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CONTROVERSY ON THE FERROELECTRICITY IN METAL–FORMATE FRAMEWORKS

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The metal–organic frameworks (MOFs) crystallizing in a perovskite-like architecture became extremely interesting for scientists due to a variety of applications including memory devices, energy conversion and drug delivery. These compounds are constructed from a metal–oxygen or metal–nitrogen octahedral coordinated by organic ligands. They exhibit various interesting properties due to their hybrid organic–inorganic nature. However, ferroelectric MOFs still remain scarce and the topic of ferroelectricity raises a lot of controversies. In this article, we will discuss the actual state of knowledge of these specific compounds with a focus on ferroelectric properties. We will try to create an order out of the current confusion that followed attributing ferroelectric properties to metal–formate frameworks without a direct proof.

Keywords: ferroelectricity, phase transitions, metal–formate frameworks, pyroelectric physics

1. Introduction

In the world of science, no one questions the notion that the metal–organic frameworks belong to the more exciting compounds. The definition of metal–organic materials encompasses a very large number of compounds with a wide variety of chemical compositions and structures. A property that unites the whole family is the homogeneity of the size and shape of the pores in this specific type of compound that allows one to selectively absorb only molecules smaller than the pore size [1]. The desirable physical and chemical properties of these structures result from the versatile feature of different organic and inorganic components. An additional advantage of the metal–organic frameworks is the possible applications of the hybrid compounds such as efficient solar cells [2], gas storage devices [3, 4] or multiferroic memories [5, 6]. The potential applications of these structures have resulted from their structure consisting of two main elements: metal ion centres (nodes) and organic ligand connected with each other by coordination bonds [7]. The metal centres and various organic ligands are responsible for different optical [8], electric [9], magnetic [10] and gas-absorption related [11–13] properties of these materials. We will focus on one of the families of metal–organic frameworks, metal–formate frameworks, that have formate as the organic ligand. The first properties that have been explored in metal–organic frameworks were magnetic ordering [14]. The long distance that the formate ligand occupies can only mediate a weak magnetic coupling, therefore the metal–formate frameworks only exhibit a long-range magnetic coupling below 50 K, hence they are less attractive in terms of practical applications [15]. The most interesting, application-wise, feature of these structures is ferroelectricity. Ferroelectricity is a property of certain structures, which have a spontaneous electric polarization, that can be reversed by the applied external electric field. The characteristic feature of these materials is the P–E hysteresis loop. It is well known that all ferroelectric materials are pyroelectric, with the additional property that their natural

electrical polarization is reversible. The ferroelectricity is the most desirable feature in new materials, which is mostly controlled by the relative sizes of the ions. Several MOF families exhibit structural transitions to phases with ferroelectric properties [5]. One of the most popular subclasses of such hybrid metal–organic materials showing spontaneous polarization is metal–formate frameworks of the general chemical formula $[A][M(HCOO)_3]_n$, where A^{n+} is a molecular alkylammonium cation, and M^{2+} is the metal centre [16]. The interest in $HCOO^-$ as an organic ligand is not without a reason. It is worth mentioning that these anions are derived from the simplest carboxylic acid and keep all its characteristic properties. They can coordinate one, two or three metal ions in different ways, mediating the magnetic interaction between them. As the simplest carboxylic ligand, formate plays an important role in constructing coordinated framework structures with unique magnetic and porous properties. In addition, it may exhibit a polar structure, which means that it participates as an acceptor in the building of hydrogen bonds, while the role of donors most often belongs to the hydroxyl and amine groups of organic cations.

