Magnetization and magnetostriction of Van Vleck antiferromagnets with magnetic anisotropy of "easy-plane" type

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The magnetic properties of the antiferromagnetic state induced in the Van Vleck magnet by longitudinal magnetic field are described within thermodynamic Landau approach. We consider the case of a magnet with a single-ion anisotropy of "easy-plane" type and ion spin $S=1$. It is shown that quantum phase transition to antiferromagnetic state is related to appearance of the spontaneous spin polarization parallel to an "easy-plane." Application of longitudinal field gives rise to the tilt of sublattice magnetizations toward the field direction and increase in their modula as well. Linear field dependence of the net magnetization (similar to that observed in the classical antiferromagnets) can be attained only in the limit of large interion "easy-plane" anisotropy comparable to the single-ion one. We also study peculiarities of the induced magnetostriction of the Van Vleck antiferromagnet and show that: (i) like the magnetization, magnetostriction has a singularity at the phase-transition point and (ii) the sign of magnetostriction can be reversed during the magnetization process due to the influence of the spin tilt. An attempt is made to qualitatively compare the obtained results with the available experimental data.

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I. INTRODUCTION

It is well known that magnetization of the classical or weakly anisotropic antiferromagnets (AFMs) at low temperatures (far below Néel temperature T_N) is related only to canting of sublattice magnetizations.[1] Based on this fact, it is usually supposed that the module of corresponding vectors is fixed and the external magnetic field may influence only the direction of sublattice magnetization. The character and peculiarities of the magnetization process (spin flip, spin flop, and also reorientational phase transitions of the first kind) in AFMs depend on the following parameters: value and direction of the external magnetic field, anisotropy constants, and magnitude of the intersublattice exchange.[2–5] For example, field dependence of net magnetization for two dichalcogenides of iron group, $NiCl_2$ or $CoCl_2$,[6–10] can be appropriately described within a quasiclassical approach although these magnets are markedly different. While both magnets are "easy-plane" two-sublattice AFMs, the ion orbital moment is almost completely frozen by crystal field in $NiCl_2$ (due to the fact that the value of an "easy-plane" single-ion anisotropy is much smaller than the exchange constant) and is only partially frozen in $CoCl_2$ (where an "easy-plane" single-ion anisotropy is only two times smaller than the exchange constant[7]). Field dependence of the induced magnetostriction in these crystals[11–13] also agrees with the assumption that the sublattice magnetizations have fixed modula and may only rotate.

However, among AFMs there is a family of crystals where the single-ion anisotropy exceeds the interion exchange.[14,15] These are the so-called Van Vleck, or singlet, antiferromagnets (VVAs). VVAs show no magnetic ordering at any temperature down to $T=0$. Such materials include, in particular, hexagonal crystals of ABX_3 type, where A is an ion of alkali metal ($A=$Cs, Rb), B is a transition metal ($B=$Fe), and X is a chalcogenide ($X=$Cl, Br). In these crystals the magnetic moments induced by the external field at paramagnetic ions B^{2+} form simultaneously antiferromagnetic chains along C_3 axis and also triangular structures in the basis plane (see, for reviews, Refs. 16–19).

There are also some other compounds classed with VVAs, including the so-called DTN (dichloro-tetrakisthioureanickel), the chemical formula of which is $NiCl_2 \cdot 4SC(NH_2)_2$.[20–23] DTN also shows (AFM) Ni-Cl-Cl-Ni chains along a "hard" magnetic axis, although in the absence of field the mean spin at each site is zero. Such a behavior can be ascribed to the fact that the single-ion anisotropy exceeds both the intrasublattice and intersublattice exchange parameters. It should be emphasized that DTN can be classified as a two-sublattice VVA which differs from $NiCl_2$ by crystal structure and character of the exchange interactions that are much weaker than the single-ion anisotropy.[22,23]

The magnetization process in VVAs is fundamentally different from that in the classical Néel AFMs.[24–27] First, VVAs show no magnetic ordering in the absence of the external magnetic field. Hence, they have no magnetic sublattices. Second, magnetic or, strictly speaking, antiferromagnetic ordering in VVAs may appear spontaneously in the course of the quantum (in definition of Ref. 28) field-induced phase transition.[16–23] Thus, the formed AFM phase has one impor-

tant peculiarity: the corresponding magnetic susceptibility weakly depends on external magnetic field. As a result, the observed magnetization actually follows the linear field behavior.[22,23,29,30] In other words, such a behavior of net magnetization in AFM phase turns out to be similar to the magnetization induced by the external field in the Néel AFMs.

One can understand such a behavior in case of the first-order transition to the AFM phase when sublattice magnetizations abruptly appear at the transition point (if temperature or field dependence of susceptibility has a proper singularity). Further application of the magnetic field can induce only rotation of corresponding vectors.

However, experiment shows that transformation of the nonmagnetic (singlet) state into the AFM one takes place continuously, i.e., this magnetic transformation is a second-order phase transition.[22,23,29,30] This also implies continuous variation in sublattice magnetizations from the initial zero to saturation value. Therefore, it is principally impossible to describe VVAs within the classical approach based on assumption of the fixed module of average sublattice spin.

The induced magnetostriction in DTN is experimentally studied by Zapf *et al.*[22,23] They show, in particular, that the magnetostriction appears in DTN only in AFM phase. They also found that the external field may induce sign reversal of the relative elongation (contraction) along the hard magnetic axis.

Such a behavior of DTN striction was attributed, in Ref. 23, to the prevailing role of the intersublattice magnetoelastic interaction of an exchange nature.[20,21] On the other hand, sign reversal of magnetostriction is observed also in some classical Néel AFMs, for example in $CoCl_2$ (Refs. 11–13) where it is conditioned by the anisotropic intrasublattice magnetoelastic interaction.

So, one can specify some problems in the theory of VVAs that need to be solved, namely, description of the field-induced transition into antiferromagnetic phase and magnetic properties of this phase (field dependencies of sublattice magnetizations and net magnetization of crystal, magnetic susceptibility, and magnetostriction).

The present paper is aimed at the description of the induced magnetostriction in the VVAs with the pronounced anisotropy. In such materials the constant of anisotropic magnetoelastic coupling also can be comparable (or even larger) to that of isotropic magnetoelastic coupling. In contrast to quasiclassical approach, our model strictly accounts for the appreciable field dependence of the modula of sublattice magnetizations in AFM phase which arises from the initially singlet state.

