PHYSICAL REVIEW B, VOLUME 64, 174403

Magnetic ordering in the mixed-valence compound β-$Na_{0.33}V_2O_5$

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(Received 15 December 2000; published 1 October 2001)

The low-temperature electron spin resonance (ESR) spectra and the static magnetization data obtained for the stoichiometric single crystals of β-$Na_{0.33}V_2O_5$ indicate that this quasi-one-dimensional mixed-valence compound demonstrates at $T_N = 22$ K the phase transition into the canted antiferromagnetically ordered state. The spontaneous magnetization of 3.4×10^{-3} μ_B per V^{4+} ion was found to be oriented along the twofold b axis of the monoclinic structure, the vector of antiferromagnetism is aligned with the a axis and the Dzyaloshinsky vector is parallel to the c axis. The experimental data were successfully described in the frame of the macroscopic spin dynamics and the following values for the macroscopic parameters of the spin system were obtained: the Dzyaloshinsky field $H_D = 6$ kOe and the energy gaps of two branches of the spin wave spectrum $\Delta_1/(2\pi) = 48$ GHz and $\Delta_2/(2\pi) = 24$ GHz.

DOI: 10.1103/PhysRevB.64.174403 PACS number(s): 76.50.+g, 75.50.Ee, 75.25.+z

I. INTRODUCTION

The quasi-one-dimensional mixed-valence compound β-$Na_{0.33}V_2O_5$ exhibits various phase transitions of a considerable interest.[1–3] Below 230 K the $1\times2\times1$ crystal lattice superstructure appears, indicating probably the ordering of Na ions. At $T_c = 136$ K this one-dimensional conductor exhibits a metal-insulator phase transition of a charge ordering type and at $T = T_N = 22$ K the charge-ordered structure undergoes an antiferromagnetic phase transition.

This behavior is to be compared with that of the quasi-one-dimensional magnet α-NaV_2O_5 in which the lattice, charge and spin subsystems transform simultaneously. The charge ordering in this related system causes the opening of the spin gap in the spectrum of magnetic excitations and the appearance of a nonmagnetic singlet state.[4–6]

The β-$Na_{0.33}V_2O_5$ has the monoclinic structure $C2/m$ (see Fig. 1) with the unit cell containing two NaV_6O_{15} formula units. The sodium ions are located in the tunnels formed by a V-O framework. The Na^+ ions occupy only one of the two nearest-neighboring sites A in the a-c plane. The V-O framework consists of the three distinct kinds of double chains directed along the b axis.[7,8] The V1-sites have a sixfold octahedral coordination and form a zigzag chain of edge-sharing VO_6 octahedra. The V2 sites with a similar octahedral coordination form a two-leg ladder chain of corner-sharing VO_6 octahedra, and the V3 sites, having a fivefold square pyramidal coordination form a zigzag chain of edge-sharing VO_5 pyramids.

The absence of the Knight shift in NMR experiments on ^{23}Na nuclei[9] shows that the outer s-shell electrons of the Na-ions are transferred into the d-shells of V ions. Therefore, the V ions are in the mixed valence states V^{4+} and V^{5+}. The V^{4+} ions are in a magnetic $S=\frac{1}{2}$ state, while the V^{5+} ions with $S=0$ are nonmagnetic. Basing on interatomic distances[10] and on NMR measurements[11,12] it was concluded that in the high temperature phase $T > T_c$ the donated electrons are situated at the V1 sites, with one half of these sites being V^{4+}. The recent NMR experiments on V ions[13] confirm the charge ordering nature of the transition at $T = T_c$ and reveal that the number of inequivalent V positions below T_c is increased. Two possible models of the charge ordering (zigzag and linear chains of V^{4+} ions) are proposed but the exact crystal structure in a low temperature phase is still unknown.

