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Influence of the Jahn-Teller effect on magnetic anisotropy in single crystals of fluorine hexahydrates of transition metals

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The magnetic properties of fluorine hexahydrates of transition metals have been studied. It was found that the presence of spin-orbit interaction of the transition metal ion has a significant effect on anisotropy of magnetic properties. Depending on the direction of interaction of the orbital magnetic moment of a transition metal cation with a crystal field easy direction of magnetization changes from the crystallographic *b*-axis to the *c*-axis.

Keywords: single crystal, magnetic anisotropy, Jahn-Teller effect.

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1. Introduction

Interaction of orbital electron states with the distortion of crystalline lattice field — the Jahn-Teller effect — is typical for compounds with transition ions with a non-zero orbital moment [1].

In addition to the well-known static Jahn-Teller effect a dynamic effect is observed. The static effect, i.e., the formation of local strains of a crystalline lattice, is a result of interaction between electrons and vibrations of nuclei. These states in the lattice occur as a result of splitting of an unstable electron state of a Jahn-Teller ion [1,2]. In case of the dynamic Jahn-Teller effect coupled vibrations of nuclei and electrons (so-called vibronic states) arise. In this case the system appeared to be delocalized over all minima of energy and tunneling takes place between individual low-symmetry states [3].

Vibronic excitations arise in molecular crystals, i.e., crystals formed by molecules bound by intermolecular forces. These, as a rule, are crystals with the van der Waals or hydrogen bonds [4,5]. These excitations are composed of an electron molecular exciton and one or several internal phonons. Internal phonons correspond to vibration branches of the crystal arising from the intramolecular vibrations when molecules are united to form the crystal. Molecular excitons are electron excitations (quasi-particles) in molecular crystals. It means that molecules in ground and excited states keep their identity and are weakly disturbed by the crystal field, and wave functions of neighboring molecules are weakly overlapped. The excited state of a molecule is not localized and can move from one molecule to another.

Compounds belonging to a wide family of $AB\mathrm{F}_6 \cdot 6\mathrm{H}_2\mathrm{O}$ (A = Mg, Zn, Fe, Co, Ni, Mn, Cd; B = Ti, Si, Ge, Sn, Zr) also are vibronic crystals, because alternating $[A(\mathrm{H}_2\mathrm{O})_6]^{2+}$ and $[B\mathrm{F}_6]^{2-}$ octahedra are coupled by hydrogen bonds $\mathrm{O{-}H\cdots F}$ [6,7].

There is an extensive data on the magnetic anisotropy of $\mathrm{FeSiF_6 \cdot 6H_2O}$, $\mathrm{NiTiF_6 \cdot 6H_2O}$, and $\mathrm{FeTiF_6 \cdot 6H_2O}$ crystals [8–13], that demonstrate a behavior typical for antiferromagnetics when a field is applied in the plane of symmetry, and a paramagnetic behavior under normal direction of magnetic field, i.e,. they are two-dimension or frustrate antiferromagnetics [8–13]. Ions of iron, Fe^{2+}, and nickel, Ni^{2+}, in these compounds have an orbital moment, that results in the presence of spin-orbital interaction and, as a consequence, possible emergence of excitations and anisotropy of magnetic properties. In this work we studied magnetic properties of the following single crystals: $\mathrm{CoTiF_6 \cdot 6H_2O}$, $\mathrm{CoSiF_6 \cdot 6H_2O}$, $\mathrm{FeGeF_6 \cdot 6H_2O}$, $\mathrm{MnSiF_6 \cdot 6H_2O}$, and $\mathrm{MnTiF_6 \cdot 6H_2O}$. Fe^{2+} and Co^{2+} ions possess an orbital moment, while Mn^{2+} ion has five electrons at the 3d orbital and, as a consequence, the orbital moment of this ion is zero. Substitutions in the $[B\mathrm{F}_6]^{2-}$ subsystem were made to verify the effect of B^{4+} quadrivalent ion on the character of magnetic anisotropy in these systems.