Regarding the issue of ferroelectricity in metal–organic frameworks, the majority of such hybrid frameworks exhibit structural phase transition due to the cooperative ordering of these cations followed by the deformation of the framework [17, 18]. In some cases, the transition occurs to a noncentrosymmetric phase with ferroelectric properties [19]. Additionally, most of the structures with paramagnetic transition metal ions exhibit magnetic ordering in the low temperatures. The simultaneous coexistence of the spontaneous electric and magnetic polarizations makes such materials single phase multiferroics that are highly attractive for application in four-state memory devices. Spontaneous polarization below the Curie temperature and the possibility to change the direction of polarization by reversing the applied electric field are the two basic requirements for ferroelectricity. The most popular and simplest method of demonstrating the ferroelectric properties is, of course, the *P*–*E* hysteresis loop observations. However, the order–disorder phase transition is relatively often considered ferroelectric despite no direct proof. In addition, the dispute over the ferroelectricity of the banana skin highlighted the problem of assigning ferroelectricity and cautioned the interpretation of electrical polarization loops [20]. In recent years, there has been a worrying increase in scientific articles where ferroelectric properties have been assigned without conclusive evidence [21, 22]. In this article, we will look at the current state of knowledge about ferroelectricity in metal–formate frameworks. In order to determine ferroelectricity in the compounds, it is possible to use several measurements, from pyroelectric measurements, complex dielectric permittivity, to the direct proof, which is the *P*–*E* hysteresis loop.

2. The *P*–*E* hysteresis loop measurements

Characteristic of all ferroelectric compounds is the presence of a *P*–*E* hysteresis loop. For such measurements, the sample must be oriented along the polar axis, which is troublesome for many metal–formate frameworks, because the single crystals are too small. In addition, it should be remembered that this technique requires the ability to interpret the obtained results, because often due to the so-called banana effect, ferroelectricity has been incorrectly assigned (Fig. 1) [22].

The most important result is the successful measurement of the electric polarization loop during the measurement of polarization dependent on the applied external electric field in $NH_4[Zn(HCOO)_3]$ below the phase transition temperature (191 K). The experimentally determined spontaneous polarization (1.03 $\mu C/cm^2$) agrees with the theoretical value of spontaneous polarization (0.96 $\mu C/cm^2$) [23]. The magnetic members of this family also exhibit ferromagnetic ($NH_4[Co(HCOO)_3]$ and $NH_4[Ni(HCOO)_3]$) and antiferromagnetic ($NH_4[Mn(HCOO)_3]$) [21, 24] properties.

The first reported and the most thoroughly studied member of the hybrid metal–formate frameworks is dimethylammonium ($[(CH_3)_2NH_2]$, DMA) [22, 25–31]. Most of these compounds exhibit a single structural phase transition that involves a cooperative ordering of organic cations. Depending on a metal centre, the phase transition temperatures fall between 160–180 K [25, 27, 29, 32–34] with an exception of the Mg compound (270 K) [35]. Several publications revealed indications of the ferroelectric behaviour of the low-temperature phase in some of these hybrid perovskites,

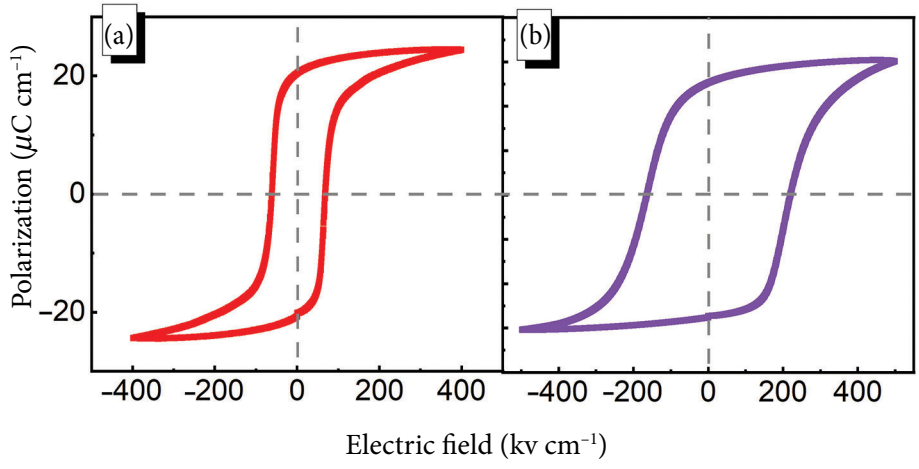

Fig. 1. (a) Saturated hysteresis loops for ferroelectric compounds, (b) non-saturated hysteresis loops.

