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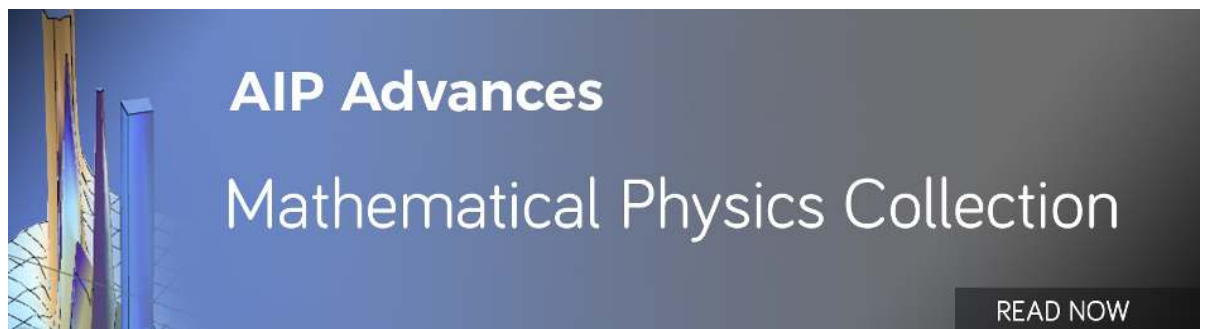
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ABSTRACT

We report the magnetocapacitance effect and the magnetostriction in the spin-crossover (SCO) complex $[\text{Mn}^{\text{III}}(\text{taa})]$ ($\text{H}_3\text{taa} = \text{tris}(1-(2\text{-azolyl})-2\text{-azabuten-4-yl})\text{amine}$). It is shown that huge enhancements of dielectric constant and lattice volume are caused by the field-induced SCO transition from the low-spin to the high-spin states in $[\text{Mn}^{\text{III}}(\text{taa})]$. In addition, the temperature-field phase diagram of the field-induced SCO in thermal equilibrium state is clarified up to 28 T. Our analysis suggests that a large magnetocaloric effect can also be caused by the field-induced SCO. These results indicate the possibility of multiple control of various material properties by the field-induced SCO.

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Tuning the physical properties of materials by magnetic fields has attracted increasing interest from both fundamental and practical points of view. Not only magnetic properties but also dielectric, thermal and mechanical properties can be tuned by magnetic fields. Typical phenomena to realize such tuning by applied field are the magnetoelectric (ME), magnetodielectric (MD) or magnetocaloric effects and magnetostriction. The MD effect, which is a change in the dielectric constant by the magnetic field, is important because it enables the development of, for instance, the field tunable capacitor. A large MD effect is known to be caused by the strong ME coupling between spins and electric dipoles.¹ A huge MD effect of ~ 500% due to the field-induced reorientation of the spiral spin structure was reported in the ME multiferroic material DyMnO_3 .² Moreover, giant magnetocaloric effect, which is demanded for magnetic refrigeration³⁻⁷ and magnetostriction, which is applicable to magnetic actuators,⁸ are known to occur with the field-induced martensitic transformation in Heusler alloys and field-induced transition from the antiferromagnetic to ferromagnetic state in FeRh alloys.⁹⁻¹¹ So far, reported giant changes of physical properties by magnetic field, are mainly caused by field-induced changes of the magnetic structure or the magnetic order.²⁻¹¹ The observation of giant changes in

multiple properties by the applied magnetic field in one material are still rare.

In this research, as a new approach to tune the various properties of a material by the magnetic field, we focus the magnetic-field-induced spin-crossover (SCO) transition. The SCO is a transition between the low-spin (LS) and the high-spin (HS) states in transition metal compounds from $3d^4$ to $3d^7$. The SCO can be induced by several kinds of external stimulation, such as temperature, pressure, magnetic field, or photonic irradiation.¹² Because the SCO is caused by a variation of the $3d$ electric configuration, it is accompanied not only by a change of the spin quantum number but also by drastic changes of lattice volume, color and/or entropy.¹²⁻¹⁴ Therefore, we can expect to achieve tuning of various kinds of material properties using magnetic-field-induced SCO transition. In this letter, we report the huge MD effect and magnetostriction accompanying the magnetic-field-induced SCO. Furthermore, from our measurements in high fields, the temperature-field phase diagram of the field-induced SCO of $[\text{Mn}^{\text{III}}(\text{taa})]$ in thermal equilibrium state is obtained. From the analysis of this phase diagram, we indicate that the field-induced SCO can also bring about a large magnetocaloric effect.

