PEROVSKITE TYPE SEIGNETTOMAGNETS

Yu. Venevtsev, V. Lyubimov, V. Ivanova, G. Zhdanov

JOURNAL DE PHYSIQUE *Colloque* C2, *supplément au n°* 4, *Tome* 33, *Avril* 1972, *page* C2-255

PEROVSKITE TYPE SEIGNETTOMAGNETS

Yu. N. VENEVTSEV, V. N. LYUBIMOV, V. V. IVANOVA and G. S. ZHDANOV

Karpov Institute of Physical Chemistry, Moscow, U. S. S. R.

Résumé. — Nous avons donné une rapide revue des recherches expérimentales et théoriques de l'institut Karpov pour la synthèse et l'étude des ferromagnétiques de type perovskites.

Abstract. — A short review of exprimental and theoretical investigations of Karpov Institute in the synthesis and study of perovskite type seignettomagnets has been given.

In 1916-1917 S. A. Boguslavskii admitted the existence of substances with moleculas possessing simultaneously electric and magnetic dipoles [1]. It is known also that in 1958 G. A. Smolenskii and coworkers synthesized Fe-containing seignettoelectrics and supposed that these substances are at the same time antiferromagnets [2]-[4]. However the experimental evidences of the existence of seignettomagnets (ferroelectric with a magnetic ordering) were obtained only in late 1961 and early 1962 independently in the Institute of semiconductors (under the Academy Sciences, U. S. S. R.) [5], [6] and in our Institute [7], [8]. The discovery of the first seignettomagnets stimulated further investigations of similar substances. The main results of Karpov Institute in a study of seignettomagnets are as follows :

I. It is known that one of the first seignettomagnets is bismuth ferrite ($BiFeO_3$). This seignettomagnet has been discovered [7], [8] and studied in detail [9]-[11] in Karpov Institute. In accordance our later data $BiFeO_3$ is a seignettoelectric-compensated antiferromagnetic with Curie temperature and Neel point 850 and 375 °C respectively [11].

It is necessary to note for an justice that for a definite time Smolenskii school refused the existence of the spontaneously-polarized state at $BiFeO_3$ [12]. Now a discussion is transfered in another plane. This school became to keep to an opinion, that $BiFeO_3$ is similar on a character of its dielectric properties to a known antiseignettoelectric $PbZrO_3$ [13].

At the same time a recent data of american investigators [14], [15] confirmed the seignettoelectric character of dielectric properties of $BiFeO_3$.

II. Electric and magnetic properties of a seignettoelectric-ferromagnetic have been investigated on the base of the Landau thermodynamic theory of the second-order phase transitions [16]. In this theory a connection between electric and magnetic characteristics is realized through a linear magnettoelectric (M. E.) effect. The last causes an « weak » electric polarization (« weak » ferromagnetism) when an initial ferromagnetic (seignettoelectric) ordering occurs only. This phenomenon has been described also on a base of the effective field theory [16].

III. Crystals, admitting, M. E.-effect (including of seignettomagnets) desplay some particularities when electromagnetic waves and for example a light propagate in their [17]-[19]. It has been shown theoretically that velosity of « forward » propagation differs from that of « backward » propagation. Such phenomenon takes place in 47 classes of a symmetry from 68 crystallographic and the limited groops of a magnetic symmetry, admiting M. E.-effect. The last influences not only on refractive indices (velosities of the propagation) this effect influences also on a polarization of waves. For example, in a case of a perpendicular falling of a light on a face of the cubic crystal a polarizations plane of a reflective light is turned on an angle proportional to M. E.-effect [18]. When the light passes through a plate of a crystal Cr_2O_3, possessing M. E.-effect, arises a characteristic ellipsoidal polarization of the light [19].

IV. A magnetic symmetry of possible seignettoelectric-ferromagnetic phases for perovskite-type crystals with different mutual orientations of a spontaneous electrical polarization and spontaneous magnetization has been studied [20].

Moreover, all positions in unit cells (of 230 space groups) in which can be placed electric and magnetic dipoles have been found [21]. Symmetry conditions of an existence and an coexistence of seignetto-, antiseignetto-electric and ferro-, antiferromagnetic dipole arrangements have been analysed [22].

We have studied also symmetry restrictions on different effects of an interrelation of electric, magnetic and mechanical properties of crystals [23].

V. Table I contains a number of seignettomagnetic perovskite-type compounds, which have been synthesized and investigated (N 5 ÷ 8) or only investigated (N 1 ÷ 4,9) by us [7], [8], [24]-[29].

