Phase transitions and crossover at high magnetic fields in the Jahn-Teller compound $DyVO_4$

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The influence of a high magnetic field applied along the [001] axis on the magnetic properties of the Jahn-Teller compound $DyVO_4$ is studied. Two phase transitions and a crossover effect are discovered. For $T<T_N=3$ K the destruction of antiferromagnetic ordering of the magnetic moments of Dy^{3+} ions along the [100] direction takes place at the fields around 12 T. In the neighborhood of 21 T the destruction of quadrupole ordering resulting in the change of the crystal symmetry occurs for all temperatures below the Jahn-Teller distortion temperature, $T<T_C=14$ K. The orthorhombic-tetragonal phase diagram in the $H-T$ plane is constructed. At higher fields the approaching of the low-lying energy levels of Dy^{3+} ions (crossover) exists in the tetragonal phase. These phase transitions and the crossover manifest themselves as pronounced anomalies of the differential magnetic susceptibility dM/dH, which is measured at the fields up to 36 T in the temperature range from 1.4 to 15 K. The effects under investigation are accounted for in the context of the unified approach, which is based on the crystal-field calculations and mean-field approximation.

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I. INTRODUCTION

Systems with two types of ordering, Jahn-Teller and magnetic, attract considerable interest because of the diverse crystallographic and magnetic transitions which occur at low temperatures. Dysprosium vanadate, $DyVO_4$, belongs to such systems. For $T>14$ K it is a paramagnet with the tetragonal zircon structure (D_{4h}^{19}), at $T_C=14$ K $DyVO_4$ undergoes a structural phase transition, and below $T_N=3$ K it becomes an Ising antiferromagnet. The miscellaneous properties of this compound are investigated in many papers; a survey of the work that has been done is given in Ref. 1. Spectroscopic and thermodynamic characteristics of $DyVO_4$ have been studied in subsequent work, but investigations in high magnetic fields are absent, as well as are missing sufficient spectroscopic data for the ground multiplet of Dy^{3+} in $DyVO_4$. High-field investigations allow one to observe new phase transitions and to obtain information about the higher-lying energy levels which usually are not involved in the consideration of spontaneous and low-field characteristics and effects. Hence high-field experiments require the interpretation in the framework of more general approaches.

The influence of a high magnetic field on the quadrupole and magnetic orderings in dysprosium vanadate at low temperatures is explored in this work. Below the temperature of a structural phase transition $T_C=14$ K the structure of dysprosium vanadate is orthorhombic, with space group D_{2h}^{28}, resulting from a crystal distortion along the [100] axis (B_{1g} strain). The structural phase transition is a cooperative Jahn-Teller effect,[2] which is conventional to consider as an ordering of the quadrupole moments of the Dy^{3+} ions, associated with a peculiar character of energy levels of two low-lying Kramers doublets. The mean-field theory has been shown to provide a good description of the quadrupole effects in the majority of Jahn-Teller compounds, $TbVO_4$ and $TmVO_4$ included. The validity of the mean-field approximation is a consequence of the dominance of the long-wavelength acoustic phonons in causing the cooperative behavior. In contrast, $DyVO_4$ shows the breakdown of mean-field theory, which is usually attributed to the existence of strong short-range interactions, arising through coupling of the Dy electronic levels to optic phone modes.[2,3] Below $T_N=3$ K an external magnetic field along the ordering direction a induces a metamagnetic phase transition at 0.21 T with a rather complicated phase diagram (see, e.g., Ref. 4).

The magnetic field is known to have a pronounced effect on the quadrupole ordering in rare-earth (RE) compounds, both an increase and decrease of the quadrupole order parameter being observed depending on the magnetic field direction related to symmetry axes of the crystal. The induced quadrupole ordering has been studied by different experimental techniques for a number of oxide and intermetallic RE compounds, whereas the destruction of quadrupole ordering is explored poorly. One can note the ultrasonic studies of the destruction of quadrupole ordering by a magnetic field in another RE compound with the zircon structure, $TmVO_4$ ($T_C=2.15$ K, $\mu_0 H_C \approx 0.6$ T).[5] The calculations of this effect were carried out in the pseudospin formalism considering two lowest-lying energy levels.[3,5]

II. EXPERIMENT

The measurements were performed on single-crystal samples, grown by the well-known method of spontaneous crystallization from solution, with a typical size $1\times1\times5$ mm^3 where their length was parallel to the [001] direction. The differential magnetic susceptibility dM/dH of $DyVO_4$ was measured by the induction method in the temperature range 1.4–15 K at the pulsed field along the [001] direction. The magnetic field was generated by the discharge of capacity bank on the copper coil. The maximum field value of 36 T was reached in 100 ms, the downsweep time