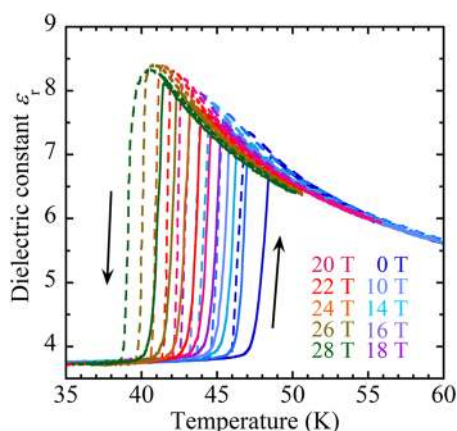


FIG. 1. Temperature dependence of the dielectric constant ϵ_r observed in $[\text{Mn}^{\text{III}}(\text{taa})]$. The data observed in temperature rising and lowering processes are shown in solid and dashed curves, respectively.

The $3d^4$ complex $[\text{Mn}^{\text{III}}(\text{taa})]$ ($\text{H}_3\text{taa} = \text{tris}(1-(2\text{-azoly})-2\text{-azabuten-4-yl})\text{amine}$) shows an SCO transition between the LS state with a spin $S = 1$ and the HS state with $S = 2$ at $T_{\text{SCO}} \cong 47$ K in the absence of magnetic field.^{15,16} Because the internal energy difference ΔE between the LS and HS states in $[\text{Mn}^{\text{III}}(\text{taa})]$ is relatively small, the complete field-induced SCO transition can be realized by experimentally accessible magnetic fields.¹⁷ An important feature of $[\text{Mn}^{\text{III}}(\text{taa})]$ is that reorientation of the electric dipole moments appear owing to the dynamic Jahn-Teller (JT) effect in its HS state.^{18,19} Previous X-ray diffraction experiments at room temperature revealed a trigonal symmetry in the HS state,¹⁵ in which a two-fold degeneracy of the d_y orbitals remains. Because the d_y orbitals are occupied by one electron in the HS state of a $3d^4$ system, a JT instability arises in the HS state of $[\text{Mn}^{\text{III}}(\text{taa})]$.¹⁸⁻²¹ Reflecting the trigonal symmetry, the molecular elongation by JT distortion in $[\text{Mn}^{\text{III}}(\text{taa})]$ has three equal directions, and generates an electric dipole moment perpendicular to both the trigonal axis and the JT elongation axis.¹⁹ Because the direction of the JT elongation is disordered, the electric dipole shows random reorientation, resulting in a

Curie-Weiss-like paraelectric behavior.^{18,19} Moreover, the molecule in the LS state with no JT distortion has a small dielectric constant. Therefore, we expect that the field-induced SCO transition from the LS to the HS state causes a large MD effect. In addition to this MD effect, a large magnetostriction by field-induced SCO is also expected because the SCO causes a large change in the molecular volume from the smaller LS to larger HS molecule.

Single crystals of $[\text{Mn}^{\text{III}}(\text{taa})]$, which belongs to a cubic symmetry with an $I\bar{4}3d$ space group, were prepared by a method described by Sim and Sinn.^{15,16} The dielectric constant of a single crystal of $[\text{Mn}^{\text{III}}(\text{taa})]$ was measured by an LCR meter (Agilent, E4980A) in temperature range from 35 K to 70 K in magnetic fields B along $[001]$ up to 28 T. A silver paste (Du Pont, 4922N) was used as electrodes on the sample. A 10 kHz AC electric field E was applied along $[001]$ to measure the dielectric constant. The longitudinal and lateral magnetostrictions in magnetic fields along $[001]$ up to 14 T were measured in temperature range from 4.2 K to 70 K using a home-made capacitance cell and a capacitance bridge (Andeen Hagerling, 2500A). Steady magnetic field was applied using the 28T-cryogen-free hybrid magnet (28T-CHM) and the 15T-, 20T-superconducting magnets (15T-SM, 20T-SM) at High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University.