VI. One of the first experimental evidences of the existence of an interrelation between electric and magnetic properties of seignettomagnets appeared gamma-resonance data on $BiFeO_3$ [30].

TABLE I

Perovskite-type seignettomagnets
(*of Karpov Institute*)

N	Compounds	Properties (*)	T_{KE} °C	T_{KM} °C
1	$BiFeO_3$	se-afm	850	375
2	$BiMnO_3$	ase-fm	500	— 170
3	$Pb(Fe_{1/2}Ta_{1/2})O_3$	se-fim	— 40	— 140
4	$Pb(Mn_{1/2}Nb_{1/2})O_3$	ase-afm	20	— 262
5	$PbMn_{2/3}W_{1/3}O_3$ (*)	ase-afm	200	— 180
6	$PbFe^{3+}_{1/2}Mn^{4+}_{1/4}W^{6+}_{1/4}O_3$	se-fim	— 10	— 130
7*a*	$Pb_2Mn^{2+}Re^{6+}O_6$	ase-fim	95	— 150
7*b*	$Pb_2Mn^{3+}Re^{5+}O_6$	ase-fim	120	— 170
8	$Cd(Fe_{1/2}Nb_{1/2})O_3$	ase-afm	450	— 225
9	Sr_2CuWO_6	se-afm	920	— 230

(*) Compositions are given without a count of possible superstructure.

(**) se, ase, fm, fim, afm — seignetto, antiseignettoelectric, ferro-, ferri- and antiferromagnetic respectively.

In accordance to [30], [31] in the crystals $BiFeO_3$ magnetic moments are perpendicular to a vector of the spontaneous polarization P_s. It allows to conclude that a reorientation of P_s (for example, with an electric field) on an other threefold axis of a similar crystals must cause a change of the directions of the magnetic momentums and consequently a change of magnetic properties of crystals in the whole.

In this connection our data [32]-[34] are interesting also.

VII. Seignettomagnetic solid solutions with different combinations of dielectric and magnetic properties (seignettoelectric-ferrimagnetic [32], [35], antiseignettoelectric-ferromagnetic [25] and others) have been obtained and studied.

Scientific and practical interests demand of a continuation of the investigation of seignettomagnets and the creation of seignettomagnetic materials.