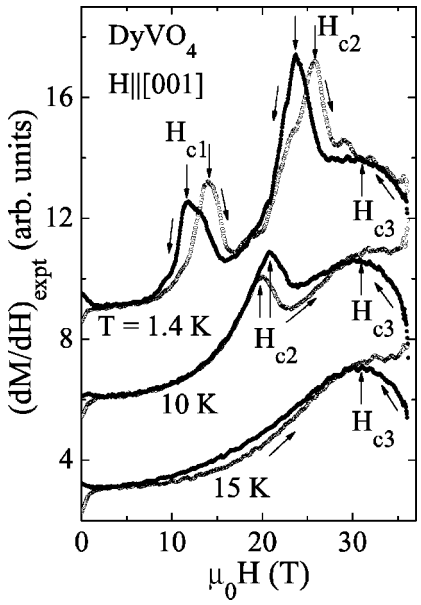

FIG. 1. Experimental differential magnetic susceptibility dM/dH of $DyVO_4$ for upsweep (open circles) and downsweep (solid circles) at various initial temperatures, $H\|[001]$. The curves for $T=10$ and 1.4 K are shifted along the vertical axis by three and six units, respectively.

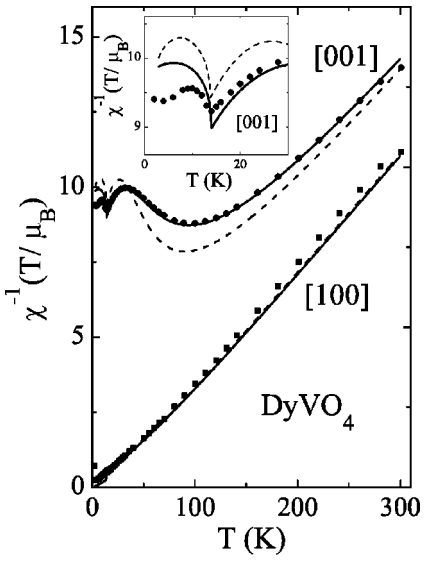

FIG. 2. Temperature dependencies of the reciprocal initial magnetic susceptibility along the [001] axis and in the basal plane in $DyVO_4$. The lines are variations calculated with CF of this work (continuous) and of Ref. 6 (broken).

was about 1 s. The digital recording of the signals from the measuring $M(t)$ and field $H(t)$ coils was made with the step ~0.05 T during the field pulse (about 800 points). The decompensation signal of the measuring coil was recorded under the same conditions in the absence of a sample and subtracted by a program. The programmed experimental data processing consisted in calculating smoothed magnetization function $M(H)$ and its derivative dM/dH. The pulse durations were such that the magnetization regimes can be considered as being close to adiabatic for upsweep and isothermal for downsweep, except a transition process which accompanies the change of dH/dt sign. The misorientation of the field with respect to the [001] direction in the conditions of our high-field experiment was equal for all runs and did not exceed 2°. The magnetization measurements in steady magnetic fields up to 8 T were also performed in order to derive the initial magnetic susceptibility in the temperature range 1.6–300 K.

Experimental curves of differential magnetic susceptibility $dM/dH(H)$ of $DyVO_4$ at $H\|[001]$ are presented in Fig. 1 for the temperatures from three characteristic intervals. At $T=1.4\ \mathrm{K}<T_N$ three anomalies are seen in the susceptibility curve: sharp peaks at H_{c1} and H_{c2} and a less pronounced anomaly at H_{c3}. For $T_N<T=10\ \mathrm{K}<T_C$ one can see two anomalies, and at $T=15\ \mathrm{K}>T_C$ a wide maximum of dM/dH takes place in the high-field region, which is better seen at downsweep.

Figure 2 shows the experimental temperature variations of reciprocal initial susceptibility along the [001] axis and in the basal plane. Distinct anomalies connected with the spontaneous structural phase transition (quadrupole ordering) at 14 K and with the onset of the antiferromagnetic ordering along the [100] axis at 3 K are seen. The inset in Fig. 2 demonstrates that the susceptibility along the hard axis [001] is very sensitive to the change of electronic structure of the Dy^{3+} ion caused by the quadrupole ordering. We note that the domain state of a sample (both for the quadrupole and magnetic ordered states) has no effect on these anomalies since any possible type of domain yields the same contribution for this case.

III. THEORY

To calculate the influence of high magnetic fields on the phase transitions and magnetic properties of $DyVO_4$, we use a Hamiltonian $\mathcal{H}$ which incorporates the crystal-field (CF) Hamiltonian $\mathcal{H}_{\mathrm{CF}}$ written in terms of the equivalent operators O_n^m, the Zeeman term $\mathcal{H}_Z$ and the Hamiltonians of exchange/dipole $\mathcal{H}_M$ and quadrupole $\mathcal{H}_{\mathrm{QT}}$ interactions, responsible for the antiferromagnetic and quadrupole orderings of relevant moments of Dy^{3+} ions:

$$\mathcal{H}=\mathcal{H}_{\mathrm{CF}}+\mathcal{H}_{\mathrm{Z}}+\mathcal{H}_{\mathrm{M}}+\mathcal{H}_{\mathrm{QT}},$$

$$\mathcal{H}_{\mathrm{CF}}=\alpha_{\mathrm{J}}B_2^0O_2^0+\beta_{\mathrm{J}}(B_4^0O_4^0+B_4^4O_4^4)+\gamma_{\mathrm{J}}(B_6^0O_6^0+B_6^4O_6^4),$$
$$\mathcal{H}_Z=-g_J\mu_B\mathbf{HJ}. \tag{1}$$

