Jahn-Teller crystals – new class of smart materials

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Abstract. Jahn-Teller crystals represent a promising class in the search for new smart materials. Jahn-Teller multiferroics are of a special interest. We show that the properties of these crystals are not only “of interest for future applications”, but are already used and protected by various patents. Special attention is paid to some new results on magnetic shape memory effects in dielectrics because the physics of the corresponding materials is not yet completely clarified.

1. Introduction
This paper is written to call attention to a set of materials, which have heretofore been neglected in the search for 'smart' materials. Those materials are Jahn-Teller materials which undergo drastic changes as a function of externally applied forces. The development of any technologically advanced society constantly requires new materials with specific properties that could be used for various applications – smart materials. The term “smart” means that the materials are characterized by properties that can be significantly and quickly changed by means of an external and controllable medium/force (temperature, pressure (hydrostatic or uniaxial), light intensity, magnetic or electric external fields, pH, etc.).

In order to further illustrate the concept, we list in figure 1 different properties of possible smart materials. This figure and the definition of “smartness” of the materials may facilitate the formulation of the criteria in the search for smart materials. Since most of the material properties are defined by their electronic energy spectra it should be clear that those materials with the electronic orbital degeneracies should be of primary interest. In those materials it is easy to significantly change the material properties with the application of external forces. One should also note that the most dramatic (anomalous) property changes take place in materials at the phase transitions. The above considerations point to the Jahn-Teller crystals–multiferroics as a likely class of compounds for the search for smart materials.

The term “smart material” was coined more than 40 years ago in connection with the discovery of the smart memory compound Nitinol (Ni-Ti alloy discovered at the Naval Research Laboratory (Maryland, USA) [1]). This material undergoes a first order structural phase transition from the cubic (austenite) to the tetragonal (martensite) phase as a function of temperature. Correspondingly Nitinol can be changed from a state with one shape to another shape and back, with the change of temperature...
or external pressure. Therefore that material "remembers" its shape. The strain change at these transformations is huge – up to 7-10%.

Here we point out that in Jahn-Teller ferroelastics the spontaneous strain is also large [2] and can reach magnitudes similar to that of Nitinol. Similarly, materials with the first order Jahn-Teller structural transition exhibit hysteresis and memory effect.

It was found by [3] that big strains in smart memory materials could be related to domain reorientation in the martensite crystal phase. Soon after that magnetic shape memory materials were discovered [4]. In these materials the initial sample shape was recovered by an external magnetic field. It was suggested that the mechanism of the crystal memory is based on the domain magnetic reorientation accompanied by huge martensite reorientation magnetostriction. The reorientation of the domains, according to reference [5], depends significantly upon the magnetic anisotropy of the compounds.

| Type of smart material                  | Input          | Output               |
|-----------------------------------------|----------------|----------------------|
| Piezoelectric                           | Deformation    | Potential difference |
| Electrostrictive                        | Potential difference | Deformation         |
| Magnetostrictive                        | Magnetic field | Deformation          |
| Thermoelectric                          | Temperature    | Potential difference |
| Shape memory crystals                   | Temperature    | Deformation          |
| Magnetic shape memory crystals          | Magnetic field | Deformation          |
| Photochromic                            | Radiation      | Color change         |
| Thermochromic                           | Temperature    | Color change         |

Figure 1. Examples of types of smart materials and their properties.

2. Jahn-Teller magnetic shape memory materials

Jahn-Teller crystals are characterized by huge static and dynamic magnetostriction [6]. Figure 2 shows some experimental and theoretical results for static and dynamic magnetostriction of Jahn-Teller elastics [7, 8]. Due to the huge magnetostriction of Jahn-Teller crystals, domain reorientation by an external magnetic field in these materials is also possible. That indicates that magnetic shape memory materials exist among the Jahn-Teller elastics. Moreover the mechanism of the domain reorientation in Jahn-Teller systems is quite well understood. Therefore the elastic anisotropy can play a much more significant role in the reorientation than the magnetic anisotropy. The magnetic shape memory effect in Jahn-Teller crystals can take place even in completely non-magnetic crystals. The magnetostriction of the paramagnetic systems is big enough for the reorientation processes.