References

[1] BOGUSLAVSKII (S. A.), Izbrannie trudi po fizike, Moskva, 1961, p. 231.
[2] SMOLENSKII (G. A.), AGRANOVSKAYA (A. I.), *Zh. Tekhnich. fiz.*, 1958, **28**, 1491.
[3] SMOLENSKII (G. A.), AGRANOVSKAYA (A. I.), POPOV (S. N.), ISYPOV (V. A.), *Zh. Tekhnich. fiz.*, 1958, **28**, 2152.
[4] SMOLENSKII (G. A.), IOFFE (W. A.), Communications du Colloque international de magnétisme de Grenoble (France, 2-6 juillet, 1958). Communication, 71.
[5] SMOLENSKII (G. A.), ISYPOV (V. A.), KRAINIK (N. N.), AGRANOVSKAYA (A. I.), *Izv. Akad. Nauk S. S. S. R. Ser. fiz.*, 1961, **25**, 1333.
[6] BOKOV (V. A.), MILNIKOVA (I. E.), SMOLENSKII (G. A.), *Zh. exper. theor. fiz.*, 1962, **42**, 643.
[7] VENEVTSEV (Yu. N.), ZHDANOV (G. S.), SOLOVIJEV (S. P.), BEZUS (Ye. V.), IVANOVA (V. V.), FEDULOV (S. A.) and KAPYSHEV (A. G.), *Kristallografiya*, 1960, **5**, 620.
[8] KISELEV (S. V.), OZEROV (R. P.), ZHDANOV (G. S.), *Dokl. Akad. Nauk, S. S. S. R.*, 1962, **145**, 1255.
[9] FEDULOV (S. A.), VENEVTSEV (Yu. N.), ZHDANOV (G. S.), SMAGEVSKAYA (E. G.), REZ (I. S.), *Kristallografiya*, 1962, **7**, 77.
[10] TOMASHPOL'SKII (Yu. Ja.), VENEVTSEV (Yu. N.), ZHDANOV (G. S.), *Dokl. Akad. Nauk S. S. S. R.*, 1963, **153**, 1313 ; *Kristallografiya*, 1964, **9**, 746 ; 1967, **12**, 252.
[11] ROGINSKAYA (Yu. Ye.), TOMASHPOL'SKII (Yu. Ya.), VENEVTSEV (Yu. N.), PETROV (V. M.), ZHDANOV (G. S.), *Zh. exper. theor. fiz.*, 1966, **50**, 69.
[12] SMOLENSKII (G. A.), BOKOV (V. A.), *J. Appl. Physics*, 1964, **35**, 915.
[13] SMOLENSKII (G. A.), BOKOV (V. A.), ISYPOV (V. A.), KRAINIK (N. N.), NEDLIN (G. M.), *Helv. Phys. Acta*, 1968, **41**, 1187.
[14] MICHEL (C.), MOREAU (Y. M.), ACHENBACH (G. D.), GERSON (R.), JAMES (W. J.), *Solid State Comm.*, 1969, **7**, 701.
[15] TEAQUE (J. R.), GERSON (R.), JAMES (W. J.), *Solid State Comm.*, 1970, **8**, 1073.
[16] LYUBIMOV (V. N.), *Izv. Akad. Nauk S. S. S. R., Ser. fiz.*, 1964, **28**, 626.
[17] LYUBIMOV (V. N.), *Dokl. Akad. Nauk S. S. S. R.*, 1968, **181**, 858.
[18] LYUBIMOV (V. N.), *Kristallografiya.* 1968, **13**, 1008 ; **14**, 213.
[19] LYUBIMOV (V. N.), *Fiz. Tverdogo Tela*, 1968, **10**, 3502.
[20] LYUBIMOV (V. N.), *Kristallografiya*, 1965, **10**, 420.
[21] LYUBIMOV (V. N.), ZHELUDEV (I. S.), *Kristallografiya*, 1963, **7**, 313.
[22] LYUBIMOV (V. N.), *Kristallografiya*, 1963, **8**, 699 ; *Izv. Akad. Nauk S. S. S. R., Ser. fiz.*, 1964, **28**, 658.
[23] LYUBIMOV (V. N.), *Kristallografiya*, 1967, **12**, 708.
[24] TOMASHPOL'SKII (Yu. Ja.), ZUBOVA (Ye. V.), BURDINA (K. P.), VENEVTSEV (Yu. N.), *Izv. Akad. Nauk S. S. S. R., Ser. Neorg. Mater.*, 1967, **3**, 2132.
[25] IVANOVA (V. V.), VENEVTSEV (Yu. N.), *Izv. Akad. Nauk S. S. S. R., Ser. fiz.*, 1967, **31**, 1803.
[26] SHVORNEVA (L. I.), VENEVTSEV (Yu. N.), *Zh. exper. theor. fiz.*, 1965, **49**, 1038.
[27] ROGINSKAYA (Yu. Ye.), VENEVTSEV (Yu. N.), ZHDANOV (G. S.), *Zh. exper. theor. fiz.*, 1965, **48**, 1231.
[28] DROBISHEV (L. A.), AL'SHIN (B. I.), TOMASHPOL'SKII (Yu. Ya.), VENEVTSEV (Yu. N.), 1969, **14**, 736.
[29] VENEVTSEV (Yu. N.), IVANOVA (V. V.), GOLOVNIN (V. A.), KASHLINSKII (A. I.), KOZLOVA (L. A.), KUZ'MIN (R. N.), *Izv. Akad. Nauk S. S. S. R., Ser. fiz.*, 1971, **35**, 1829.
[30] MITROFANOV (K. P.), VISCOW (A. S.), PLOTNIKOVA (M. V.), VENEVTSEV (Yu. N.), SHPINEL (V. S.), *Izv. Akad. Nauk S. S. S. R., Ser. fiz.*, 1965, **29**, 2029.
[31] SOSNOVSKA (I.), SOSNOVSKI (E.), KISELEV (S. B.), KSHNYAKINA (A. N.), OZEROV (R. P.), Preprint N 2653, Ob'edin. Inst. Jadern. Issledov., Dubna, 1966.
[32] TOMASHPOL'SKII (Yu. Ja.), VENEVTSEV (Yu. N.), ANTONOV (G. N.), *Zh. exper. theor. fiz.*, 1965, **49**, 367.
[33] TOMASHPOL'SKII (Yu. Ja.), VENEVTSEV (Yu. N.), BEZNOZDREV (V. N.), KASHLINSKII (A. I.), *Zh. exper. theor. fiz.*, 1967, **52**, 100.
[34] ASTROV (D. N.), AL'SHIN (B. I.), ZORIN (R. V.), DROBISHEV (L. A.), *Zh. exper. theor. fiz.*, 1968, **55**, 2122.
[35] SHVORNEVA (L. I.), VENEVTSEV (Yu. N.), *Izv. Akd. Nauk S. S. S. R., Ser. Neorg. Mater.*, 1966, **2**, 1856.