We start from an assumption that the intrinsic spontaneous magnetic (or AFM) moment in VVAs is zero. So, in the absence of the external magnetic field the concept of the magnetic ordering temperature is meaningless. From the fact that the magnetic (dipole) moment or, in other words, magnetization (spin) at a site is zero, one can mistakenly deduce not only the absence of any magnetic ordering but also the absence of any magnetic contributions to physical properties of the corresponding systems. However, this is not the case because the absence of ordinary (exchange-induced) spin ordering does not exclude the presence the ordering of other type, e.g., the quadrupole one. The latter, in that or in the other way, is peculiar to the all Van Vleck magnets that, in turn, are a special case of the magnetic crystals with more specific (nematic) type of spin ordering.[31,32]

This or other spin ordering shows up not only in formation of new (spin-) electron-excitation branches in crystals[33] but also in such an observed and computable characteristic as magnetostriction whose peculiarities for VVA are not completely studied yet. At the same time, such a necessity does exist in context of recent measurements of magnetoelastic properties of DTNs.[22,23]

It should be noted that some studies (e.g., Refs. 34–37) describe the phase transition between the singlet and induced AFM states in terms of the representation of Bose-Einstein condensation of magnons. Indeed, appearance of magnetization at the finite magnetic field value can be formally described in the terms of condensation of certain magnetic excitations. However, in reality no true condensation of quasiparticles occurs in the observed systems because, and it will be shown below, one should speak about transformation of the ground state only and, hence, about virtual, rather than real, magnons.[38]

Below we consider the model of strongly anisotropic two-sublattice AFM with ion spin $S=1$. In the framework of quantum approach an attempt is made to describe the behavior of the net magnetization, magnetic susceptibility, and magnetostriction in the course of the field-induced phase transition from the initial singlet state to the spin-ordered one. To calculate the physical characteristics of the system, we take into account the following contributions into the internal energy E of VVAs:

$$E = E_{\text{exch}} + E_{\text{an}} + E_h + E_{\text{el}} + E_{\text{m-el}}. \quad (1)$$

Here E_{exch} is the exchange energy, E_{an} is the magnetic anisotropy energy, E_h is Zeeman energy, E_{el} is the elastic energy, and $E_{\text{m-el}}$ is the magnetoelastic energy or the energy of spin-lattice coupling. It is also supposed that the value of magnetoelastic coupling is much smaller than that of the exchange. So, magnetoelastic coupling has no noticeable feedback influence on the magnetic ordering. Hence, without loss of generality one can calculate the parameters of the magnetic phases neglecting magnetoelastic effects and then calculate the induced striction in a standard approximation of linear elasticity.[39]

II. GROUND STATE OF A SINGLET ANTIFERROMAGNET IN THE LONGITUDINAL MAGNETIC FIELD

Following the method of successive approximations described above, we first take into account only the first three summands in Eq. (1), namely, bilinear anisotropic (intrasublattice and intersublattice) exchange coupling, single-ion "easy-plane" anisotropy, and Zeeman contribution. In this case, the simplest model Hamiltonian of a system can be written down as follows:

$$H = \frac{1}{2}\sum_{\mathbf{n}_\alpha,\mathbf{m}_\beta} J_{\mathbf{n}_\alpha\mathbf{m}_\beta}\mathbf{S}_{\mathbf{n}_\alpha}\mathbf{S}_{\mathbf{m}_\beta} + \frac{1}{2}\sum_{\mathbf{n}_\alpha,\mathbf{m}_\beta} J^Z_{\mathbf{n}_\alpha\mathbf{m}_\beta} S^Z_{\mathbf{n}_\alpha} S^Z_{\mathbf{m}_\beta} + D\sum_{\mathbf{n}_\alpha}(S^Z_{\mathbf{n}_\alpha})^2 - \mathbf{h}\sum_{\mathbf{n}_\alpha}\mathbf{S}_{\mathbf{n}_\alpha}, \quad (2)$$

where $\alpha,\beta=1,2$ enumerate the magnetic sublattices, vectors $\mathbf{n}$ and $\mathbf{m}$ specify the spins position within the magnetic sublattice, $\mathbf{S}_{\mathbf{n}_\alpha}$ are corresponding spin operators, $D>0$ is a constant that reflects an "easy-plane" magnetic structure, and magnetic field $\mathbf{h}$ is determined in energy units; hence, $\mathbf{h}=\mu_B g\mathbf{H}$, where $\mathbf{H}$ is the magnetic field, μ_B is Bohr magneton, and g is gyromagnetic ratio. Crystallographic symmetry axis OZ is perpendicular to the "easy-plane." Longitudinal, $\mathbf{h}\|\mathrm{OZ}$, magnetic field induces the phase transition to the antiferromagnetic state, while transverse field $\mathbf{h}\perp\mathrm{OZ}$ in two-sublattice VVA does not induce any phase transition. Parameter $J_{\mathbf{n}_\alpha\mathbf{m}_\beta}$ characterizes the value of an isotropic part of the exchange coupling and $J^Z_{\mathbf{n}_\alpha\mathbf{m}_\beta}$ characterizes the exchange anisotropy which, in principle, can be of either "easy-axis" or "easy-plane" type. However, we assume that the interion anisotropy, such as the single-ion one, is of the same, i.e., "easy-plane" type.

It should be emphasized that Hamiltonian (2) differs from that we considered in Refs. 26 and 27 because the exchange striction is taken into account. Moreover, in the above studies the three-sublattice AFM were described. It should be borne in mind in this case that the magnetization of two- and three-sublattice VVAs proceeds in a similar way in the longitudinal field, differing only in values of the critical fields and rates of magnetization. Magnetization of three-sublattice AFM in the transverse field is complicated by the frustration phenomenon, while two-sublattice VVA is magnetized in a common way. In this study, we compare the magnetization of two-sublattice VVA in the longitudinal and transverse magnetic fields.

In Ref. 23 the process of magnetization of the system described by Hamiltonian (2) was analyzed by using the Monte-Carlo technique. This method is helpful in computation of field dependencies of different parameters, but it does not allow determining the type (but not the order) of phase transition. It should be also mentioned that the results of numerical calculations obtained by Monte-Carlo technique strongly depend on the number of steps and nodes. So, correctness of the results thus obtained is usually proved by comparison with experimental data that is not always a good criterion of computation accuracy. In addition, the problem of AFM eigenstate remains open within the Monte-Carlo technique because sublattices are artificially fixed in the calculations. Moreover, using the formally precise method of computation, the authors of Ref. 23 face with the problem of degeneracy of the direction of AFM vector in the basis plane at $\mathbf{h}\|\mathrm{OZ}$. This degeneracy can be removed by application of small exchange field that gives rise to the lowering of the initial Hamiltonian (2) symmetry.