Figure 1 shows the temperature dependence of dielectric constant ϵ_r . At 0 T, a Curie-Weiss-like paraelectric behavior is observed in the HS state above the transition temperature T_{SCO} as previously reported.^{18,19} Then, ϵ_r abruptly decreases at T_{SCO} with decreasing temperature owing to the SCO transition to the LS state. Almost constant ϵ_r is observed in the LS state below T_{SCO} . A hysteresis with a width of ~ 2 K is observed around T_{SCO} . By applying magnetic field, T_{SCO} shifts toward lower temperature because the HS (high spin) state is stabilized.

Figures 2 (a) and (b) show the MD effect, defined by $\Delta\epsilon_r(B)/\epsilon_r(B=0) = \{\epsilon_r(B) - \epsilon_r(B=0)\}/\epsilon_r(B=0)$, in fields from 0 T to 16 T and from 14 T to 28 T, respectively. At temperatures below T_{SCO} , the LS state at low field shows almost no field dependence of ϵ_r . However, as the field is further increased ϵ_r increases abruptly owing to the field-induced SCO to the HS state, showing a huge positive MD effect, which reaches over 100%. With increasing temperature,

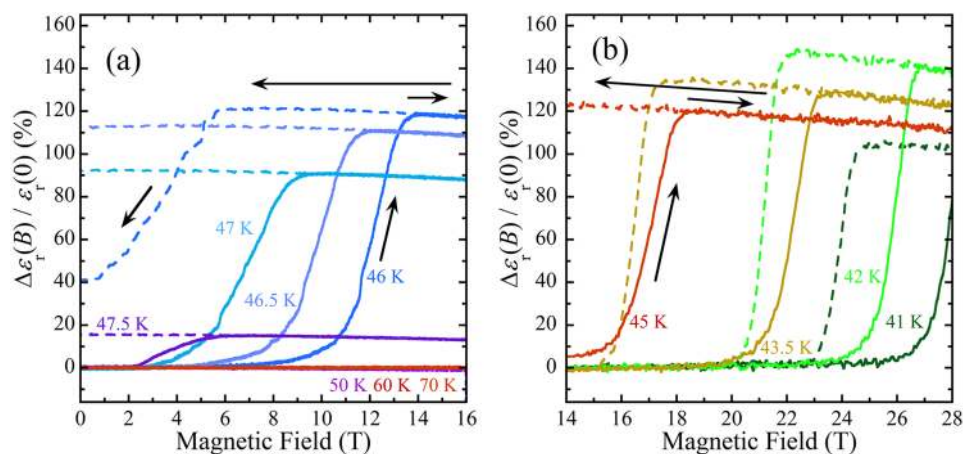


FIG. 2. Magnetodielectric (MD) effect $\Delta\epsilon_r(B)/\epsilon_r(B=0) = \{\epsilon_r(B) - \epsilon_r(B=0)\}/\epsilon_r(B=0)$ observed in the magnetic field (a) from 0 T to 16 T and (b) from 14 T to 28 T. Huge MD effect appears with the SCO transition. The data, observed in up and down sweep of the magnetic field, are shown by solid and dashed curves, respectively.

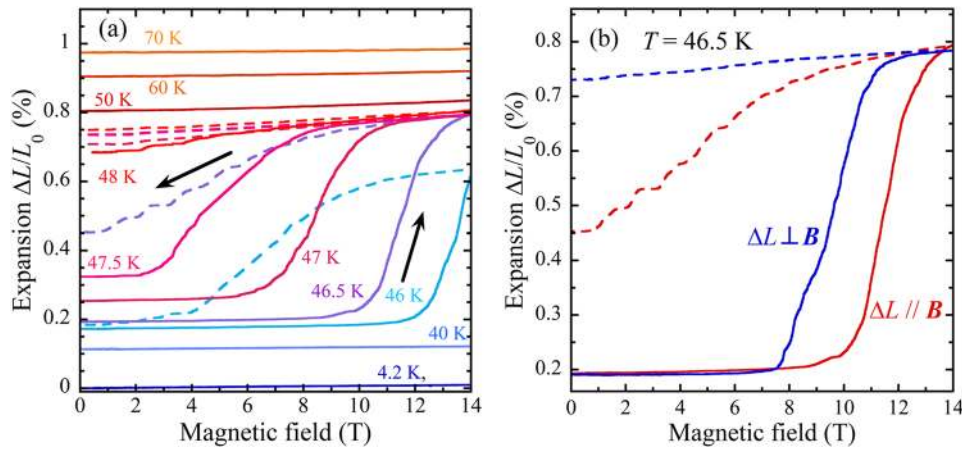


FIG. 3. (a) Longitudinal magnetostriction of [Mn^{III}(taa)] along [001] for $\mathbf{B} \parallel [001]$. Magnetostriction, observed in up and down sweep of the magnetic field, are described in solid and dashed curves, respectively. (b) The longitudinal and transverse magnetostrictions at 46.5 K.

the transition field of the field-induced SCO shifts toward lower field, and disappears above 50 K.