2. Experiment

Single crystals were synthesized in the Institute of Chemistry of FEB RAS using the technology described in earlier papers [14,15]. X-ray diffraction analysis has shown that all the studied samples are single crystals corresponding to the declared chemical formulae with space symmetry group $R\bar{3}$. Atoms A and B in the crystalline structure of

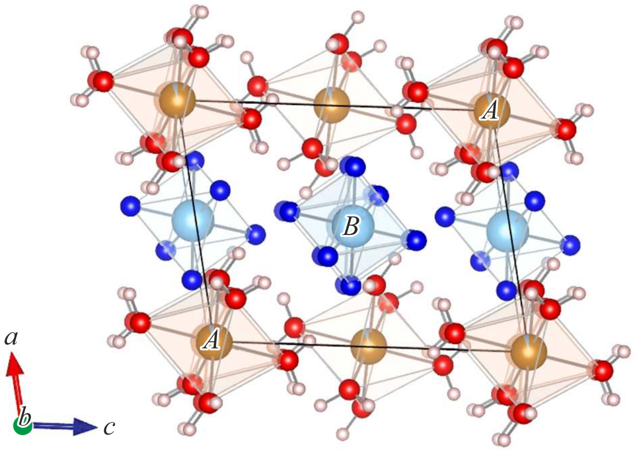

Figure 1. The crystalline structure of $ABF_6 \cdot 6H_2O$ single crystals. A (Mn, Co, Fe) atoms are surrounded by water molecules, B (Si, Ge, Ti) atoms have an environment of fluorine atoms.

samples form alternating layers bound between themselves by hydrogen bonds only (Fig. 1). At the same time the environment of type A atoms (Mn, Fe, Co) is composed of water molecules, atoms of type B have an octahedral environment of F^- fluorine anion.

Magnetization was measured by a vibration magnetometer [16] and PPMS 9T by Quantum Design. Single crystals with a length of 5–6 mm and a weight of 10–30 mg were placed in a cylinder measuring cell to prevent rotation of the sample in the applied magnetic field. Magnetic field was applied along the c crystallographic axis (Fig. 1) as for the parallelness of magnetic field to the third-order axis, and along the b direction (Fig. 1) as for the case of $H \perp c$.

3. Results and discussion

Fig. 2 shows dependencies of magnetization on temperature and applied magnetic field for single crystal