In what follows we analyze the possible eigenstates of Hamiltonian (2) at $\mathbf{h}\|\mathrm{OZ}$ in approximation of self-consistent field. This approximation allows one to derive the analytical expressions for the vectors of average sublattices spins. In this case it is possible at all stages of calculations to trace over the spin system parameters and to separate those responsible for the series of phase transitions—from the singlet to the AFM state, then from the AFM one to the paramagnetic state. In the approximation of self-consistent field the spin fluctuations can be ignored, so the averages of product of different site spin operators can be replaced by a product of the averages. We concentrate our attention mainly on the magnetically induced phase transition to AFM state, which belongs to the displacementlike phase transitions, and which is caused by competition between single-ion and interion spin interactions.

It should be stressed that in contrast to order-disorder phase transition, the displacementlike phase transition can take place even at $T=0$. So, while description of the order-disorder transition needs the analysis of the free energy (with account of temperature-dependent contribution) of the system, displacementlike transition can be analyzed on the basis of the internal energy only. The entropy contribution related to fluctuations is negligible in this case.

An expression for energy E_{gr} of the ground state per unit cell of AFM phase with account of nearest neighbors is equal to

$$E_{\mathrm{gr}} = \frac{1}{2}\sum_{\alpha\beta} J_{\alpha\beta} z_{\alpha\beta}\mathbf{s}_\alpha\mathbf{s}_\beta + \frac{1}{2}\sum_{\alpha\beta} J^Z_{\alpha\beta} z_{\alpha\beta} s^Z_\alpha s^Z_\beta + D\sum_\alpha Q^{ZZ}_\alpha - h_\parallel\sum_\alpha s^Z_\alpha, \quad (3)$$

where $\mathbf{s}_\alpha$ is the quantum-mechanical average of the spin vector of the αth sublattice in the ground ion state and $z_{\alpha\beta}$ is the number of the nearest neighbors within the same ($z_{\alpha\alpha}$) and within the different ($z_{\alpha\beta}\equiv z_{12}$) sublattices. Introduced also are the averages for components of spin quadrupole moment Q^{ZZ}_α.[42,45,46] Note that for AFM the intersublattice exchange parameter is $J_{12}z_{12}\equiv I>0$. At the same time, the parameter $J_{11}z_{11}=J_{22}z_{22}\equiv J$ of intrasublattice exchange can have any sign. We take for simplicity $J<0$, so that intrasublattice exchange favor the AFM ordering. The exchange anisotropy, in this case, satisfies the conditions of its "easy-plane" type: $J^Z_{12}z_{12}\equiv\triangle I<0$ and $J^Z_{11}z_{11}=J^Z_{22}z_{22}\equiv\triangle J>0$.

Let us impose for spins of each sublattice their proper (rotating) coordinate systems $\xi_\alpha\eta_\alpha\zeta_\alpha$ such that αth sublattice average spin is always oriented along ζ_α axis, which means that this axis is the quantization one for this spin sublattice, and ξ_α axis is parallel to $Z\zeta_\alpha$ plane. Then the appropriate wave function of the ground spin state of the αth sublattice in such a coordinate system, as it is well known, takes the following form:[43,44]

$$\psi^{(0)}_\alpha = \cos\phi_\alpha|1\rangle + \sin\phi_\alpha|-1\rangle, \quad (4)$$

where $|\pm1\rangle$ and $|0\rangle$ are the eigenfunctions of the operator $S^\zeta_{\mathbf{n}_\alpha}$ in bra-ket representation. Then we can calculate the quantum-mechanical spin and quadrupole averages by using Eq. (4) as follows:

$$s = \cos 2\phi, \quad Q^{\zeta\zeta} = 1, \quad Q^{\xi\xi} = \frac{1}{2}(1 + \sin 2\phi),$$

$$Q^{\eta\eta} = \frac{1}{2}(1 - \sin 2\phi). \tag{5}$$

In the expressions (5) the sublattice indices are omitted because of the assumed homogeneity mentioned above.

Substituting Eq. (4) into Eq. (3) with the assumption $\mathbf{h} \| OZ$, we obtain the following expression for the energy of ground state:

$$E_{gr} = I \cos^2 2\phi \cos 2\theta - |J| \cos^2 2\phi + J_Z \cos^2 2\phi \cos^2 \theta + 2D\left[\cos^2 \theta + \frac{\sin^2 \theta}{2}(1 + \sin 2\phi)\right] - 2h_{\|} \cos \theta \cos 2\phi, \tag{6}$$

where $J_Z \equiv \triangle J - \triangle I$ and θ is the angle between the sublattice magnetization and OZ axis.

As was reported in Refs. 40 and 41, spin configuration in the magnetic field can be found from minimization of expression (6) with respect to all the unknown variables: the geometric angle θ and [see Eq. (4)] the angle ϕ of quantum states mixture. Such an approach is completely equivalent to the solution of quantum self-consistent problem; but at the same time it is more convenient and consistent, because it allows generalization for the case of finite temperature.[26,27]

The equations for both angles are

$$\frac{\partial E_{gr}}{\partial \phi} = -2(I \cos 2\theta - |J| + J_Z \cos^2 \theta) \sin 4\phi + 2D \sin^2 \theta \cos 2\phi + 4h_{\|} \cos \theta \sin 2\phi = 0, \tag{7}$$

$$\frac{\partial E_{gr}}{\partial \theta} = -(2I + J_Z) \sin 2\theta \cos^2 2\phi - D \sin 2\theta (1 - \sin 2\phi) + 2h_{\|} \sin \theta \cos 2\phi = 0. \tag{8}$$

As known from Ref. 38, in the absence of external magnetic field, set of Eqs. (7) and (8) has two solutions: nonmagnetic one, $s=0$, stable at $D > 2(I+|J|)$ and "magnetic," stable at $D \leq 2(I+|J|)$. For the latter case the reduced value of single-site mean spin is

$$s = \sqrt{1 - \frac{D^2}{4(I + |J|)^2}} < 1. \tag{9}$$

The initial ground state of the system should be the singlet one, $s=0$, so that the quantum phase transition (at the magnetic field $\mathbf{h} \| OZ$) from this state to magnetically ordered one occurs. So, let us assume that the above explicit inequality, i.e., $D > 2(I+|J|)$, is satisfied. Then, the ground state of the system is really nonmagnetic, and in the absence of magnetic field no ordering takes place at any temperature.[41] In other words, expression (9) determines the condition of singletness of magnet ground state, which is a Van Vleck one. Solution $s=0$ is satisfied in the interval $h_{\|} < h_s = \sqrt{1 - (I + |J|/D)}$.