Figure 3 (a) shows the result of the longitudinal magnetostriction measurement. $L_0 = 0.4$ mm is the length of the sample in the room temperature and ΔL is the elongation from the point 4.2 K and zero magnetic field. At the temperatures below 50 K, a large positive magnetostriction, which reaches $\sim 0.6\%$, appears owing to the field-induced SCO to the HS state. This magnetostriction value agrees with the change of the lattice constant accompanying the thermally-induced SCO $\cong 0.65\%$, which was obtained from the previous X-ray diffraction measurement.²²

With increasing temperature, the magnetostriction shifts toward lower field and disappear above T_{SCO} as well as the large MD effect mentioned above. Figure 3 (b) shows the longitudinal and transverse magnetostriction at 46.5 K. The lattice changes in both measurements almost coincident each other. This coincident suggests that the magnetostriction comes from an isotropic volume increase due to the field induced SCO transition. The difference of the transition fields, seen in $\Delta L \perp \mathbf{B}$ and $\Delta L \parallel \mathbf{B}$ probably comes from slight difference of the measurement temperature. In addition to the large MD effect and magnetostriction accompanying the field-induced SCO, a slight positive magnetostriction and a negative MD effect are observed in the HS state. We estimate that these behaviors come from the alignment of dynamic JT elongation in the HS state by the magnetic field under the influence of the spin-orbit interaction.

From the results of dielectric constant and magnetostriction measurements, the temperature-field phase diagram of the SCO transition is obtained in Fig. 4. Previously, the field-induced SCO in [Mn^{III}(taa)] was observed in pulsed magnetic fields whose duration were less than 100 ms.¹⁷ The fast sweep of the pulsed fields, however, gives rise to a very large hysteresis accompanying the field-induced SCO,¹⁷ and the width of that hysteresis strongly depends on the sweeping speed. Therefore, the phase diagram in a thermal equilibrium state was impossible to obtain from the measurements in pulsed fields. In this study, by using steady magnetic fields, we succeeded in clarifying the thermal equilibrium phase diagram up to 28 T. The SCO transition points determined by different measurements are in good agreement with each other as shown in Fig. 4.

The phase boundaries between the LS and HS states can be calculated with the assumption that the free energies of the LS and the HS states, F_{LS} and F_{HS} , are equal.¹⁷ F_{LS} is considered to be equal to the free energy $F_{S=1}$ of a free spin with $S = 1$. On the other hand, F_{HS} is expressed as follows.

$$F_{HS} = F_{S=2} - S_{JT}T - S_{ext}T + \Delta E \quad (1)$$

Here, the first term $F_{S=2}$ is the free energy of the spin $S = 2$, the second term with $S_{JT} = k_B \ln(3)$ is the entropy contribution from the three equal direction of the JT distortion,¹⁸ the third term is the entropy contribution other than the JT effect and spin degrees of freedom, which was not taken into account in the previous study,¹⁷ and the fourth term ΔE is the energy difference between the LS and the HS states at zero field. From the condition $F_{LS} = F_{HS}$, the phase boundary is given as:

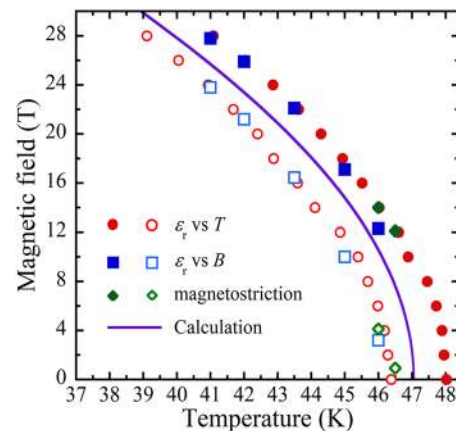


FIG. 4. Phase diagram of the SCO transition, obtained from the dielectric constant and magnetostriction measurements. Closed and open circles are the transition points, obtained from the temperature dependence of dielectric constant ϵ_r . Squares and diamonds are the transition points, obtained from the field dependence of ϵ_r and the magnetostriction, respectively. Solid curve is the calculated phase boundary. See text for detail.