We will here focus our discussion on the mechanism of the magnetic shape memory of the crystals. Analysis of the magnetoelastic properties of the Jahn-Teller crystals has shown [9] that the multisublattice crystals exhibit a property similar to metamagnetism in Ising antiferromagnets. That property was named metamagneetoelasticity – the overturn of a sublattice of the local distortions in sufficiently strong external magnetic fields. This effect was first experimentally observed in some rare earth compounds [10], then explained theoretically [11], and after that observed in different Jahn-Teller compounds (figures 3 and 4). It is important to mention that the experimental data corresponding to domain reorientation look very much like metamagneetoelasticity curves: the crystal strain jumps up in magnitude as a function of the external magnetic field when it reaches some critical value. However, the mechanisms of these two phenomena are different. In case of the domain
reorientation the magnetic field (Zeeman interaction) has to overcome the structural sublattice anisotropy, but at the metamagnetoelasticity the overturn of the sublattice distortions takes place when the Zeeman interaction becomes stronger than the intersublattice virtual phonon exchange interaction responsible for the cooperative Jahn-Teller effect. Naturally the magnitudes of the magnetic fields for these two phenomena are different. New magnetostriction experiments with the single domain crystals will elucidate the correct mechanism of the shape memory effect.

Figure 2. The top two graphs are experimental data by V.I Sokolov and Z.A. Kazey [7], the two graphs below are the theoretical data for the dynamic magnetostriction in TbVO₄ and Tb₁₋ₓGdₓVO₄ crystals by M.D. Kaplan and B.G. Vekhter [8].

While initially the magnetic smart memory was found among the semiconducting and metallic compounds, lately the Jahn-Teller dielectrics with XY-ordering attracted attention for that smart
property [12, 13]. On one hand these types of magnetic crystals are undergoing a transition (figure 5) responsible for the jump of the crystal strain with the field. On another hand, it was shown in [13] that the strain change with the magnetic field is much faster in dielectrics than in conductive materials. The explanation of that is related to the absence of eddy currents in dielectrics. This property makes the Jahn-Teller dielectric crystals more attractive for different applications. On figures 6-8 different domain magnetostriction and hysteresis are shown for the XY-ordered MnV₂O₄ crystal. Similar effects were observed [14] and explained [15] in the colossal magnetoresistance LaMnO₃ compounds.

The above argument supports the statement that memory (temperature and/or magnetic field induced) is a smart property typical of the Jahn-Teller crystals. However in case of the magnetic shape memory effects the future magnetostriction measurements in single and multidomain crystal samples will elucidate the real mechanism responsible for these properties.

![Figure 3](image_url)

**Figure 3.** Magnetic field dependence of magnetostriction in colossal resistance compound [14].
Figure 4. Metagnetoelasticity manifestation in XY-ordered materials [15] (A, H_x, T, and Δ are given in units of energy Δ).

Figure 5. Example of a 3-dimensional surface of the crystal free energy as a function of the structural order parameters X and Z for different molecular field constants A and B at competing XY and ZZ structural orderings (all parameters are dimensionless, the minima of the free energy correspond to the different crystal spontaneous strains/shapes).
Figure 6. Hysteresis curve calculated from the 3-d free energy surfaces similar to shown in figure 5.

Figure 7. Temperature dependence of the magnetostriction at different orientation of magnetic field [13].

3. Jahn-Teller multiferroics as smart materials
A group of smart properties is found in Jahn-Teller multiferroics. These are crystals with simultaneous structural, magnetic, and/or electric (ferro-, antiferrotype) ordering. They all contain at least one sublattice of ions (structural units) with orbital electronic degeneracy or pseudo degeneracy. Some examples of ordered structures in Jahn-Teller multiferroics were discussed earlier [6, 16]. A smart
property – magnetoelectricity – was also widely discussed [16, 17] for a Jahn-Teller ferroelastic, antiferromagnetic, antiferroelectric TbPO$_4$ crystal.

Among the multiferroics, the vibronic magnets [18] are of a special interest. The Jahn-Teller vibronic magnets are characterized by magnetic moments whose magnitude is linearly proportional to the vibronic (electron-phonon) coupling:

$$M_z = g_z \beta \bar{S}_z$$

$$Z_0 = e^{\Delta/\lambda T} \left( 1 + e^{\frac{4kT}{\lambda T}} \right) + e^{\frac{E^2_0}{\lambda T}}$$

Here the increase of symmetry strain $\bar{P}$ induces an increase of the magnetic moment. The constant $A$ in (1) is the Jahn-Teller molecular field constant that is proportional to the square of the electron-phonon coupling. This effect is similar to the macroscopic effect of piezomagnetism which is one of the smart material properties. Some vibronic magnets could additionally have a ferro- or antiferroelectric ordering. In this case the corresponding smart properties are electrostriction and the dielectric response (susceptibility).