In the mean-field approximation for a magnetic field in the xz plane, for an ion from ith sublattice ($i=1$ and 2) $\mathcal{H}_M$ takes the form:

$$\mathcal{H}_{Mi}=\lambda_x M_{jx}J_{ix}+\lambda_z M_{jz}J_{iz};\quad \mathbf{M}_j=g_J\mu_B\langle\mathbf{J}_j\rangle;$$
$$j=1,2;\quad j\neq i. \tag{2}$$

In these expressions B_n^m are the crystal-field parameters, α_J, β_J, γ_J are the Stevens coefficients, g_J is the Lande factor, **J** is the angular momentum operator of the RE ion.

As is well known, the cooperative Jahn-Teller effect is a phase transition which is driven by the interaction between

localized orbital electronic states and the crystal lattice.[2] In the case of $DyVO_4$ the quadrupole moment $Q_2=\alpha_J\langle O_2^2\rangle$ is the order parameter, in so far as below T_C the distortion is of B_{1g} type, and the Hamiltonian of quadrupole interaction can be reduced to the expression (see Ref. 7):

$$\mathcal{H}_{\mathrm{QT}} = -\alpha_J^2 G^{\gamma}\langle O_2^2\rangle O_2^2 = \alpha_J B_2^2 O_2^2, \quad B_2^2 = -\alpha_J G^{\gamma}\langle O_2^2\rangle, \quad (3)$$

where the total quadrupole coefficient G^{γ} includes contributions from both the one-ion magnetoelastic and two-ion quadrupole interactions. Note that $\mathcal{H}_{\mathrm{QT}}$ is equivalent, in principal, to the term $\alpha_J B_2^2 O_2^2$ of the CF Hamiltonian. Hence in the ordinary mean-field approximation the parameter B_2^2 depends on T and H as does the quadrupole moment Q_2. The mean-field approximation, meanwhile, is known[2,3] to be of limited validity for description of the Jahn-Teller correlations in $DyVO_4$. For instance, the Jahn-Teller transition temperature T_C calculated in the mean-field approximation is about 19 K, instead of 14 K in reality.

To account for the first-order Jahn-Teller phase transition in $DyAsO_4$, Page *et al.*[8] in the framework of pseudospin formalism introduced a modified mean-field model analogous to the compressible Ising model of magnetic systems. The effective interaction was assumed to increase with ordering as $J'=J_0'(1+\xi\langle\sigma^z\rangle^2)$, where ξ measures the strength of the "compressibility" and $\langle\sigma^z\rangle$ is the order parameter. X-ray diffraction data suggest that the origin of the parameter ξ in $DyAsO_4$ is anharmonic interaction involving an A_{1g} zone-center phonon. Comparable x-ray data are not available for $DyVO_4$ but a similar interaction is likely to be present although it must be weaker since the Jahn-Teller phase transition appears to be of second order. The "compressible" model was successfully used for interpretation of experimental data for the specific heat[9] and for changes in linear birefringence[10] associated with the cooperative Jahn-Teller phase transition in $DyVO_4$.

In pseudospin formalism, the Pauli spin operator σ^z in the order parameter $\langle\sigma^z\rangle$ operates between the two low-lying Kramers doublets of the Dy^{3+} ions. In our more general approach, the order parameter is the quadrupole moment, calculated on the basis of the whole ground multiplet. The generalization of the compressible model introduced in Ref. 8 for B_2^2 in Eq. (3) gives

$$B_2^2 = B_2^2(0)\frac{Q_2(T,H)}{Q_2(0,0)}\left\{1+\xi\left[\frac{Q_2(T,H)}{Q_2(0,0)}\right]^2\right\}, \quad (4)$$

where $\xi=0$ corresponds to an ordinary mean-field approximation. The value of B_2^2 at $H=0$ and low temperatures, $B_2^2(0)$, is found from the appropriate splitting of the low-lying Kramers doublets, equal to 27 cm^{-1}.[11,12]

The magnetization M,

$$M = g_J\mu_B\langle J\rangle = g_J\mu_B\frac{1}{Z}\sum_i e^{-E_i/k_BT}\langle i|\mathbf{J}|i\rangle,\ Z=\sum_i e^{-E_i/k_BT}, \quad (5)$$

the differential magnetic susceptibility dM/dH and the quadrupole moment Q_2,

$$Q_2 = \alpha_J\langle O_2^2\rangle = \alpha_J\frac{1}{Z}\sum_i e^{-E_i/k_BT}\langle i|O_2^2|i\rangle, \quad (6)$$

are calculated for the spectrum and wave functions of the Dy^{3+} ion which are deduced from a numerical diagonalization of the total Hamiltonian $\mathcal{H}$ (1) for every H and T with the solution of necessary self-consistent problems. For adiabatic regime a magnetocaloric effect ΔT under the field change from H to $H+\Delta H$ is calculated by the formula:

