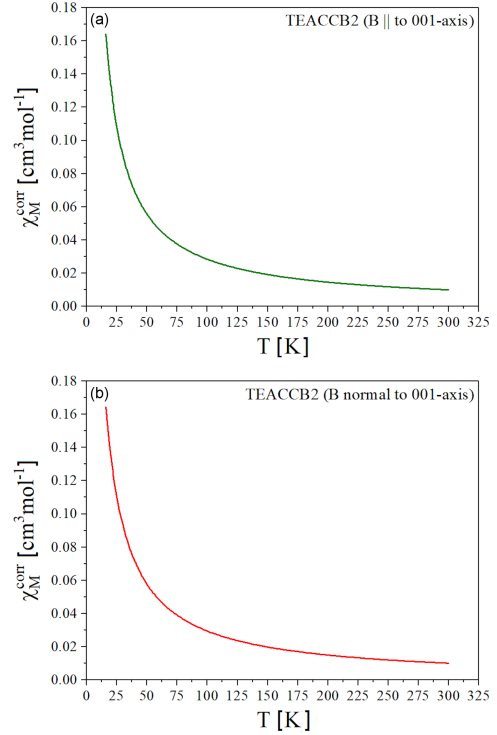


Fig. 2. Temperature dependences of the corrected magnetic susceptibilities measured at two different orientation of the magnetic field: along the axis (001) (a) and in the perpendicular direction (b).

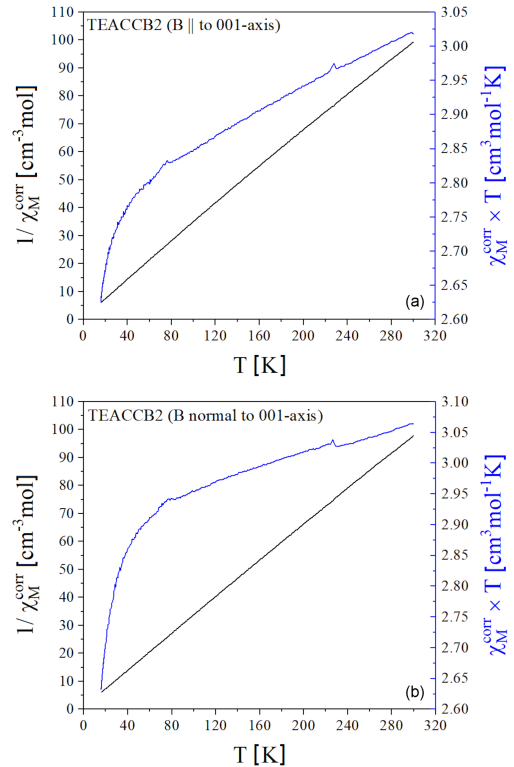


Fig. 3. The temperature dependences of magnetic susceptibility reciprocal values and $\chi_m^{\text{corr}}T$ for different orientation of the magnetic field: along the axis (001) (a) and in the perpendicular direction (b).

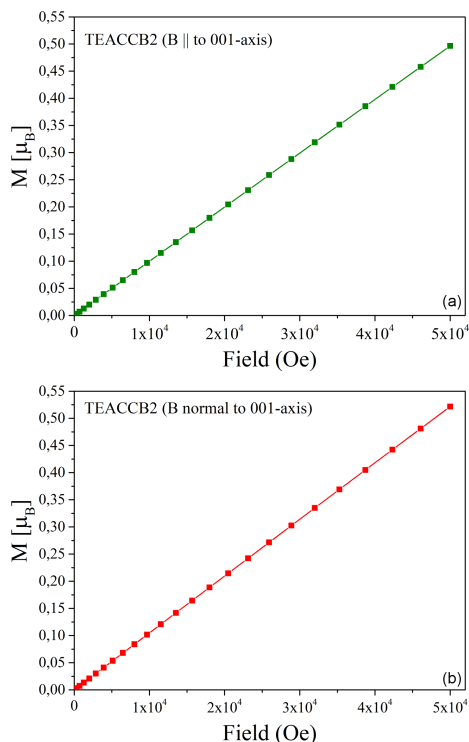


Fig. 4. Field dependences of the magnetization for two different orientations of the magnetic field obtained at $T = 50$ K.

The effective magnetic moment values experimentally determined in the range of 16–300 K change from 4.58 to 4.92 μ_B for the orientation of the magnetic field along c axis and 4.59 μ_B for its orientation in the perpendicular direction.

The magnetic moment values experimentally determined for the investigated compound seems to be close to spin only values for the respective ions calculated from the equation $\mu_{\text{eff}} = [4s(s+1)]^{1/2}$, $s = n/2$ in the absence of the magnetic interactions for present spin-system. This theoretical value calculated at room temperature for Co(II) is equal to 3.88 μ_B .

In the case of the magnetic field oriented along and perpendicularly to c axis the values of $\chi_M^{\text{corr}}T$ vs T change from 2.6255 $\text{cm}^3 \text{mol}^{-1} \text{K}$ (16 K) to 3.0176 $\text{cm}^3 \text{mol}^{-1} \text{K}$ (300 K) and from 2.6326 $\text{cm}^3 \text{mol}^{-1} \text{K}$ (16 K) to 3.0634 $\text{cm}^3 \text{mol}^{-1} \text{K}$ (300 K), respectively. But on the both analyzed curves two peaks appear with a maximum at 227.7 K and 74.9 K for the magnetic field parallel to c axis and at 226.4 K and 77 K for the magnetic field oriented in a perpendicular direction. These increases in $\chi_M^{\text{corr}}T$ vs T values are due to the appearance of ferromagnetic interactions in a very small temperature range around these points.