4. Applications of Jahn-Teller smart materials

One of the “traditional” smart properties of the Jahn-Teller crystals is the dependence of the ultrasound velocity upon temperature and external magnetic field. Examples of the measurements and calculations of these properties in rare earth and transition metal compounds at the low and room temperatures were discussed by Kaplan and Vekhter in reference [6].

Lately a new smart material property attracted much attention in connection with its numerous applications of self-assembly. This property could be considered as a special type of structural phase transition. It is not surprising that it was observed in the class of the Jahn-Teller crystals with spinel structure. An example of experimentally found self-assembly among the Jahn-Teller compounds is shown on the figure 8.

Overall, it should be mentioned that the idea of the Jahn-Teller smart materials had already been recognized in industry for a long time. That is why some applications of the Jahn-Teller compounds have been known for many years and are protected by various patents.

One of the first patents related to the Jahn-Teller effect was received by Bell Telephone Laboratories Inc. about 50 years ago – “Temperature-stable Sonic Transmission Elements Comprising Crystalline Materials Containing Jahn-Teller Ions” (inventors are D. Fraser, E. Gyorgy, R. Le Craw, F. Schnettler). The application of the materials is based on the properties discussed before in this presentation, the temperature dependence of the velocity of the acoustic waves in Jahn-Teller crystals that is proportional to the square-root of the modulus of elasticity ($V=(C/Q)^{1/2}$) and the possibility of changing this velocity by means of the external magnetic and fields.
In the seventies a Patent US 3961289 was awarded to Matsushita Electric Industrial Co., Ltd for “Ultrasonic Delay Material” (inventor Y. Kino). The material under discussion is “a spinel-type oxide exhibiting a cooperative Jahn-Teller effect”. This material shows an extraordinary reduction of sound velocity “there through at temperatures near the Jahn-Teller phase transition temperature.”

M. Kaplan, B. Vekhter, I. Bersuker, M. Maizenberg, V. Moshkovich, V. Bobrov (Patent SU 1013837 A) in the eighties suggested a new method for measuring the external magnetic fields based on the dynamic magnetostriction of the Jahn-Teller crystals. This method has many different applications. One of them is related to the non-destructive testing of materials. The corresponding device is shown in figure 9.

In the nineteen nineties it was established that the Jahn-Teller effect is fundamentally important for the understanding of the mechanism of the working of the lithium batteries. For these batteries the best positive active electrode is a crystal with the cooperative Jahn-Teller effect. The first positive electrode material for the lithium batteries was patented by Japan Storage Battery Co, Ltd. (this material is LiMn2O4, inventors - K. Amine, H. Yasuda, Y. Fujita, 1997). The first Jahn-Teller materials for the lithium batteries were developed by J. Goodenough and his co-workers [21]. Today there are many different patented Jahn-Teller materials applicable as the electrodes for lithium batteries.
Figure 9. Acousto-electronic device for magnetic field measurements. The attached converter contains the Jahn-Teller crystal with big dynamic magnetostriction.

Lately a Patent WO 2006133129 A2 was issued to Rutgers University for “Nano-Scale Self Assembly in Spinel Doped by Jahn-Teller Distortion” (inventors – S.-W. Cheong, S.Yeo). It is about a method for making a self-assembled spinel having an ordered nanocrystal superlattice. Without using any organic liquids it is possible to fabricate a nanoscale checkerboard pattern of square rods. The ordered array is the result of the spinodal decomposition between Jahn-Teller-active and – inactive ions in ZnMnGaO₄ compounds. The picture of the ordered ion structure is shown on the figure 8.

5. Conclusion
In conclusion we want to emphasize and call attention to the fact that it should be accepted that a) the Jahn-Teller materials are mostly smart materials; b) in the search of a material with a required smart property the Jahn-Teller class of materials is very attractive; c) the Jahn-Teller multiferroics are especially promising type of smart materials [20]; d) new magnetostriction experiments with single domain crystals are necessary for elucidating the mechanism of the magnetic shape memory.

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