$$-T \left[S_{\text{ext}} + k_B \ln \left\{ \frac{3 \sinh\left(\frac{5g\mu_B H}{2k_B T}\right)}{\sinh\left(\frac{3g\mu_B H}{2k_B T}\right)} \right\} \right] + \Delta E = 0 \quad (2)$$

Here, $g = 2$ represents the g -factor. The experimental phase boundary is well explained by that equation, calculated with $S_{\text{ext}} = k_B \ln(3)$ and $\Delta E/k_B = 127.3$ K, as shown in Fig. 4.

Mentioning the entropy change of the SCO transition in $[\text{Mn}^{\text{III}}(\text{taa})]$, Garcia *et al.* suggested from DFT calculations that the vibrational contribution is not negligible.²³ In addition to this phonon contribution, we indicate the entropy contribution from the pseudo rotation of the dynamic Jahn-Teller distortion to S_{ext} .²⁴ The first and the second excited energy levels of pseudo rotation of the distortion in an $E \times e$ Jahn-Teller system are nearly triply degenerated, giving rise to an entropy contribution $S \cong k_B \ln(3)$.²⁴

As described above, we have succeeded in observing the giant MD effect and magnetostriction accompanying the magnetic field-induced SCO, and have clarified the thermodynamic properties of field-induced SCO in $[\text{Mn}^{\text{III}}(\text{taa})]$. In addition to the MD effect and magnetostriction, as described above, other properties can be also changed by the field-induced SCO. In fact, the magnetochromic effect, which is a change in color by the field, was previously observed in $[\text{Mn}^{\text{III}}(\text{taa})]$.²¹ Moreover, because of the large entropy change across the phase boundary of the SCO, a giant magnetocaloric effect is expected. The entropy change ΔS from the LS to HS states is obtained from N_A times difference between differentials of the free energies $N_A \{(-\partial F_{\text{HS}}/\partial T) - (-\partial F_{\text{LS}}/\partial T)\}$ and given as:

$$\Delta S = R \ln \left\{ \frac{\sinh\left(\frac{5g\mu_B H}{2k_B T}\right)}{\sinh\left(\frac{3g\mu_B H}{2k_B T}\right)} \right\} + \frac{g\mu_B H N_A}{2T} \left\{ \frac{5 \cosh\left(\frac{5g\mu_B H}{2k_B T}\right)}{\sinh\left(\frac{5g\mu_B H}{2k_B T}\right)} - \frac{3 \cosh\left(\frac{3g\mu_B H}{2k_B T}\right)}{\sinh\left(\frac{3g\mu_B H}{2k_B T}\right)} \right\} + R \ln(3) + N_A S_{\text{ext}} \quad (3)$$

Here, $R = k_B N_A = 8.31$ is the gas constant and $N_A = 6.02 \times 10^{23}$ is the Avogadro constant. From the calculation using S_{ext} , obtained from the analysis, the magnetocaloric effect reaching ~ 51 J/kg K (~ 22.1 J/mol K) at 46.8 K and under 5 T is predicted. This value is comparable with the giant magnetocaloric effect ~ 50 J/kg K, reported in $\text{MnFeP}_{0.5}\text{As}_{0.3}\text{Si}_{0.2}$.⁵ The entropy value ~ 22.1 J/kg K contains three parts, $S_{\text{JT}} = S_{\text{ext}} = k_B \ln(3) = 9.1$ J/mol K and $\Delta S_{\text{mag}} = 3.9$ J/mol K. Here, ΔS_{mag} is difference of the magnetic entropy between the LS and HS states. Because ΔS_{mag} decreases upon cooling, ΔS approaches to 18.2 J/mol K in low temperature region. On the other hand, it was reported that the slope of the phase boundary in low temperature region, obtained from the previous pulsed magnetic field measurement, seems to agree with Clausius-Clapeyron equation $(\partial H_c/\partial T_c) = -(\partial S/\partial M)$ with $\Delta S = 9.1$ J/mol K which includes only S_{JT} . However, the steady magnetic field measurements in this study showed a larger slope of the phase boundary, This requires the additional entropy $S_{\text{ext}} = k_B \ln(3)$.