As the field grows, the finite value ($s \neq 0$) of the mean spin at a site appears, and at $h_{\|} > h_s$ the two-sublattice AFM phase is formed. In this phase the ground state of ions corresponds to that with nonzero spin polarization. AFM phase appears spontaneously at the critical-field value; corresponding vector of spin polarization is parallel to the basis plane. Field increase gives rise to both rotation of sublattice magnetizations and increase in their modula.

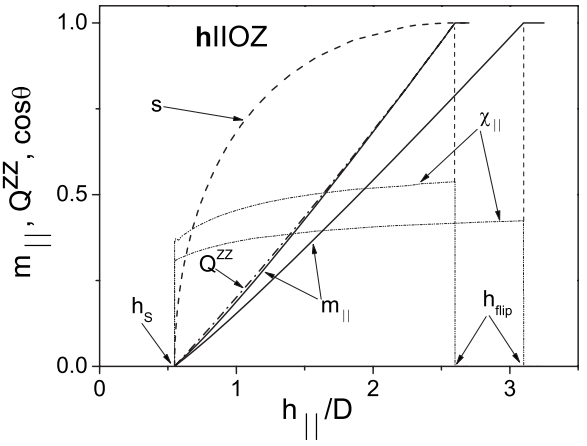

FIG. 1. Longitudinal magnetization $m_{\|}$ and magnetic susceptibility $\chi_{\|}$ versus field at $|J|/D=0.05$, $I/D=0.3$, and $J_Z/D=1$ and 1.5. Functions $s(h_{\|})$ and $Q(h_{\|})$ are shown only for $|J|/D=0.05$, $I/D=0.3$, and $J_Z/D=1$.

It follows from Eq. (7) that at large field value, $h_{\|} \geq h_{flip}$ (where $h_{flip} \equiv D+2I+J_Z$), the paramagnetic state in which spins of both sublattices are directed along the hard ($\theta=0$) axis is stable. In this case the projection of the average spin on the external field direction attains its maximal, $s=S=1$, value. At $h_s < h_{\|} < h_{flip}$, the vectors of the sublattice spins make a finite angle $0 < \theta < \pi/2$ with the hard axis. The modula of these vectors do not depend on the $s(h_{\|})$ field. The behavior of two-sublattice AFM at $\mathbf{h} \| OZ$ is in qualitative agreement with that of three-sublattice AFM.

Phase transition induced by the longitudinal field from singlet state to the AFM one in three-sublattice VVAs is described in Refs. 26 and 27 within the Landau thermodynamic approach. According to this approach, the energy of the ground state is described as a power series in order parameter, which, in the framework of this problem, is the spin polarization. Using this approach for the two-sublattice system (2), it is easy to find that in the vicinity of critical field $(h_{\|} - h_s)/h_s \ll 1$ the net magnetization follows a linear field dependence:

$$m_{\|} \equiv m(h_{\|}) = s(h_{\|}) \cos \theta = \frac{2h_s^2(h_{\|} - h_s)}{D^3 + 2h_s^2(2I + J_Z)}, \tag{10}$$

where $m(h_{\|})$ is the net magnetization per magnetic ion. For $h_{\|} < h_s$ net magnetization vanishes, $m_{\|}=0$. However, expression (10) obtained within the phenomenological theory is applicable only in the vicinity of the critical point h_s at $h_{\|} \geq h_s$.

So, magnetization of AFM phase in the whole field range, i.e., at $h_s < h_{\|} < h_{flip}$, should be described on the basis of more accurate expressions (7) and (8). Figure 1 represents field dependencies of sublattice magnetization $s(h_{\|})$, its orientation $\theta(h_{\|})$, net magnetization $m_{\|}(h_{\|})$, the quadrupole spin

moment $Q^{ZZ}(h_\parallel)$, and magnetic susceptibility $\chi_\parallel(h_\parallel) = dm_\parallel/dh_\parallel$ calculated using Eqs. (7) and (8). As seen from Fig. 1, $m_\parallel(h_\parallel)$ dependence shows weak nonlinearity in the interval $h \in [h_s, h_{\text{flip}}]$. This nonlinearity decreases with increasing exchange "easy-plane" anisotropy. Nevertheless, in this case, nonlinearity is not fully suppressed even when the exchange anisotropy is comparable to the single-ion one.

It also follows from Fig. 1 that the field dependence of the ZZ component of spin quadrupole moment $Q^{ZZ}(h_\parallel)$ almost coincides with the field dependence of $m_\parallel(h_\parallel)$. At model parameter values $|J|/D=0.05$, $I/D=0.3$, and $J_Z/D=1.5$ used in Fig. 1, the critical-field ratio is equal to $h_{\text{flip}}/h_s \approx 5.6$, which corresponds to the ratio of these fields determined in the experiment[22,23] for DTN.

The quantum process in the magnetization prevails near h_s, and the magnetization is determined by the appearance and growth of $s(h_\parallel)$ as mentioned above. On the contrary, in the vicinity of $h_\parallel \leq h_{\text{flip}}$, the classical canting of sublattice spins to the field direction becomes more important. At the same time, the role of the change in ground ion state spin value is essentially smaller (but not absent). It is apparent that field dependence of susceptibility in this region is weak. So, it can be assumed that spin flip of AFM sublattices or field-induced transition of the Van Vleck system from two- to one-sublattice ordered states is similar to orientation phase transition in classical AFM, where, as was already mentioned, only rotation of sublattices magnetizations takes place. Nevertheless, even for these transitions the quasiclassical approach does not give the correct result for the $m(h_\parallel)$ dependence in spin nematics.

The magnetic susceptibility of system (2) calculated within the quasiclassical approach takes the following form:

$$\tilde{\chi}_\parallel = \frac{1}{D + 2I + J_Z} \equiv \frac{1}{h_{\text{flip}}} = \text{const}. \tag{11}$$

This value of magnetization obtained at $h_\parallel \to h_{\text{flip}}$ suggests that $m_\parallel$ is proportional to $h_\parallel$ and that $m_\parallel$ should asymptotically tend to zero at $h_\parallel \to 0$. From Fig. 1 one can see that in contrast to classical AFMs, field dependence $m_\parallel(h_\parallel)$ of VVAs magnetization, although linear, is shifted along field axis. This means that the quasiclassical approach is inapplicable even for a region of the fields where the spin polarization reaches saturation, $s \to 1$.