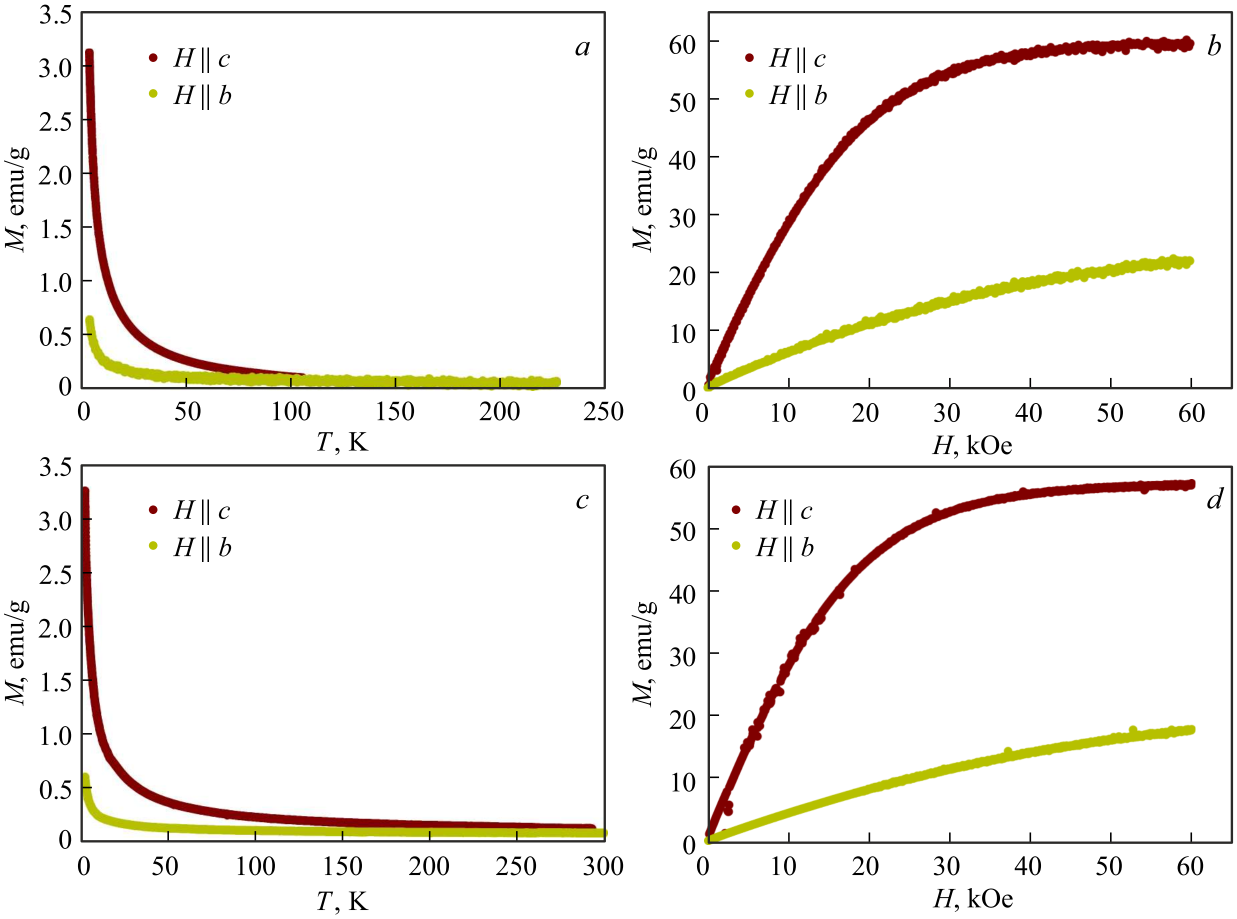

Figure 2. a, b — dependencies of magnetization on temperature at a magnetic field of $H = 1$ kOe (a) and on the applied magnetic field at a temperature of $T = 4.2$ K (b) for a sample of $CoTiF_6 \cdot 6H_2O$; c, d: dependencies of magnetization on temperature at a magnetic field of $H = 1$ kOe (c) and on the applied magnetic field at a temperature of $T = 4.2$ K (d) for a sample of $CoSiF_6 \cdot 6H_2O$; orientation of the applied field relative to the sample is shown in the figure.