In conclusion, a huge MD effect (over 100%) and the magnetostriction of $\sim 0.6\%$, caused by the field induced SCO transition,

were observed in $[\text{Mn}^{\text{III}}(\text{taa})]$. Furthermore, this study suggests from the analysis of the temperature-field phase diagram that the field induced SCO causes a large magnetocaloric effect (~ 52 J/kg K). Our results demonstrated that huge changes of various kinds of physical properties can be caused by the field-induced SCO. The field-induced SCO opens new ways to achieve effective and multiple tuning of material properties by the magnetic field.

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REFERENCES

- Y. Tokura, S. Seki, and N. Nagaosa, *Rep. Prog. Phys.* **77**, 076501 (2014).
- T. Goto, T. Kimura, G. Lawes, A. P. Ramirez, and Y. Tokura, *Phys. Rev. Lett.* **92**, 257201 (2004).
- V. K. Pecharsky and K. A. Gschneidner, Jr., *J. Magn. Magn. Mater.* **200**, 44 (1999).
- V. K. Pecharsky and K. A. Gschneidner, Jr., *Phys. Rev. Lett.* **78**, 4494 (1997).
- W. Dagula, O. Tegus, X. W. Li, L. Song, E. Brück, D. T. C. Thanh, F. R. de Boer, and K. H. J. Buschow, *J. Appl. Phys.* **99**, 08Q105 (2006).
- E. Brück, *J. Phys. D: Appl. Phys.* **38**, R381 (2005).
- E. Brück, O. Tegus, D. T. C. Thanh, and K. H. J. Buschow, *J. Magn. Magn. Mater.* **310**, 2793 (2007).
- J. Schafer and H. Janocha, *Sensors and Actuators A* **49**, 97 (1995).
- K. Ullakko, J. K. Huang, C. Kantner, R. C. O'Handley, and V. V. Kokorin, *Appl. Phys. Lett.* **69**, 1966 (1996).
- M. Sato, T. Okazaki, Y. Furuya, and M. Wuttig, *Mater. Transactions* **44**, 372 (2003).
- K. Ohtake, Y. Mitsui, K. Takahashi, R. Onodera, S. Kimura, K. Watanabe, and K. Koyama, *IEEE Trans. Magn.* **50**, 1 (2014).
- P. Gütllich, A. Hauser, and H. Spiering, *Angew. Chem. Int. Ed. Engl.* **33**, 2024 (1994).
- P. Gütllich, A. B. Gaspar, and Y. Garcia, *Beilstein J. Org. Chem.* **9**, 342 (2013).
- M. Sorai and S. Seki, *J. Phys. Chem. Sol.* **35**, 555 (1974).
- P. G. Sim and E. Sinn, *J. Am. Chem. Soc.* **103**, 241 (1981).
- Y. Garcia, O. Kahn, J. P. Ader, A. Buzdin, Y. Meurdesoif, and M. Guillot, *Phys. Lett. A* **271**, 145 (2000).
- S. Kimura, Y. Narumi, K. Kindo, M. Nakano, and G. Matsubayashi, *Phys. Rev. B* **72**, 064448 (2005).
- M. Nakano and G. Matsubayashi, *Phys. Rev. B* **66**, 212412 (2002).
- M. Nakano, G. Matsubayashi, and T. Matsuo, *Adv. Quantum Chem.* **44**, 617 (2003).
- S. Kimura, T. Otani, Y. Narumi, K. Kindo, M. Nakano, and G. Matsubayashi, *J. Magn. Magn. Mater.* **272**, 1102 (2004).
- Y. Sawada, S. Kimura, K. Watanabe, and M. Nakano, *J. Low. Temp. Phys.* **170**, 424 (2013).
- P. Guionneau, M. Marchivie, Y. Garcia, J. A. K. Howard, and D. Chasseau, *Phys. Rev. B* **72**, 214408 (2005).
- Y. Garcia, H. Paulsen, V. Schunemann, A. X. Trautwein, and J. A. Wolny, *Phys. Chem. Chem. Phys.* **9**, 1194 (2007).
- I. B. Bersuker, *The Jahn-Teller Effect* (Cambridge University Press, Cambridge, 2006).