Phase transition to an AFM state does not occur at $\mathbf{h} \perp \text{OZ}$. Such a field, even at $h_\perp \to 0$, only monotonously polarizes ions while magnetizing the crystal. So, at $\mathbf{h} \perp \text{OZ}$ the ground-state energy has rather a trivial form

$$E_{\text{gr}} = (I - |J|)s^2 + D(1 - \sqrt{1 - s^2}) - 2h_\perp s. \tag{12}$$

It should be also noted that at $\mathbf{h} \perp \text{OZ}$ the spin polarization is always equal to magnetization, which is directed along $\mathbf{h}$, i.e., $m_\perp = s$. Minimization of the energy (12) yields the following equation:

$$\frac{\partial E_{\text{gr}}}{\partial s} = 2(I - |J|)s + D\frac{s}{\sqrt{1 - s^2}} - 2h_\perp = 0, \tag{13}$$

which makes it possible to determine dependence of spin polarization on the transverse field.

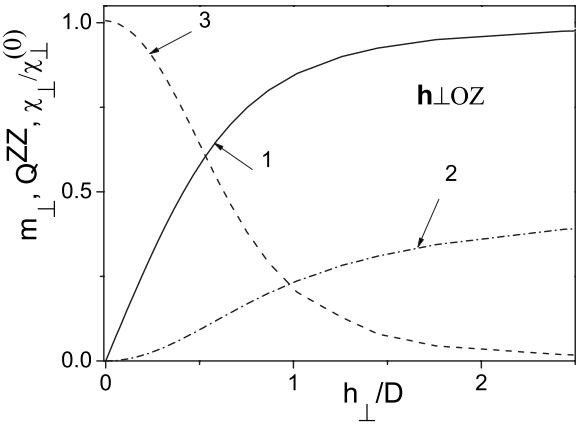

FIG. 2. Field dependencies of $m(h_\perp)$ (curve 1), $Q^{ZZ}(h_\perp)$ (curve 2), and $\chi_\perp$ (curve 3) for $\mathbf{h} \perp \text{OZ}$ and model parameters $|J|/D = 0.05$ and $I=0.3$.

Figure 2 shows the field dependencies of $m_\perp(h_\perp)$, magnetic susceptibility $\chi_\perp(h_\perp) = dm_\perp/dh_\perp$, and components of spin quadrupole moment $Q^{ZZ}(h_\perp)$. The field derivative of magnetization in the transverse field decreases with field growth as can be seen from the behavior of $\chi_\perp(h_\perp)$. Despite the interion exchange interaction, the $\chi_\perp(h_\perp)$ value is typical for the Van Vleck magnets. The only difference arises from the fact that the AFM exchange coupling while decreasing the magnetic susceptibility prevents it from saturation.

Another important conclusion follows from Figs. 1 and 2: Saturation of magnetization in the transverse field occurs at smaller field value than in the longitudinal field. This result completely agrees with the data for DTN where, as reported in Refs. 21–23, the difference was revealed between the saturation fields at their longitudinal and transverse orientations.

III. INDUCED MAGNETOSTRICTION IN THE LONGITUDINAL MAGNETIC FIELD

The peculiarity of the magnetostriction field behavior in the Van Vleck magnets in the course of magnetization was predicted in Ref. 47 where, however, ferromagnetic spin system has been considered. Moreover, description of the induced striction was limited to the vicinity of critical point $h_s: (h_\parallel - h_s)/h_s \ll 1$.

Magnetoelastic contribution to the internal energy, which arises from canting of the sublattices spins, should be taken into account for large field values where this canting is pronounced. Considering the striction properties of VVA, we assume for certainty that a crystal has hexagonal structure. In magnetoelastic energy [see Eq. (1)] we take into account spin-lattice contribution proportional to second power of the average spin[47] and the single-ion terms proportional to the averaged components of spin quadrupole tensor.[48,49] Thus, the elastic and magnetoelastic contributions to the total energy (1) can be written down as follows:

$$E_{\text{el}} = \frac{1}{2}c_{11}(u_{xx}^2 + u_{yy}^2) + \frac{1}{2}c_{33}u_{zz}^2 + c_{12}u_{xx}u_{yy} + c_{13}(u_{xx} + u_{yy})u_{zz} + 2c_{44}(u_{xz}^2 + u_{yz}^2) + 2c_{66}u_{xy}^2, \tag{14}$$

$$E_{\text{m-el}} = \sum_{\alpha\beta} [\lambda_{\alpha\beta} u_{zz} + \gamma_{\alpha\beta}(u_{xx} + u_{yy})]\mathbf{s}_\alpha \mathbf{s}_\beta + \sum_{\alpha} [B_{11}^{(s-i)}(Q_\alpha^{XX} u_{xx} + Q_\alpha^{YY} u_{yy}) + B_{33}^{(s-i)} Q_\alpha^{ZZ} u_{zz} + B_{12}^{(s-i)}(Q_\alpha^{XX} u_{yy} + Q_\alpha^{YY} u_{xx}) + 4B_{44}^{(s-i)}(Q_\alpha^{YZ} u_{yz} + Q_\alpha^{XZ} u_{xz}) + 4B_{66}^{(s-i)} Q_\alpha^{XY} u_{xy}] + \sum_{\alpha\beta} [B_{11}^{(\alpha\beta)}(s_\alpha^X s_\beta^X u_{xx} + s_\alpha^Y s_\beta^Y u_{yy}) + B_{33}^{(2)} s_\alpha^Z s_\beta^Z u_{zz} + B_{12}^{(\alpha\beta)}(s_\alpha^X s_\beta^X u_{yy} + s_\alpha^Y s_\beta^Y u_{xx}) + 4B_{44}^{(\alpha\beta)}(s_\alpha^Y s_\beta^Z u_{yz} + s_\alpha^X s_\beta^Z u_{xz}) + 4B_{66}^{(\alpha\beta)} s_\alpha^X s_\beta^Y u_{xy}], \tag{15}$$

where $\lambda_{\alpha\beta}$ and $\gamma_{\alpha\beta}$ are the parameters of the magnetoelastic exchange coupling, in which indices α and β, as above, are the numbers of the spin sublattices; $B_{jl}^{(s-i)}$ and $B_{jl}^{(\alpha\beta)}$ are the parameters of anisotropic magnetoelastic coupling,[47] where the upper index indicates either the single-ion or interion origin, respectively; u_{ij} are the components of the elastic strain tensor; and c_{jl} are elasticity modula. Note that the constants of the single-ion magnetoelastic coupling in Eq. (15) are written down in crystallographic coordinate systems XYZ, so in contrast to Eq. (5) the indices of spin quadrupole tensor components $Q^{jl} = \frac{1}{2}\langle s^j s^l + s^k s^l \rangle$ are also defined in this system.