though a proper polarization hysteresis loop was only obtained for $[(CH_3)_2NH_2][Co(HCOO)_3]$ [36] and $[(CD_3)_2ND_2][Co(DCOO)_3]$ [37, 38]. Surprisingly, $[(CD_3)_2ND_2][Co(DCOO)_3]$ has a new phase transition above the room temperature at around 319 K [38], as well as a low-temperature structural phase transition, in contrast to $[(CH_3)_2NH_2][Co(HCOO)_3]$ with only one temperature phase transition about 155 K [36]. The dielectric properties above 151 K between II and III phases show 'classical' dipolar relaxation. Very similar dielectric behaviours were observed in $NaNo_2$, which is a typical order–disorder type ferroelectric [39]. The proper dielectric hysteresis loop with a saturation polarization of 1.04 $\mu C/cm^2$ is comparable to that of $NH_4[Zn(HCOO)_3]$. This hysteresis loop and the SHG measurement and dielectric properties clearly prove that $[(CH_3)_2NH_2][Co(HCOO)_3]$ and $[(CD_3)_2ND_2][Co(DCOO)_3]$ are relaxor-type ferroelectrics. These types of ferroelectrics have received attention, in part because of their excellent electromechanical properties.

3. The structural measurements

Structural measurements make it possible to indicate changes in symmetry and a non-centrosymmetric crystal structure. The determination of the symmetry of high-temperature and low-temperature phases allows for the determination of potential ferroic properties in accordance with the Aizu classification. As expected, ferroelectric materials exhibit a second harmonic generation (SHG) effect that is sensitive to symmetry breaking during temperature changes (only non-centrosymmetric materials display SHG signals). This technology is used in ceramic ferroelectrics, mainly for confirming symmetry breaking and detecting ferroelectric domains [39, 40]. Similarly, the determination of the dipole moment in two possible states in a unit cell proves the ferroelectricity. However, due to the chemical and geometric complexity of the structures in MOF compounds, an accurate determination of symmetry in phases is troublesome and sometimes even impossible.

For the single crystal $NH_4[Mg(HCOO)_3]$, X-ray diffraction showed that it crystallizes in the hexagonal space group $P6_322$, with orientation disordered NH_4^+ ions located inside of frameworks. After cooling down, the compound undergoes a phase transition at around 255 K, interestingly to the ferroelectric structure $P6_3$ [41]. The authors noted that the same structural changes had previously been reported for other compounds in this family. The data presented in the article indicates that in the ordered phase $NH_4[Mg(HCOO)_3]$ three nitrogen atoms are heterogeneous on the X-ray timescale, but the rotation of the NH_4^+ does not freeze completely on the phase transition but shows a further slowdown below 255 K on the Raman and IR timescales [41]. This behaviour proves the highly dynamic nature of hydrogen bonds. Authors have noticed that the phase transition temperature increases with a decrease in mass and an increase in the size of metal cations [41]. According to the authors, the obtained results indicate a method of modulating the phase transition temperature and ferroelectric properties by changing

the cation type in the metal formate structure. In our opinion, based on Raman, IR and structural measurements it is difficult to determine the ferroelectric properties of a compound. No hysteresis loop or pyroelectric current measurements were demonstrated for the tested compound. The dielectric measurements were compared with the only compound with the NH_4 cation, for which ferroelectric properties were demonstrated, namely $NH_4[Zn(HCOO)_3]$ [23, 42, 43], but can ferroelectric properties be determined from the similarity? This proposal raises serious concerns.

4. The pyroelectric current measurements

The pyroelectric measurement as a function of temperature is an alternative method. It is a direct measurement of the polarization derivative over temperature. Due to the averaging of the polarization vector component for polycrystalline samples, this method does not allow for a precise determination of the value of spontaneous polarization, but it gives a picture of changes in this value as a function of temperature.