Hypothetical models of the magnetic structure with the localized electrons suggest that only one-sixth part of the V ions has the magnetic moments and the magnetic subsystem of β-$Na_{0.33}V_2O_5$ appears to be strongly diluted. Nevertheless, the transition to the long-range magnetically ordered state occurs at an appreciably high temperature $T_N = 22$ K. The aim of the present work was to study in details the magnetic ordering in β-$Na_{0.33}V_2O_5$ by means of magnetic resonance and static magnetization measurements.

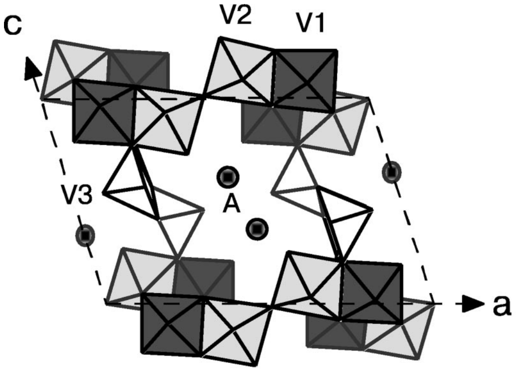

FIG. 1. The crystal structure of β-$Na_{0.33}V_2O_5$.

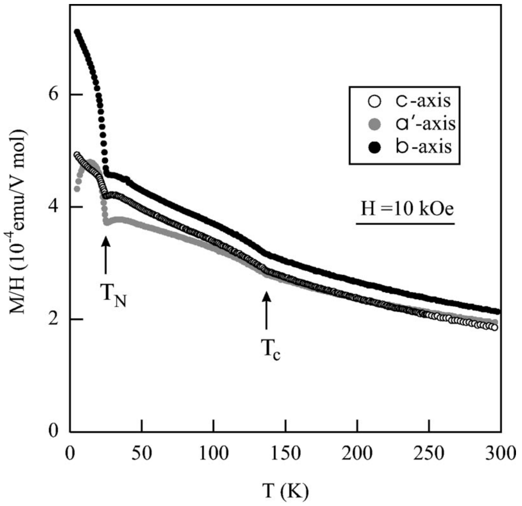

FIG. 2. The temperature dependences of the susceptibility M/H for three principal orientations of the magnetic field.

II. EXPERIMENTAL

The single crystals of a stoichiometric β-$Na_{0.33}V_2O_5$ were grown by a self-flux technique using NaV_3O_8 as a flux. The crystals of a typical size $5\times0.5\times0.2$ mm^3 were obtained by melting the mixture of one part of $Na_{0.33}V_2O_5$ powder and thirty parts (weight ratio) of NaV_3O_8 powder. The melting at 740 °C and cooling down to 600 °C with a rate of 0.5 °C/h were performed in a vacuum. The flux was removed by diluted hydrochloric acid. The longest dimension of the rectangular sample was aligned with the b axis, the middle dimension was aligned with the c axis, and the shortest dimension, denoted below as a' was perpendicular to the b-c plane. The crystallographic a axis is directed at an angle of 18° with respect to a' axis in the a'-c plane. The static magnetization measurements were done by the Quantum Design SQUID magnetometer. The magnetic resonance measurements in the frequency range 18–80 GHz were performed by the transmission type microwave spectrometer. The sample was put into the rectangular resonator having a set of eigen-frequencies in this range.

The temperature dependences of the magnetization of β-$Na_{0.33}V_2O_5$ sample measured along the a', b, and c axes at the magnetic field $H=10$ kOe are shown in Fig. 2. The change of the slope on these curves at $T_c=136$ K marks the metal-insulator transition associated with the charge redistribution between the vanadium sites. The sharp increase in magnetization is observed at $T=T_N$.