$$\Delta T = -T\left(\frac{\partial M}{\partial T}\right)_H\cdot\frac{\Delta H}{C_H} \equiv -T\left(\frac{\partial S_{\mathrm{mag}}}{\partial H}\right)_T\cdot\frac{\Delta H}{C_H}, \quad (7)$$

with a step size ΔH small enough to provide a conversion of the numerical procedure. In relation (7) the total heat capacity C_H includes the lattice heat capacity $C_{\mathrm{lat}}=12\pi^4/5k_B\nu(T/T_D)^3$ (the Debye temperature for the zircon lattice being $T_D=275$ K,[13] $\nu=6$) and the magnetic heat capacity C_{mag}. The magnetic contribution to the entropy is given by the expression (per one RE ion):

$$S_{\mathrm{mag}} = k_B\left(\ln Z + \frac{\langle E\rangle}{k_BT}\right), \quad (8)$$

where $\langle E\rangle$ is the mean energy. C_{mag} and other quantities in Eq. (7) are calculated with the help of above-mentioned numerical diagonalization of the total Hamiltonian.

IV. CRYSTAL FIELD AND INITIAL MAGNETIC SUSCEPTIBILITY

The CF parameters of $DyVO_4$ are actually unknown, since there are no sufficient spectroscopic data for the Dy^{3+} ion in $DyVO_4$ in tetragonal and orthorhombic phases. In Ref. 14 the CF parameters of the tetragonal $DyVO_4$ were derived with the usage of some interpolation procedure. They give the value of energy gap between the two low-lying Kramers doublets ΔE less than 1.5 cm^{-1}. ΔE is of crucial importance for the effects under consideration as will be seen from what follows. In our work,[6] devoted to experimental and theoretical investigations of the thermal expansion anomalies in $DyVO_4$ associated with the cooperative Jahn-Teller phase transition, the CF parameters were derived when taking into account that $\Delta E\approx 9$ cm^{-1}. Those CF parameters are equal (in cm^{-1}): $B_2^0=-79$, $B_4^0=35$, $B_6^0=-41$, $B_4^4=676$, $B_6^4=126$. The value of ground state splitting in the tetragonal phase $\Delta E\approx 9$ cm^{-1} was found in the optical absorption spectroscopy studies of the low-lying energy levels of $DyVO_4$ under uniaxial stress (Ref. 15), then it was presented in the review[2] fundamental for understanding of Jahn-Teller transitions and further was used and cited in the works concerning $DyVO_4$.

Calculations have shown that our experimental data for temperature variations of initial magnetic susceptibility $\chi(T)$ and anomalies of magnetic properties in high fields could not be interpreted with the help of those CF parameters. So we have derived a new set of CF parameters on the basis of our experimental data for $\chi(T)$, values of g-tensor components and available information on the structure of ground multiplet.[1] We emphasize that our findings for the high-field magnetic properties are not used in this fitting. From the sets

best describing the experimental data we have chosen a set which is the closest to that of $HoVO_4$,[16] because the CF of $HoVO_4$ is considered to be very reliable and the CF parameters for neighboring ions in the same compound are known to differ only slightly. The used CF parameters are equal (in cm^{-1}):

$$B_2^0 = -92,\ B_4^0 = 47.3,\ B_6^0 = -40.6,\ B_4^4 = 900,\ B_6^4 = -75.8. \tag{9}$$

For them the splitting ΔE comprises $\sim 3.5\ cm^{-1}$. This splitting is in accordance with Raman and UV studies of the energy spectrum of the Dy^{3+} ion in $DyVO_4$ above 14 K (Refs. 11 and 12) giving $\Delta E < 5\ cm^{-1}$ and contradicts the data of Ref. 15 discussed above with $\Delta E = 9\ cm^{-1}$.

The best fit to the magnetic data with the CF parameters ((9)) are shown in Fig. 2 as continuous lines. For $T < T_C = 14$ K the calculations are performed with regard to B_2^2 [Eq. (4)]. Curves calculated with CF from Ref. 6 demonstrate that the susceptibility along the hard direction, [001], is poorly described (Fig. 2, broken curve). We note that any other set of CF parameters which yields the splitting $\Delta E \approx 9\ cm^{-1}$ does not give a better description. The susceptibility in the easy basal plane is not that sensitive to the value of this splitting, as is seen from Fig. 2.

V. MAGNETIC SUSCEPTIBILITY IN HIGH FIELDS

(a) $T > T_C$: In the tetragonal phase of $DyVO_4$ the field along the tetragonal axis, $H \| [001]$, results in increasing of susceptibility dM/dH with a maximum around $\mu_0 H_{c3} \approx 31$ T (Fig. 3, lower part). Analogous anomalies in susceptibility take place for other temperatures as well (Fig. 1), the field H_{c3} being weakly dependent on temperature. As calculations indicate, the increase in susceptibility is caused by approaching of energy levels (crossover) (Fig. 3, upper part). It occurs when the lower level of the third doublet with a large component of the g-tensor g_z approaches the ground level and changes its wave function. The anomalies of the $dM/dH(H)$ curves caused by the crossover were observed and studied earlier for a number of RE zircons (see, e.g., Ref. 17).