In 2017, it was reported that the compound $[(CH_3)_2NH_2][Mn(HCOO)_3]$ exhibits a first-order ferroelectric phase transition with a high polarization, induced by the order–disorder transition of hydrogen bonds [44]. The authors found the ferroelectricity of the compound based on a pyroelectric measurement. It has been suggested that the sharp first-order ferroelectric transition is related to the hydrogen bond ordering process, therefore single crystals $[(CH_3)_2NH_2][Mn(HCOO)_3]$ show a high pyroelectric coefficient ($5.16 \cdot 10^{-2}$ C/m^{2}K) and a high thermal expansion coefficient [44–48]. In our opinion, the measurement of pyroelectric current alone cannot provide sufficient evidence for the existence of the ferroelectric transition. However, it should be remembered that earlier Sanchez-Andujar and others showed the structure for $[(CH_3)_2NH_2][Mn(HCOO)_3]$ and assigned a monoclinic eccentric space group Cc, which could suggest ferroelectricity [47]. It would seem that the demonstration of the change in symmetry and non-centrosymmetricity and, additionally, a large coefficient of pyroelectric current are a sufficient proof of ferroelectric properties. It is worth noting that the measurements of $[(CH_3)_2NH_2][Mn(HCOO)_3]$ in the form of mesoscale particles do not show a detectable pyroelectric current [49]. Surface polarization effects limit spontaneous polarization and this is a consequence of a relatively low electrical polarization in this formate family. A similar behaviour can be observed for the analogue $[(CH_3)_3NH_2](Mg(HCOO)_3)$ [50].

Let us look at other structures with the $(CH_3)_2NH_2$ cation. Another compound for which pyroelectric measurements have been made is $[(CH_3)_2NH_2][Fe(HCOO)_3]$ [51]. The strong dependence of dielectric permittivity on the frequency indicates the relaxor nature of the electrical order. The pyroelectric current was measured – a small, sharp anomaly is observed at the phase transition temperature. The resulting electrical polarization of 18 μC/m^2 [51] suggests a weak ferroelectricity. It is worth noting that currently all measurements of the second harmonic generation (SHG) and pyroelectric current measurements in DMA^+ analogue structures indicate only a pyroelectric, but not a ferroelectric behaviour. Assigning ferroelectric properties to these structures is, in our opinion, improper and it still hampers the widely discussed potential applications of compounds with this cation in ferroelectric devices. Additionally, we should distinguish proper and improper ferroelectricity [52, 53]. For the improper ferroelectrics, it will not be possible to measure the hysteresis loop. An interesting case is the compounds with the general formula $[CH_3NH_2NH_2][M(HCOO)_3]$ for which it was not possible to obtain direct evidence in the form of a hysteresis loop, but the measurements made allowed one to determine the ferroelectricity [54, 55]. These compounds show the two structural phase transitions. The first phase transition temperature is practically independent of the type of divalent metal and is observed in 310–327 K from the nonpolar phase $R\bar{3}c$ to the polar R3c phase. It is a second type of phase transition associated with the partial ordering of methylhydrazinium cations. The second, low-temperature phase transition indicates the first-order character and is related to the complete ordering of methylhydrazinium cations and deformation of the metal–formate frameworks. The pyroelectric measurements show the ferroelectric nature of the phase transition at room temperature (Fig. 2). Based on the analysis of dielectric measurements, the improper ferroelectricity was indicated.

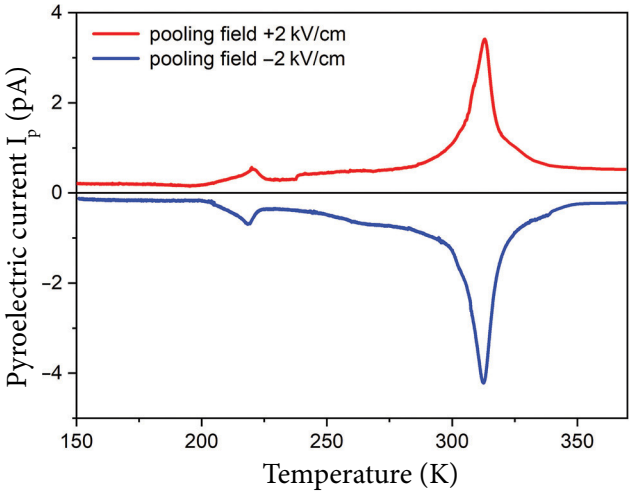

Fig. 2. Pyroelectric current as a function of temperature after poling $[CH_3NH_2NH_2][M(HCOO)_3]$ from 350 to 150 K with ±2 kV/cm, during heating with the temperature rate of 1 K/min.