Elastic strains resulting from a change in the spin configurations are found by minimizing energies (14) and (15) by corresponding components of strain tensor. This yields the following expressions:

$$u_{xx} + u_{yy} = -\frac{1}{c_{11} + c_{12} - 2c_{13}^2/c_{33}} \left[2\sum_{\alpha\beta} \gamma_{\alpha\beta} \mathbf{s}_\alpha \mathbf{s}_\beta + \sum_{\alpha} (B_{11}^{(s-i)} + B_{12}^{(s-i)})(Q_\alpha^{XX} + Q_\alpha^{YY}) + \sum_{\alpha\beta} (B_{11}^{(\alpha\beta)} + B_{12}^{(\alpha\beta)})(s_\alpha^X s_\beta^X + s_\alpha^Y s_\beta^Y) - \frac{2c_{13}}{c_{33}} \left(\sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{s}_\alpha \mathbf{s}_\beta + \sum_{\alpha} B_{33}^{(s-i)} Q_\alpha^{ZZ} + \sum_{\alpha\beta} B_{33}^{(\alpha\beta)} s_\alpha^Z s_\beta^Z \right) \right], \tag{16}$$

$$u_{xx} - u_{yy} = -\frac{1}{c_{11} - c_{12}} \left[\sum_{\alpha} (B_{11}^{(s-i)} - B_{12}^{(s-i)})(Q_\alpha^{XX} - Q_\alpha^{YY}) + \sum_{\alpha\beta} (B_{11}^{(\alpha\beta)} - B_{12}^{(\alpha\beta)})(s_\alpha^X s_\beta^X - s_\alpha^Y s_\beta^Y) \right], \tag{17}$$

$$u_{zz} = -\frac{(c_{11} + c_{12})}{c_{33}(c_{11} + c_{12}) - 2c_{13}^2} \left[\sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{s}_\alpha \mathbf{s}_\beta + \sum_{\alpha} B_{33}^{(s-i)} Q_\alpha^{ZZ} + \sum_{\alpha\beta} B_{33}^{(\alpha\beta)} s_\alpha^Z s_\beta^Z - \frac{c_{13}}{c_{11} + c_{12}} \left\{ 2\sum_{\alpha\beta} \gamma_{\alpha\beta} \mathbf{s}_\alpha \mathbf{s}_\beta + \sum_{\alpha} [B_{11}^{(s-i)} + B_{12}^{(s-i)}](Q_\alpha^{XX} + Q_\alpha^{YY}) + \sum_{\alpha\beta} [B_{11}^{(\alpha\beta)} + B_{12}^{(\alpha\beta)}](s_\alpha^X s_\beta^X + s_\alpha^Y s_\beta^Y) \right\} \right]. \tag{18}$$

Equation (16) determines the isotropic striction in "easy-plane" or, similarly, its expansion (or contraction, depending on the signs of magnetoelastic constants), while Eq. (18) determines its expansion or contraction along the crystal symmetry axis.

Spontaneous strain in the singlet phase is defined by substituting in Eqs. (16)–(18) the corresponding values $s=0$, $Q^{ZZ}=0$, and $Q^{XX}=Q^{YY}=1$. Hence, in this phase only the isotropic strain in the "easy-plane" and expansion or contraction along axis OZ is nonzero,

$$u_{xx}^{(0)} + u_{yy}^{(0)} = -4\frac{B_{11}^{(s-i)} + B_{12}^{(s-i)}}{c_{11} + c_{12} - 2c_{13}^2/c_{33}}, \tag{19}$$

$$u_{zz}^{(0)} = 4\frac{c_{13}(B_{11}^{(s-i)} + B_{12}^{(s-i)})}{(c_{11} + c_{12})c_{33} - 2c_{13}^2}, \tag{20}$$

where index (0) refers to the spontaneous magnetostriction. It can be seen that in the singlet phase the spontaneous strains are determined only by single-ion magnetoelastic coefficients and that they satisfy the following relations: $u_{xx}^{(0)} = u_{yy}^{(0)} = -u_{zz}^{(0)} c_{33}/2c_{13}$. Expressions (19) and (20) are applicable in the magnetic field as well, while $h_\parallel < h_s$, i.e., in a region of the singlet phase stability. In other words, the value of striction defined by Eqs. (19) and (20) is field independent.

The induced striction is formed only after the spin-polarization occurrence, or in fields $h_\parallel > h_s$,[49] and is de-

scribed by Eqs. (16)–(18). These equations are derived in the general form and include all the phenomenological parameters of magnetoelastic coupling that have both exchange (interionic) and single-ion origin. Below we consider some interesting cases.

First of all, let us consider the magnetostriction caused by isotopic exchange interaction. In most magnets, the corresponding magnetoelastic coupling does not depend on the spin directions and normally exceeds the anisotropic magnetoelastic one by more than an order of magnitude. However, despite the fact that the exchange magnetoelastic coupling does not depend on the spin directions in crystal, it can be easily proved that the striction generated by the external field may be anisotropic. Indeed, assume that only the magnetoelastic coefficients are finite, $\lambda_{12} \neq 0$ and $\gamma_{11} \neq 0$, as well as $c_{13} \to 0$ are finite in Eq. (15). Such situation may take place, for example, in a lamellar crystal. If the magnetic sublattices are formed by spins in the basis planes, the intersublattice AFM exchange depends primarily on interatomic distances along the crystal symmetry axis. As for intrasublattice one, it depends on the interionic distances in this plane. Then, from Eqs. (19) and (20) it follows that in singlet phase all $u_{jj}^{(0)} = 0$ and it is not influenced by the field. When spin polarization becomes finite, the exchange magnetostriction is represented by quite simple expressions

$$\frac{u_{xx}}{u_{xx}^{\text{flip}}} = \frac{u_{yy}}{u_{yy}^{\text{flip}}} = \mathbf{s}^2 = s^2, \tag{21}$$

$$\frac{u_{zz}}{u_{zz}^{\text{flip}}} = \mathbf{s}_1 \mathbf{s}_2 = s^2 \cos 2\theta, \tag{22}$$

where 2θ is, as above, the angle between the sublattice spins and $u_{xx}^{\text{flip}} = u_{yy}^{\text{flip}} = -2\gamma_{11}/(c_{11}+c_{12})$ and $u_{zz}^{\text{flip}} = -2\lambda_{12}/c_{33}$ are the values of the induced striction at $h_{\parallel} = h_{\text{flip}}$. It should be noted that $u_{xx}^{(0)} = u_{yy}^{(0)} = u_{zz}^{(0)} = 0$ for this case as well.