Figure 3 illustrates a reasonable agreement of experimental and calculated isothermal and adiabatic curves $dM/dH(H)$. (The dotted curve will be discussed below.) A difference in height of the calculated isothermal peak and the experimental one for downsweep may be attributed to the deviation of temperature from 15 K because of the magnetocaloric effect in upsweep and the following transition process. Such reasonable agreement serves as a verification of the CF ((9)) found from alternative experimental data on the temperature dependencies of initial magnetic susceptibility. We note that for any set of CF parameters giving the gap $\Delta E \approx 9\ cm^{-1}$ the crossover peak of dM/dH is much higher than in experiment, as is seen, e.g., from the dotted curve calculated with CF from Ref. 6. Our extensive calculations have shown that in all cases of CF giving $\Delta E \approx 9\ cm^{-1}$, the character of higher-lying energy levels is such that the levels in the crossover move closer together giving rise to a higher

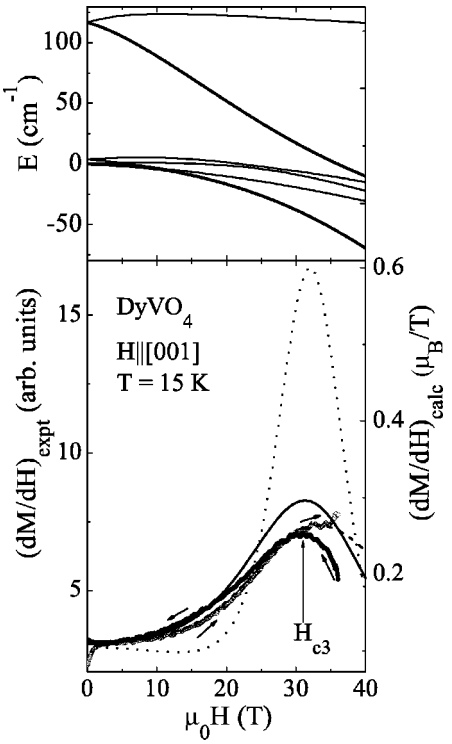

FIG. 3. Differential magnetic susceptibility dM/dH (lower part) and a fragment of Zeeman effect with three low-lying Kramers doublets, interacting levels are marked, (upper part) of $DyVO_4$ at $T = 15$ K, $H \| [001]$. Magnetic susceptibility calculated with the CF parameters (9) is given by continuous line for the isothermal regime and by dashed line for the adiabatic regime. Dotted line: calculation for CF giving $\Delta E \approx 9\ cm^{-1}$ in the isothermal regime.

susceptibility maximum. Thus information regarding the excited energy levels can be obtained from the magnetic characteristics in high magnetic fields.

(b) $T_N < T < T_C$. For this temperature range a rather sharp peak in dM/dH curve appears at the field H_{c2}. This peak existing only below T_C shows the influence of a magnetic field $H \| [001]$ on the quadrupole ordering. It destroys the quadrupole ordering and raises the crystal symmetry from orthorhombic to tetragonal. A subsequent increasing of the field gives rise to approaching of energy levels and the anomaly in susceptibility analogous to that at $T = 15$ K. This situation is displayed in Fig. 4 (lower part) for $T = 7$ K, $\mu_0 H_{c2} \approx 21$ T. The magnetocaloric effect calculation for this initial temperature gives an insignificant temperature change in the fields less than H_{c2}, so the isothermal and adiabatic $dM/dH(H)$ curves differ little from one another at $H < H_{c2}$ and in the region of the quadrupole ordering destruction.

For the field orientation strictly along the [001] axis, a destruction of quadrupole ordering occurs as a second-order phase transition. A misorientation results in a smearing out of the phase transition. In Fig. 4 (upper part) two pairs of curves are presented, for $\xi = 0$ (ordinary mean-field approximation) and $\xi = 0.3$ (compressible model). The mechanism of the suppression of the quadrupole ordering by a magnetic field may be described as follows. The application of a magnetic field to the system removes the degeneracy of Kramers doublets and rearranges the energy spectrum. The Jahn-Teller strains

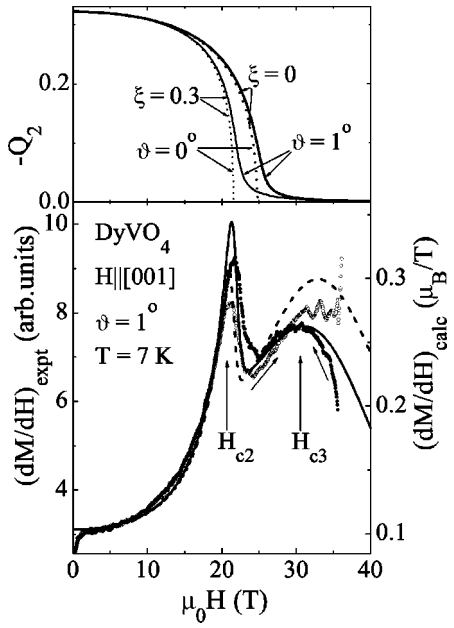

FIG. 4. Differential magnetic susceptibility dM/dH of $DyVO_4$ for $T=7$ K (lower part). Calculated curves are given by continuous line for the isothermal regime and by dashed line for the adiabatic regime, $\xi=0.3$ [see Eq. (4)], the magnetic field H is tilted by $\vartheta=1°$ with regard to the [001] direction. Calculated field dependencies of the quadrupole moment $Q_2=\alpha_J\langle O_2^2\rangle$ (upper part) are displayed for two different sets of ϑ and ξ.

change the spacings betweens the doublets. If the field-induced splittings of the low-lying doublets are sufficiently large the energy which is gained by a Jahn-Teller distortion does not overcome the associated decrease in the entropy and no distorted phase will exist.