Let us return to the already mentioned analogue with the $(CH_3)_2NH_2$ cation – for the $[(CH_3)_2NH_2)][Co(HCOO)_3]$ and $[(CD_3)_2ND_2)][Co(DCOO)_3]$ compounds it was possible to show a hysteresis loop. The static pyroelectric method, dynamic dielectric measurements and high-pressure Raman spectra were used to study the ferroelectric order–disorder transition in $[(CD_3)_2ND_2)][Co(DCOO)_3]$ [38]. The two phase transitions were noted, at 1.6 and 6.3 GPa. Near 1.6 GPa, there was some correlation between the tendency of the jumping energy of nitrogen atoms in DMA^+ cations and the tendency to order due to dipole–dipole interactions; this competition caused a slow decrease in T_c, in contrast to the sharp decrease observed with the KDP-type ferroelectric. The applied pressure suppresses the electrical polarization that is accompanied by a shift in T_c towards lower temperature. The ferroelectricity decays at 1.6 GPa, and this is related with the distortion of the anionic structure [38]. It can be seen that the application of pressure has a large influence on the dynamic behaviour of dimethylamine cations and affects the ferroelectric properties. These studies show the feasibility of fine-tuning the ferroelectric properties in MOFs under high pressure.

5. Dielectric spectroscopy

One of the extremely useful electrical techniques is broadband dielectric spectroscopy. Measurements of complex dielectric permittivity as a function of both temperature and frequencies are an often used method for identifying phase transitions. In a phase transition where the electrical polarization changes, the dielectric permittivity values must also change. In the case of ferroelectric materials, the Curie–Weiss law must be met when switching between the paraelectric and the ferroelectric phase. Measurements of the dielectric response as a function of frequency are extremely useful tools in identifying the mechanisms of ferroelectric phase transitions. This technique allows for observation of relaxation processes and connecting them with structural changes of the compound, consequently determining the factors leading to the loss of ferroelectricity.

Initially, it was suggested that the DMA-M materials indicate anti-ferroelectric properties, but this assumption – based only on the shape of the temperature dependence of the dielectric constant – turned out to be incorrect [56]. Ferroelectric phase transition is usually accompanied by a change in the symmetry of lattice constants. In addition, studies of pyroelectric current and thermal expansion may provide evidence for ferroelectricity in the studied compounds. The ferroelectric order below T_c was confirmed by measurements of the second harmonic generation (SHG) and the existence of an electrical hysteresis loop for $[(CH_3)_2NH_2)][Co(HCOO)_3]$ [36]. The estimated spontaneous polarization value for this material is 1.02 μC/cm^2, which is approximately six times the value obtained with the prototype hybrid ferroelectric (0.2 μC/cm^2) [15] of Rochelle salt (sodium potassium tartrate). Additionally, the frequency form of the dielectric permittivity indicated the Debye relaxation. The determined values of activation energy (E_a = 464 J/mol) and relaxation time ($\tau = 1.02 \cdot 10^{-15}$s) resemble analogous values obtained for traditional ferroelectric crystals showing order–disorder phase transitions, such as $NaNO_2$ [39, 57].

Another interesting metal–formate framework is a structure with the general formula $[C_2H_5NH_3][M(HCOO)_3]$. The results of experimental studies and theoretical calculations are presented for the compound $[C_2H_5NH_3][Na_{0.5}Fe_{0.5}(HCOO)_3]$ [58, 59]. Based on the results

of calorimetric tests, the phase transition temperature (360 K) of the second type from the high-temperature phase transition to the low-temperature phase was determined. Above this temperature, the dynamic disorder of the $[C_2H_5NH_3]^+$ cations does not cause a significant dispersion in the dielectric spectra. The dependence of the dielectric permittivity as a function of temperature showed strong changes in the vicinity of the phase transition temperature, which may be characteristic of ferroelectric compounds. The results of calculations based on the first principles density functional theory (DFT) clearly confirmed that the low-temperature phase is ferroelectric. The conclusions were also based on structural studies showing that non-centrosymmetric and spontaneous polarization in the ferroelectric phase results from the ordering of ethylammonium cations. The estimated value of the electric polarization in $[C_2H_5NH_3][Na_{0.5}Fe_{0.5}(HCOO)_3]$ is 0.8 μC/cm^2 and is about four times the value obtained for the prototype hybrid ferroelectric (0.2 μC/cm^2) of Rochelle salt (sodium tartrate potassium) [58, 59]. It is worth recalling here that ferroelectric MOF crystals are still rare at room temperature.