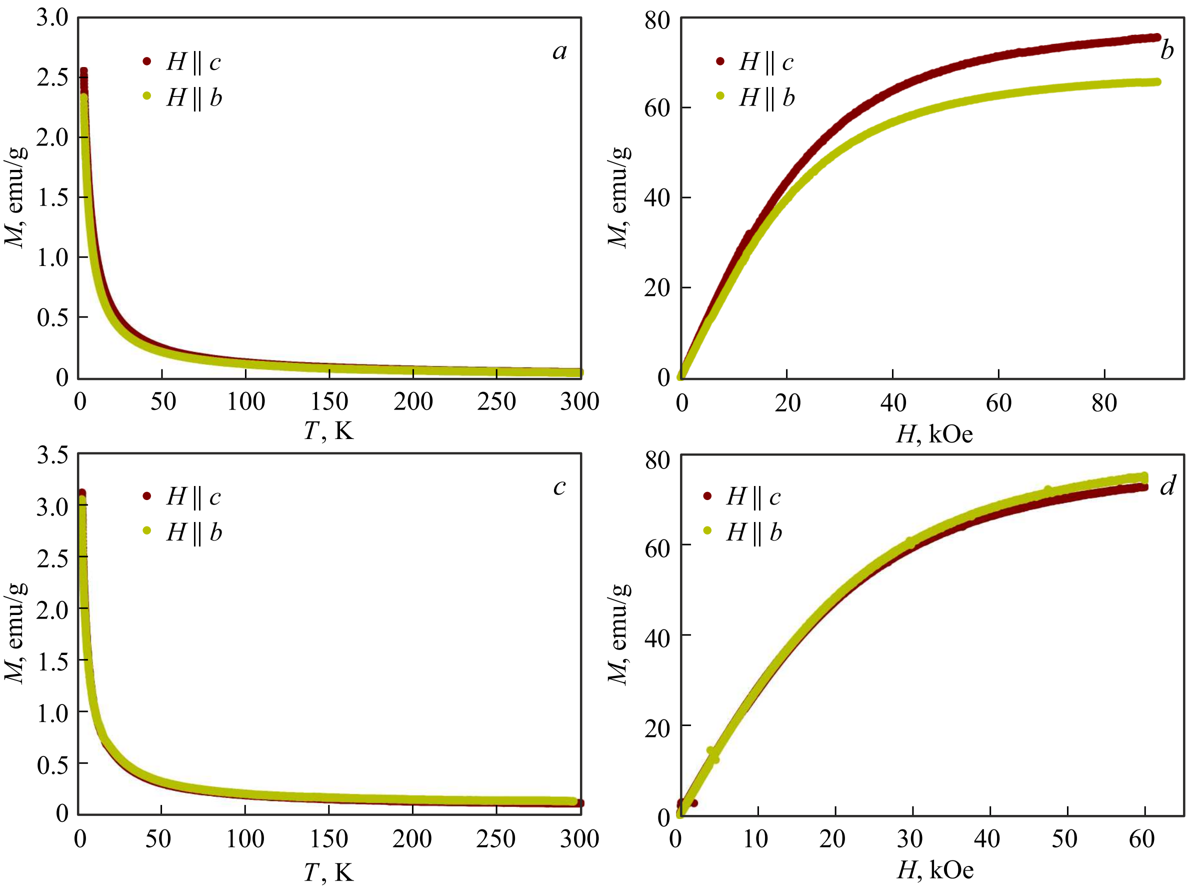

Figure 3. *a, b* — dependencies of magnetization on temperature at a magnetic field of $H = 1\,\mathrm{kOe}$ (*a*) and on the applied magnetic field at a temperature of $T = 4.2\,\mathrm{K}$ (*b*) for a sample of $MnTiF_6 \cdot 6H_2O$; *c, d*: dependencies of magnetization on temperature at a magnetic field of $H = 1\,\mathrm{kOe}$ (*c*) and on the applied magnetic field at a temperature of $T = 4.2\,\mathrm{K}$ (*d*) for a sample of $MnSiF_6 \cdot 6H_2O$; orientation of the applied field relative to the sample is shown in the figure.

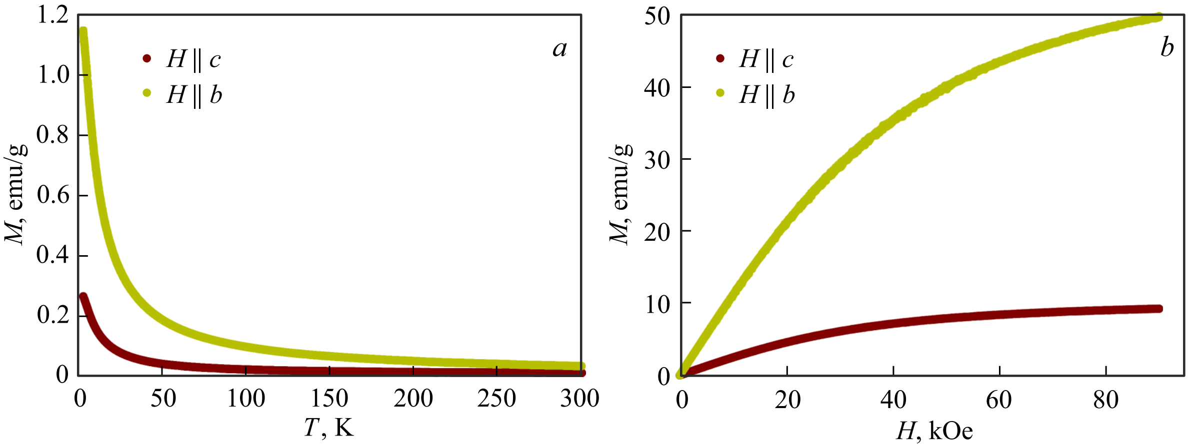

Figure 4. *a, b*: dependencies of magnetization on temperature at a magnetic field of $H = 1\,\mathrm{kOe}$ (*a*) and on the applied magnetic field at a temperature of $T = 4.2\,\mathrm{K}$ (*b*) for a sample of $FeGeF_6 \cdot 6H_2O$; orientation of the applied field relative to the sample is shown in the figure.