Experimental curves of $dM/dH(H)$ for $T_N<T<T_C$ (Figs. 1 and 4) make it apparent that in $DyVO_4$ the susceptibility peak associated with the quadrupole ordering destruction is essentially narrower and higher than the peak caused by the crossover. We emphasize that calculations with any CF giving $\Delta E\approx 9$ cm^{-1} reveal an alternative picture of a sharp peak in the crossover, similar to that presented in Fig. 3 by dotted curve, and a hardly noticeable peak at the quadrupole ordering destruction. Thus our experimental findings (Figs 2–4) suggest the energy gap in the tetragonal phase $\Delta E \approx 3.5$ cm^{-1}, in accordance with $\Delta E<5$ cm^{-1} (Refs. 11 and 12) and in contrast to $\Delta E\approx 9$ cm^{-1} (Ref. 15). The reason of this contradiction is not clear. It might be that this splitting is very sensitive to the stresses resulting from the crystal growth or the sample mounting and differs for different series of samples and experiments. But generally speaking, it is a puzzle.

The field dependencies of differential magnetic susceptibility, experimental for up-sweep and calculated in adiabatic regime, for the initial temperatures $T_0>T_N$ are shown in Fig. 5. The two sequences of curves for increasing temperature T_0 are rather similar. A variation of the character of magnetocaloric effect with increasing initial temperature should be noted (Fig. 6, upper part). The Zeeman effect calculated in the adiabatic regime for two initial temperatures 4 and 12 K (Fig. 6, lower part) helps to account for this variation. At

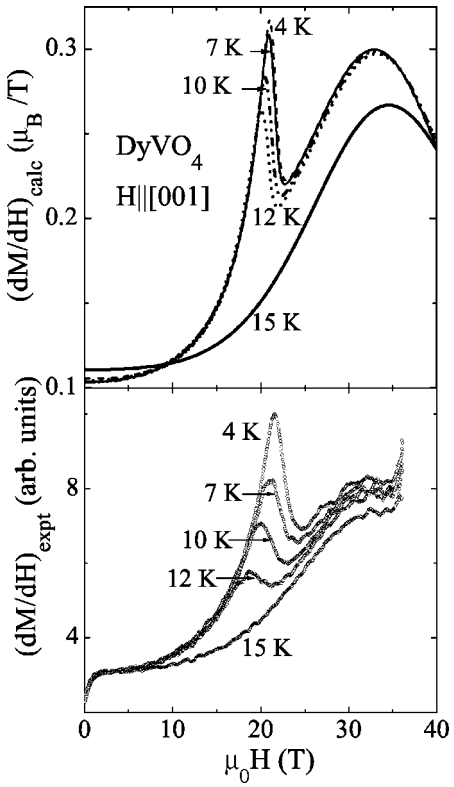

FIG. 5. Differential magnetic susceptibility dM/dH of $DyVO_4$ for various initial temperatures T_0: experimental for upsweep (lower part) and calculated in the adiabatic regime (upper part).

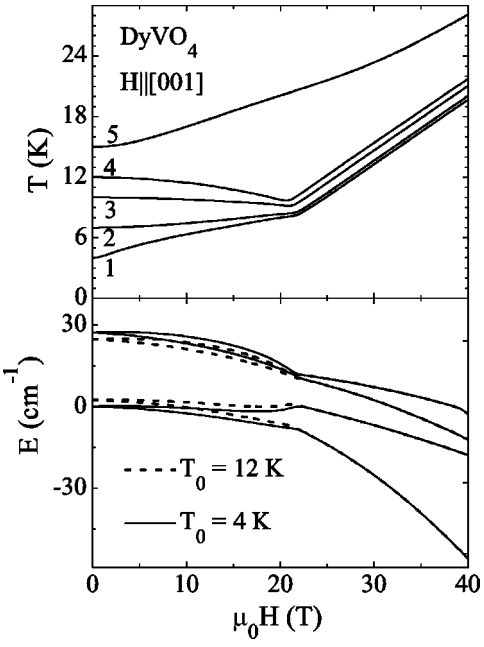

FIG. 6. Variation of the sample temperature due to magnetocaloric effect $T(H)$ for various initial temperatures T_0: (1) 4 K, (2) 7 K, (3) 10 K, (4) 12 K, and (5) 15 K (upper part). Fragment of Zeeman effect calculated in the adiabatic regime for two initial temperatures T_0 (lower part) of $DyVO_4$, two lowest-lying Kramers doublets are shown.