As follows from Eqs. (21) and (22), there are singularities in the striction field dependencies at a point of the phase transition induced by the longitudinal magnetic field at $h_{\parallel} \to h_s$. Derivatives $\partial u_{zz}/\partial h_{\parallel}$ and $\partial u_{xx}/\partial h_{\parallel}$ undergo a jump at this point.

The field behavior of the induced exchange striction defined in Eqs. (21) and (22) is shown in Fig. 3. It can be seen from this figure that in the field $\mathbf{h} \| \text{OZ}$ the exchange striction (it is normalized and, depending on the sign of γ_{11}, can be both positive or negative), which is caused by the intrasublattice interaction, does not change its sign and only "follows" the behavior $s^2(h_{\parallel})$. At the same time, the striction originated from intersublattice exchange (its sign depends on the sign of λ_{12}) is a nonmonotonic function of field for such a field orientation. This fact is a direct and simple consequence of change in $\cos 2\theta$ sign. At first, the spin polarization grows (while field increases above h_s) in such a way that spin vectors in different sublattices are practically antiparallel, so the striction (by absolute value) also increases. However, the further field growth results in a canting of spin vectors. This canting becomes more and more noticeable, causing the decrease in strain down to zero at $\theta = \pi/4$. Then,

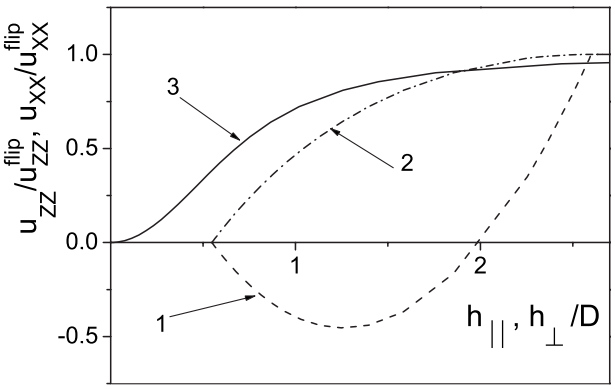

FIG. 3. Exchange striction described by Eqs. (21) and (22) for parameters $|J|/D = 0.05$, $I/D = 0.3$, and $J_Z/D = 1$. Curve 1 corresponds to the "longitudinal" strain $u_{zz}/u_{zz}^{\text{flip}}$ and curve 2 to the "transverse" strain $u_{xx}/u_{xx}^{\text{flip}}$ at $\mathbf{h} \| \text{OZ}$. Curve 3 corresponds to the "longitudinal" strain at $\mathbf{h} \perp \text{OZ}$.

after attaining configuration with $\theta \to 0$ the magnetostriction again increases, reaching a maximum in the field $h_{\parallel} = h_{\text{flip}}$.

According to Eqs. (21) and (22), field dependencies of u_{xx} and u_{zz} will be similar at $\mathbf{h} \perp \text{OZ}$. The induced exchange striction in this field changes smoothly and starts forming from the point $h_{\perp} = 0$. It should be noted that in the region $h_{\perp} \to 0$ the striction is proportional to the $h_{\perp}^2$. Derivatives $\partial u_{zz}/\partial h_{\perp}$ and $\partial u_{xx}/\partial h_{\perp}$ change continuously without jumps. Thus, the main difference in the field dependencies of the induced striction at $\mathbf{h} \| \text{OZ}$ and $\mathbf{h} \perp \text{OZ}$ is that in the longitudinal field there should be a jump in the field derivative of striction behavior versus field, and in the transverse field this derivative changes continuously.

Note that the field dependencies of magnetostriction shown in Fig. 3 are in qualitative agreement with the experimental data obtained for DTN.[22,23] Indeed, in this compound the dominating intersublattice exchange and corresponding magnetoelastic coupling are essential for the chains Ni-Cl-Ni-Cl parallel to the OZ axis. There is no doubt that the intersublattice (AFM) exchange and its anisotropy are the decisive factors in this VVA (along with the single-ion anisotropy), although it is still unclear whether Ni ions lying within the same basis plane belong to the same sublattice (the nearest chains are shifted on the half of a period along axis OZ).

Also, it cannot be excluded that in singlet magnets the anisotropy of the magnetoelastic interaction can be comparable to isotropic one. The anisotropic part of the magnetoelastic coupling may include both exchange (interion) and single-ion parts.[4] Moreover, this really should be the case provided that the magnetic system, such as DTN, possesses strong single-ion anisotropy (which is the evidence of the essential spin-orbital interaction). In DTN described by Hamiltonian (2) the single-ion anisotropy greatly exceeds the exchange coupling. As a result, singlet ground state is formed. So, in this case striction caused by anisotropic interactions may exceed that one originated from isotropic exchange.

Another example illustrative deals with the situation when all the magnetoelastic constants, except for $B_{33}^{(s-i)}$ and $B_{33}^{(\alpha\beta)}$,

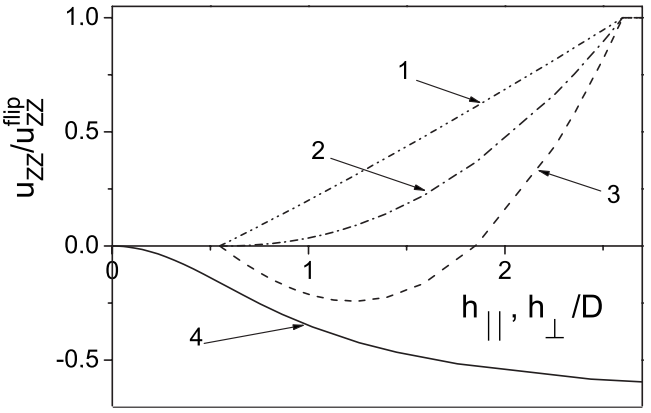

FIG. 4. Longitudinal $u_{zz}/u_{zz}^{\mathrm{flip}}$ magnetostriction versus field. Curve 1 corresponds to $B_{33}^{(s-i)} \neq 0$ and $B_{33}^{(11)}+B_{33}^{(12)}=0$, curve 2 to $B_{33}^{(s-i)}=0$ and $B_{33}^{(11)}+B_{33}^{(12)} \neq 0$, and curve 3 to $(B_{33}^{(11)}+B_{33}^{(12)})/(B_{33}^{(s-i)}+B_{33}^{(11)}+B_{33}^{(12)})=2.5$ and $B_{33}^{(s-i)}/(B_{33}^{(s-i)}+B_{33}^{(11)}+B_{33}^{(12)})=-1.5$ for $\mathbf{h} \| \mathrm{OZ}$. Curve 4 is obtained for the same parameter values as for curve 3 but at $\mathbf{h} \perp \mathrm{OZ}$.