samples of $CoTiF_6 \cdot 6H_2O$ and $CoSiF_6 \cdot 6H_2O$. Parameters of measurements are shown in the figure and in the caption to it. It can be seen that the samples containing Co^{2+} ion possess considerable magnetic anisotropy. Both single crystals have large magnetic moment when magnetic field is applied along *c* crystallographic axis, while previously studied single crystals of $FeSiF_6 \cdot 6H_2O$, $NiTiF_6 \cdot 6H_2O$, and $FeTiF_6 \cdot 6H_2O$ [8–13], in contrast, had greater magnetic moment when the magnetic field was applied alongthe *b* crystallographic axis. In addition, the above-mentioned crystals demonstrated a behavior typical for frustrated antiferromagnetics, while the compounds under study in this work demonstrate a behavior of paramagnetics for both orientations of the magnetic field relative to the crystal. The difference in the magnitude of magnetization in the applied magnetic field of $H = 60\,\text{kOe}$ is as high as 300% (≈ 20 and $\approx 60\,\text{emu/g}$ for the field orientation along b and c axes, respectively). Also, the behavior of temperature dependencies of magnetization of these compounds (Fig. 2 a, c) shows the anisotropy of magnetic properties and at a temperature of $T \approx 4.2\,\text{K}$ it achieves 600% (≈ 0.5 and $\approx 3\,\text{emu/g}$ for the field orientation along b and c axes, respectively).

Temperature dependencies of magnetization in different directions of the applied field of $MnTiF_6 \cdot 6H_2O$ and [C[C$MnSiF_6 \cdot 6H_2O$ single crystals are shown in Fig. 3. It can be seen that the behavior of magnetization of these samples differs from the magnetization of compounds containing Co^{2+} ion. It is worth noting, that no anisotropy is found for the $MnSiF_6 \cdot 6H_2O$ single crystal on the temperature dependence of magnetization in a magnetic field of $H = 1\,\text{kOe}$, and in the field dependence of magnetic moment at $T = 4.2\,\text{K}$. For $MnTiF_6 \cdot 6H_2O$, the difference between magnetizations in the applied magnetic field of $H = 60\,\text{kOe}$ is $\approx 15\%$ (≈ 62 and $\approx 72\,\text{emu/g}$ for the field orientation along b and c axes, respectively).

In order to study the effect of substitution of the B^{4+} ion on magnetic properties of fluoric hexahydrates, magnetization of the $FeGeF_6 \cdot 6H_2O$ crystal was measured (Fig. 4) that has not shown an antiferromagnetic ordering under magnetic field applied along the c crystallographic axis, that, perhaps, is connected with the fact that its Neel point, probably, is at a lower temperature. However, the character of anisotropy of this crystal differs significantly from other samples studied in this work. It was found that magnetization at the orientation of the magnetic field $H = 90\,\text{kOe}$ applied along the b axis is greater than in the case of field oriented along the c axis by about 500% (≈ 10 and $\approx 50\,\text{emu/g}$ for the field orientation along c and b axes, respectively), that makes its magnetic properties more similar to those of $FeSiF_6 \cdot 6H_2O$ and $FeTiF_6 \cdot 6H_2O$.

4. Conclusion

This work presents the studies of magnetic properties of fluoric hexahydrates of transition metals: $CoTiF_6 \cdot 6H_2O$, $CoSiF_6 \cdot 6H_2O$, $FeGeF_6 \cdot 6H_2O$, $MnSiF_6 \cdot 6H_2O$, and $MnTiF_6 \cdot 6H_2O$. It was found that the anisotropy of magnetic properties of these compounds is defined by the presence of spin-orbital interaction of ion of the transition metal. In the case of substitution of Fe^{2+} cation by the Co^{2+} Jahn-Teller ion a change in the direction of the magnetic anisotropy takes place. An in $CoTiF_6 \cdot 6H_2O$ the easy direction of magnetization changes from b to c crystallographic axis. This change in the behavior of magnetization of these compounds is caused by the difference between the direction of interaction of the orbital magnetic moment of transition metal cation and the crystalline field, that results in a change in the local minimum of energy due to the dynamic Jahn-Teller effect.

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Conflict of interest

The authors declare that they have no conflict of interest.

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