There is a general trend that in the range about of 300–50 K the values of $\chi_M^{\text{corr}}T$ alter slowly. In the range of about 50–16 K they drastically decrease for both directions of the magnetic field orientation. This drastic decrease indicates a negative θ

value which may suggest the antiferromagnetic intermolecular interaction. Therefore, the magnetic moment values are 4.58 μ_B and 4.59 μ_B , appropriately. It suggests a weak antiferromagnetic interaction between Co(II) canters [14] or a weak intermolecular hydrogen bonds in the crystal lattice [14].

We also did not observe any pronounced nonlinearity in the magnetic field dependences, measured at $T = 50$ K (see Fig. 4). This testifies that magnetic ordering in the investigated compound would be realized at much lower temperatures.

4. Conclusions

Investigations of the temperature dependence of the spontaneous polarization confirmed existence of the improper ferroelectric phase below T_2 . This temperature was found to be close to those obtained in the previous study of the temperature dependence of the real and imaginary part of the dielectric permittivity (232 K at heating) [9]. One can suggest that the spontaneous polarization exists down to the liquid nitrogen temperature (78 K).

The anomalies corresponding to the ferroelectric phase transition were also observed in the temperature dependences of the inverse magnetic susceptibility — respectively at 227.7 K and 226.4 K, depending on the orientation of the magnetic field. The observed difference in the temperatures of this phase transition obtained on the basis of the ferroelectric and magnetic studies reflects the hysteresis of the phase transition, considerably depending on the sample's size and the rate of temperature change that are different in the above mentioned experiments. Presence of the anomaly of inverse magnetic susceptibility at T_2 confirms both ferromagnetic interactions in a very small temperature range around this point and the spontaneous magnetoelectric effect arising in the phase which simultaneously is improper ferroelectric and paramagnetic. Observation of such an effect testifies that the ferroelectric ordering is closely connected with magnetic interactions between Co^{2+} ions.

Anomalous behavior of the inverse magnetic susceptibility in the vicinity of 74.9–77 K also would be related to the early unknown phase transition that demands further detailed studies.

According to SQUID method the effective magnetic moment values calculated for the Co(II) complexes change from 4.58 to 4.92 μ_B for the magnetic field parallel to c axis and from 4.59 to 4.953 μ_B for the magnetic field oriented in the perpendicular direction. They are higher than the spin-only worth which results from a spin-orbit coupling. The values of μ_{eff} calculated for the Co(II) ion using the values of L , S and J of the free ion ground term ($^4F_{9/2}$) may be different. The values may indicate that it is a complex with tetrahedral structure. Such a conclusion fairly well correlates with the data of previous spectroscopic studies [11].

The analyzed Co(II) complexes may be monomeric and characterized by antiferromagnetic interaction ($\theta < 0$ K) around the central ion. Its determined values of magnetic moment indicate a spin-orbit coupling in one Co(II) center.

Acknowledgments

This work was supported by the National Research Foundation of Ukraine in the framework of the project 2020.02/0130 “Multifunctional organic, inorganic, magnetoelectric, photovoltaic and scintillation materials” (Reg. No. 0120U104913).

References

- [1] J.F. Scott, *J. Mater. Chem.* **22**, 4567 (2012).
- [2] R. Ramesh, *Nature* **461**, 1218 (2009).
- [3] V.B. Kapustianik, *Phys. Status Solidi B* **204**, 877 (1997).
- [4] V. Kapustianyk, V. Rudyk, P. Yonak, B. Kundys, *Phys. Status Solidi B* **252**, 1778 (2015).
- [5] A.J. Wolthuis, W.J. Huiskamp, L.J. de Jongh, R.L. Carlin, *Physica B + C* **142**, 301 (1986).
- [6] G.D. Stucky, J.B. Folkers, T.J. Kistenmacher, *Acta Crystallogr.* **23**, 1064 (1967).
- [7] K. Gesi, *Ferroelectrics* **159**, 49 (1994).
- [8] V.B. Kapustianik, O.G. Vlokh, V.I. Mokryi, I.I. Polovinko, S.A. Sveleba, *Ukr. Phys. J.* **35**, 1854 (1990).
- [9] V. Rudyk, I. Kityk, V. Kapustianyk, K. Ozga, *Ferroelectrics* **330**, 19 (2006).
- [10] V. Kapustianyk, S. Sveleba, R. Tchukvinskyi, Z. Czaplá, S. Dacko, in: *Proc. III Europ. Conf. on Applications of Polar Dielectrics, Bled (Slovenia)*, 1996, p. 109.
- [11] V.B. Kapustianyk, Yu.M. Korchak, S.A. Sveleba, V.I. Mokryi, *J. Appl. Spectrosc.* **67**, 119 (2000).
- [12] V. Kapustianyk, Ya. Shchur, I. Kityk, V. Rudyk, G. Lach, L. Laskowski, S. Tkaczyk, J. Swiatek, V. Davydov, *J. Phys. Condens. Matter* **20**, 365215 (2008).
- [13] O. Kahn, *Molecular Magnetism*, VCH, New York 1993.
- [14] A.F. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York 1988, p. 955.