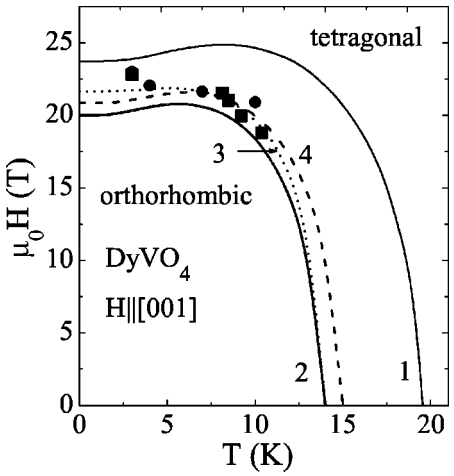

FIG. 7. $H-T$ phase diagram of $DyVO_4$. The lines are calculated with: (1) $\vartheta=0°$, $\xi=0$; (2) $\vartheta=0°$, $\xi=0.39$; (3) $\vartheta=2°$, $\xi=0.39$; and (4) $\vartheta=1°$, $\xi=0.3$. Symbols are experimental points; (■), in the up-sweep of the field (the temperatures are corrected for magnetocaloric effect); (●), in the downsweep of the field.

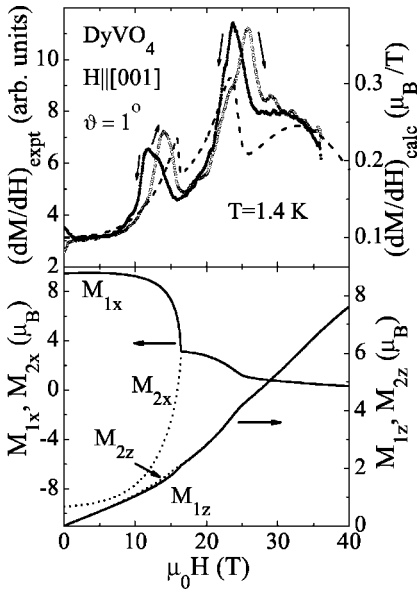

FIG. 8. Differential magnetic susceptibility dM/dH for up- and downsweeps together with the calculated curve (dashed line) (upper part) and field dependencies of the projections on x and z axes of magnetic moments $\mathbf{M}_1$ and $\mathbf{M}_2$ (lower part) of $DyVO_4$ at 1.4 K.

$T_0=4$ K the splitting of the ground Kramers doublet by a magnetic field gives rise to a decrease of the magnetic part of the entropy [see Eq. (8)] and thus to heating under magnetization. For $T_0=12$ K a contribution to the magnetic part of the entropy from the second doublet is essential because the temperature is higher and the initial gap between the doublets is less (the gap is proportional to the quadrupole moment, which is temperature dependent). In this situation the magnetic part of the entropy increases, this results in cooling of the sample up to the critical field H_{c2}. After the destruction of quadrupole ordering, the character of Zeeman effect reveals a more rapid decrease of the magnetic entropy and a more rapid heating of the sample.

In Fig. 7, the phase diagram in the $H-T$ plane for $DyVO_4$ with $H\|[001]$ is given. Theoretical curves 1 and 2 are obtained as self-consistent solutions of the equation $Q_2(T,H)=0$ for $\vartheta=0$ and different values of compressible parameter ξ [Eq. (4)]. Curve 1 in Fig. 7 corresponds to the ordinary mean-field approximation with $\xi=0$, which gives $T_C\approx 19$ K. If we take $\xi=0.39$ the Jahn-Teller phase transition temperature T_C equals its experimental value 14 K (curve 2). These curves show that the effect of "compressibility" is relatively more essential for T_C than for H_C.

In order to discuss experimental values of the field H_{c2}, the temperature dependencies of the critical fields which correspond to the peaks of the susceptibility dM/dH, calculated for a small misorientation of the field out of the [001] direction, are presented in the same phase diagram. The curves 3 and 4 are obtained for $\xi=0.39$ and the misoriention angle $\vartheta=2°$ and $\xi=0.3$ and $\vartheta=1°$, respectively. Symbols are experimental findings. The downsweep magnetization process is considered as corresponding to the isothermal regime. In upsweep the appropriate H_c, T_C points are corrected for the magnetocaloric effect. It is seen that agreement with experimental findings is more or less reasonable for both curves, 3 and 4. It we take $\vartheta=2°$ the correct value of $T_C=14$ K and a reasonable agreement of the experimental and calculated $H-T$ phase diagrams are obtained with the compressible model parameter $\xi=0.39$. This is the first attempt to construct the $H-T$ phase diagram for the field-induced destruction of quadrupole ordering in $DyVO_4$.