[AmineH$^+$]	Metal ions M^{II}	Symmetry	Activation energy E_a, eV	Temperature of phase transitions T_0, K	Physical properties
NH_4^+	Cu^{2+} Zn^{2+} Mg^{2+} Mn^{2+} Co^{2+} Ni^{2+} Fe^{2+}	Orthorhombic/ hexagonal [6]	0.76 [60] 0.17 [43] 0.28 [41] 0.09 [61] 0.094 [61]	225; 360 [60] 192 [61] 255 [61] 254 [61] 191 [24] 199 [61] 212 [61]	Multiferroicity [61] Ferroelectricity [23]
$(CH_3)_2NH_2^+$	Mn^{2+} Co^{2+} Mg^{2+} Zn^{2+} Fe^{2+} Ni^{2+}	Rhombohedral/ monoclinic [27]	~1.15 [62] 0.28 [36] 0.30 [35] 0.28 [63]	187 [48, 64] 165 [36] 270 [35] 156 [63] 160 [27] 180 [65]	Multiferroicity [36] Dielectricity [35] Magnetism [65]
$CH_3NH_2NH_2^+$	Mn^{2+} Mg^{2+} Fe^{2+} Zn^{2+}	Trigonal [54]	0.76 [66, 67]	220; 310 [54] 235; 327 [54] 181; 310 [54] 166; 322 [67]	Ferroelectricity [58]
NH_2-CH^+-NH_2	Mn^{2+}	Orthorombic [68]	0.46 [68]	280; 334 [68]	Magnetism [68]
$CH_3C(NH_2)_2^+$	Mn^{2+}	Orthorombic [69]	0.6; 1.1 [69]	304 [69]	Ferromagnetism [69]
$(CH_2)_3NH_2^+$	Cu^{2+} Mg^{2+} Mn^{2+} Zn^{2+}	Monoclinic [70] Orthorombic [70]		285 [70] 288 [71] 273 [70] 255; 300 [70]	Dielectricity [70]
$CH_3CH_2NH_3^+$	Cu^{2+} Mg^{2+}	Orthorombic [72]	0.39 [73]	357 [72] 374; 426 [73]	Magnetism [72]
$NH_2NH_3^+$	Co^{2+} Fe^{2+} Mg^{2+} Mn^{2+} Zn^{2+}	Orthorombic/hexagonal [74]	1.03 [74] 0.17; 0.11; 0.03 [75]	380 [74] 347; 336 76] 348 [74] 360; 298 [75] 367 [74]	Multiferroicity [74]
$C_3N_2H_5^+$	Mn^{2+}	Monoclinic [77]	0.83 [77]	438 [77, 78]	Ferroelectricity [78]

6. Conclusions

Searching for ferroelectric properties in metal–formate frameworks is an activity based mainly on empirical research. Despite the many experiments carried out on formate compounds of the MOF type, the topic of ferroelectricity still raises a lot of controversies. The dynamics of molecules and built-in cations can induce complex structural phase transitions that reflect the details of the interactions that occur between the various components in the structure, When the built-in organic cation and the framework molecule fit together well, creating a long-range bond, ferroelectricity will eventually occur. A key issue for ultra-fine ferroelectric materials is the depolarization effect. It is known that the ferroelectricity of conventional ferroelectric thin films is usually suppressed because the layers are thinner than the critical thickness due to the action of the depolarizing field caused by uncompensated charges in the presence of metal electrodes. Despite the technological advances made, research and the potential applications of ferroelectric metal–formates are still quite limited due to a lack of understanding of ferroelectricity, which requires extensive, complementary research. It is worth noting that ferroelectricity is an interdisciplinary topic on the border of chemistry, physics, materials science, electronics and crystallography. An important issue seems to be the theoretical calculations, such as DFT, that can unequivocally confirm or contradict the ferroelectric property of the compound. There has been a tendency in recent years to publish information about the ferroelectric properties of compounds without a direct proof. Only a set of a few experimental techniques and common results provide certainty about the ferroelectric properties of a given material. Of course, the hysteresis loop is the most desirable result, but also NMR, EPR or dielectric spectroscopy measurements can be a window to show the ferroelectric properties of the compound.

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METALO–FORMATO DARINIŲ FEROELEKTRIŠKUMO KONTROVERSIJA

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