can be neglected. If, in addition, $c_{13} \rightarrow 0$, then the only nontrivial strain component described is deformation of crystal along axis OZ as follows from Eq. (14),

$$u_{zz} = -\frac{2}{c_{33}}[B_{33}^{(s-i)} Q_{\alpha}^{ZZ} + (B_{33}^{(11)} + B_{33}^{(12)})(s \cos \theta)^2]. \quad (23)$$

The expression for striction can be written down in the normalized form

$$\frac{u_{zz}}{u_{zz}^{\mathrm{flip}}} = \frac{B_{33}^{(s-i)} Q_{\alpha}^{ZZ} + (B_{33}^{(11)} + B_{33}^{(12)})(s \cos \theta)^2}{B_{33}^{(s-i)} + B_{33}^{(11)} + B_{33}^{(12)}}, \quad (24)$$

where, according to the definition,

$$u_{zz}^{\mathrm{flip}} = -\frac{2}{c_{33}}(B_{33}^{(s-i)} + B_{33}^{(11)} + B_{33}^{(12)})$$

is the striction at $h_{\|}=h_{\mathrm{flip}}$.

The induced striction derived from Eq. (24) is shown in Fig. 4. The most interesting case is $\mathbf{h} \| \mathrm{OZ}$, where $B_{33}^{(s-i)} \neq 0$ and $B_{33}^{(11)}+B_{33}^{(12)}=0$ (curve 1 in Fig. 4). Here the magnetostriction is directly proportional to quadrupole moment Q^{ZZ}. It should be stressed that the obtained magnetoelastic contribution into the longitudinal deformation (24) depends linearly (but not quadratically, as usual) on magnetization. This can be easily seen from the fact that the quadrupole moment versus field dependence is similar to $m(h_{\|})$ (see Fig. 1). It should be taken into account that at large value of the exchange anisotropy J_Z the magnetization as a function of $h_{\|}-h_s$ changes almost linearly, or $m_{\|} \sim h_{\|}-h_s$. Therefore the magnetostriction (see curve 1 on Fig. 4) also depends almost linearly on field over the entire region of AFM phase stability.

Curve 2 in Fig. 4 corresponds to the field behavior of striction at $\mathbf{h} \| \mathrm{OZ}$ where the latter, because of the choice of numerical values of the parameters, turns out to be proportional to the square of the magnetization. Figure 4 also shows an example (curve 3) of the combined action of both anisotropic mechanisms of the magnetostriction. At these values of the parameters the competition of singe- and two-ion contributions takes place.

In particular, it can be seen from curve 3 on Fig. 4 that the striction caused by the anisotropic magnetoelastic interactions may be similar to that caused by the isotropic exchange (see Fig. 3). However, as follows from Eq. (24), at $\mathbf{h} \| \mathrm{OZ}$ the single-ion and interion contributions in striction can compete, whereas at $\mathbf{h} \perp \mathrm{OZ}$ there is only the single-ion contribution. Curve 4 in Fig. 4 shows striction at $\mathbf{h} \perp \mathrm{OZ}$ at the same values of the parameters, which were used to plot the curve 2. Thus, in the above example of the competition between magnetoelastic interactions of different nature, the longitudinal striction had opposite signs at $\mathbf{h} \| \mathrm{OZ}$ and $\mathbf{h} \perp \mathrm{OZ}$.

In DTN the components of the longitudinal striction tensor at $\mathbf{h} \| \mathrm{OZ}$ and $\mathbf{h} \perp \mathrm{OZ}$ have the same sign and almost equal values.[22] Therefore, it is highly probable that the induced longitudinal striction in this material is caused by the intersublattice isotropic exchange coupling. Nevertheless, it is necessary to make additional measurements to prove that the observed strain is really caused only by the interplane (intersublattice in DTN) exchange interaction and is not a consequence of several field contributions including the spin quadrupole moment. Also, it would be interesting to check experimentally whether the striction in the basis plane is anisotropic [see Eq. (17)] or not. To make corresponding experiment, one needs to create an AFM state, at first introducing the field $h_{\|}$ and then additionally applying the field $h_{\perp}$, which will cause the spins canting. Such an experiment can determine the dominating (single-ion or two-ion) contribution in the anisotropic striction within the basis plane.

IV. CONCLUSION

Using thermodynamic Landau approach we show that the net magnetization linearly depends on the field value in the antiferromagnetic phase induced by the longitudinal magnetic field (in the vicinity of the critical point). Such a dependence results from the spontaneous appearance of spin polarization parallel to "easy-plane." The crucial symmetrical condition for the phase transition is degeneracy of the directions of sublattice magnetizations in the "easy-plane." Striction gives rise to spontaneous lowering of the plane symmetry.

It is also shown that in the induced AFM phase the spin polarization (magnetization) of the sublattice continuously varies with magnetic field from zero up to a maximum value at the spin-flip point. In contrast to classical Néel AFM, in the magnetic phase of VVA the value of the sublattice magnetization strongly depends on the field. An angle that defines deviation of sublattice magnetization from the field direction shows the same field dependence. At the same time, the net magnetization weekly depends on the field and shows almost the linear field dependence.

The AFM phase does not form in the transverse field. Hence, the saturation field at $\mathbf{h} \perp \mathrm{OZ}$ is lower than the saturation field at $\mathbf{h} \| \mathrm{OZ}$.

The calculations show that in AFM the induced magnetostriction appears only in the magnetic phase. This magneto-

striction in low fields is related to the spontaneous formation of sublattice magnetizations. In high fields (corresponding to spin-flip field) the magnetostriction is determined primarily by the rotation of sublattice magnetizations.

There are two important points here that we want to emphasize. The first is the possibility of the induced striction resulting from the intrasublattice magnetoelastic interaction. In classical AFMs, this part of the induced magnetostriction is usually neglected because of smallness of the paraprocess. The second aspect is related to the single-ion striction. The value of which is directly proportional to the spin quadrupole moment; as a result, this part of striction shows almost linear dependence on the field.

Finally, it is necessary to make a methodical remark. The above results were obtained in an approximation of self-consistent field. It was assumed that more accurate calculations would not give any qualitative results. However, they might have a quantitative effect. Moreover, magnetoelastic energy was written down in the phenomenological form and it comprises many parameters. So, when analyzing different contributions it is necessary to take into account hierarchy of interactions in the magnetoelastic energy as what was done, for example, above. Quantitative comparison between the above calculations and available experimental data will be published elsewhere.

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