(c) $T<T_N$: Below T_N at the critical field H_{c1} the destruction of antiferromagnetic ordering along the [100] axis by the field perpendicular to the magnetic moments of Dy^{3+} ions, $H\|[001]$, and a transition to the state with magnetic moments oriented along the field direction occur in $DyVO_4$. In higher fields the effects described above take place. To account for the experimental data at $T=1.4$ K one may suggest an influence of relaxation processes on the shape of peaks and critical fields for the $dM/dH(H)$ curves. Indeed, an essential hysteresis for up- and downsweep is seen in Fig. 1 at $T=1.4$ K. Calculations of magnetocaloric effect have revealed an insignificant change of temperature (by some decimals of Kelvin). Consequently the hysteresis can not be ascribed to the magnetocaloric effect.

Figure 8 (upper part) shows a good qualitative, but not quantitative, agreement between the data and the calculated curves $dM/dH(H)$ (the isotherm and adiabat coincide because of a weak magnetocaloric effect) of $DyVO_4$ at $T=1.4$ K. Also shown in Fig. 8 (lower part) is a field dependence of projections of magnetic moments $\mathbf{M}_1$ and $\mathbf{M}_2$, which form at $H=0$ an antiferromagnetic structure along the **a** axis ($\mathbf{a}\|O_x$) for the field misorientation by 1° with respect to the **c** axis ($\mathbf{c}\|O_z$) in the xz plane. Calculations are performed on the full Hamiltonian, self-consistent problems for the five order parameters: Q_2, M_{1z}, M_{1x}, M_{2z}, M_{2x} are solved. Exchange parameters in Eq. (2) have been estimated with the help of the known value of T_N: $\lambda_x=\lambda_z=0.030$ cm$^{-1}/\mu_B$. Calculations have shown that consideration of anisotropy of exchange interaction ($\lambda_x\neq\lambda_z$) leaves the results practically unchanged.

Field dependences of the $\mathbf{M}_1$ and $\mathbf{M}_2$ projections for a small misorientation angle $\vartheta = 1°$ demonstrate a very large anisotropy which is formed by CF and is a characteristic feature of many RE compounds; it manifests itself, in particular, in highly anisotropic g tensor at low temperatures ($g_a \approx 19$, $g_c \approx 0.5$, Ref. 1) In the field H_{c1} the sublattices are parallel but the total magnetic moment is far from being parallel to the field direction, e.g., $\vartheta_M(H=H_{c1}) \approx 56°$ for $\vartheta = 1°$. In the model under consideration the transformation of the system to the state with parallel magnetic moments occurs as a second-order phase transition. A field misorientation with respect to the [001] axis does not smear out the transition in contrast to a smearing out which occurs in the case of destruction of quadrupole ordering. Therein lies the difference in the role of CF for the quadrupole and magnetic orderings in particular.

VI. CONCLUSION

Our experimental and theoretical investigations of the low-temperature phase transitions and magnetic properties of the Jahn-Teller compound $DyVO_4$ in a high magnetic field have shown that at $T < T_N$ the field along the [001] direction first destroys the antiferromagnetic ordering of magnetic moments of Dy^{3+} ions along the [100] axis forcing their alignment along the field direction. Next, the destruction of quadrupole ordering and the rise of crystal symmetry from orthorhombic to tetragonal occur, the quadrupole moment $Q_2 = \alpha_J \langle O_2^2 \rangle$ is reduced to zero. On further increasing of the field, another essential rearrangement of the energy spectrum of Dy^{3+} ions takes place, namely, an approaching of energy levels happens in the lower part of the multiplet. For $T_N < T < T_C$ the second and third events from listed above occur, at $T > T_C$ only the third one takes place. All these transitions/effects are accompanied by pronounced peaks in the field dependence of differential magnetic susceptibility. They are accounted for within the unified approach. Our calculations of the high-field magnetic properties of $DyVO_4$ in the framework of the conventional crystal-field model with regard to quadrupole and exchange interactions are in reasonably good agreement with experimental data thus confirming the validity of our interpretation.

To conclude we compare the situation in $DyVO_4$ with that in the other Jahn-Teller compound $TbVO_4$. Terbium vanadate undergoes a Jahn-Teller cooperative distortion at $T_D = 33.1$ K, determined quite precisely from the anomaly in the heat capacity. Below this temperature, the structure is orthorhombic with space group D_{2h}^{24}, resulting from a crystal deformation along the [110] axis (B_{2g} strain). The order parameter is the quadrupole moment $Q_{xy} = \alpha_J \langle \frac{1}{2}(J_x J_y + J_y J_x) \rangle$. High-field studies is of evident interest for $TbVO_4$ where the quadrupole order parameter is of different symmetry. Our preliminary calculations with available CF parameters and information on the splitting of the low-lying energy levels of this non-Kramers ion in tetragonal and orthorhombic phases have revealed the destruction of the qudrupole ordering by the field $H \| [001]$. Measurements of this phenomenon can provide valuable information on the ground multiplet structure and CF parameters, which are not reliably established.[18] We have also predicted crossing of the two lowest-lying energy levels resulting in a peak of magnetic susceptibility dM/dH in higher fields. As our calculations in adiabatic regime have shown these anomalies should be observable at pulsed fields for initial temperatures less than 10–15 K because of essential cooling of a sample near the crossover due to magnetocaloric effect.

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