The field dependences of magnetization measured along the a', b, and c axes at $T=5$ K are shown in Fig. 3. The asymptotically linear behavior of the $M(H)$ dependences indicate the existence of the antiferromagnetic ordering. The residual magnetization $M(H=0)$ for $\mathbf{H}\|b$ [as well as the anisotropic anomaly on $M(T)$ curves at $T=T_N$] are the evidence of a canting of the antiferromagnetic sublattices. The nonlinear part of the $M(H)$ curve at $\mathbf{H}\|a'$ should result from a spin-reorientation process. The extrapolation of $M(H)$ to $H=0$ at $\mathbf{H}\|b$ gives a finite value of the spontaneous magnetization with a weak ferromagnetic moment of about 3×10^{-3} μ_B per V^{4+} ion.

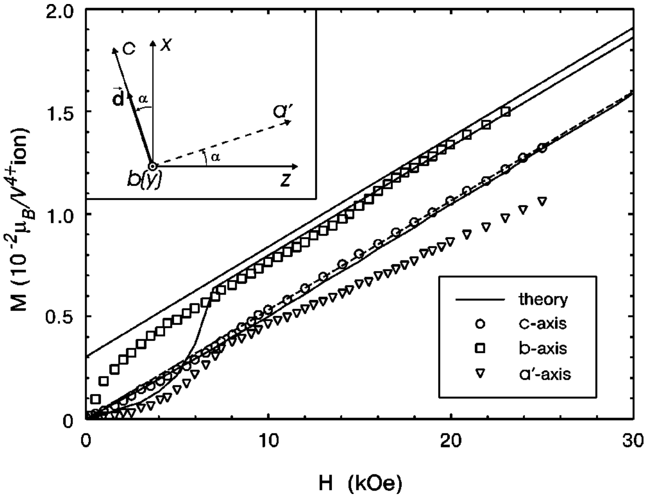

FIG. 3. The magnetization curves at $T=5$ K. Inset: The orientation of the Dzyaloshinsky vector **d**, hard, middle and easy axes (see the text) with respect to crystallographic axes.

The ESR absorption lines of β-$Na_{0.33}V_2O_5$ obtained as the field dependences of the signal transmitted through the resonator with the sample at various temperatures are shown in Fig. 4. In the paramagnetic state (at $T>T_N$) the ESR line is observed at a slightly larger field than the DPPH reference ($g=2.0$). Below T_N the ESR line rapidly shifts to lower magnetic fields.

The evolution of the ESR absorption with the frequency at $T=4.2$ K is illustrated in Fig. 5. Up to four resonant lines marked by letters A, B, C, D were present in the absorption at different frequencies and sample orientations. The C and D lines disappear above 10 K and could not be ascribed to the ordered state, while the A and B lines exist in the whole

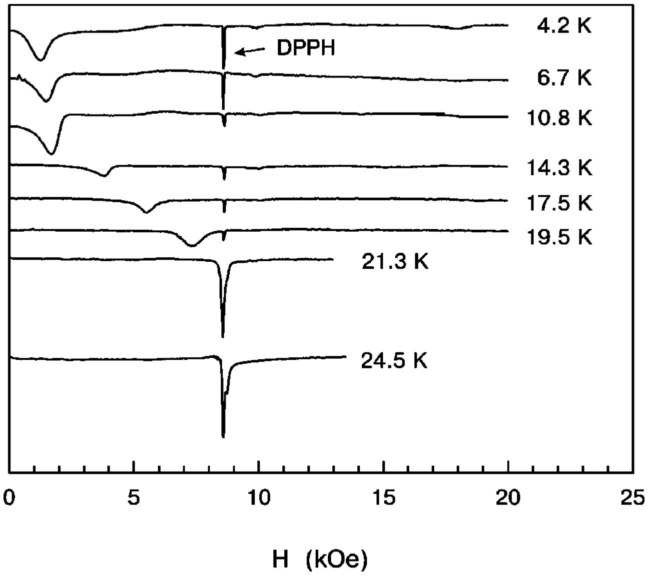

FIG. 4. The temperature evolution of the ESR absorption line measured at the frequency $f=24$ GHz ($\mathbf{H}\|b$).

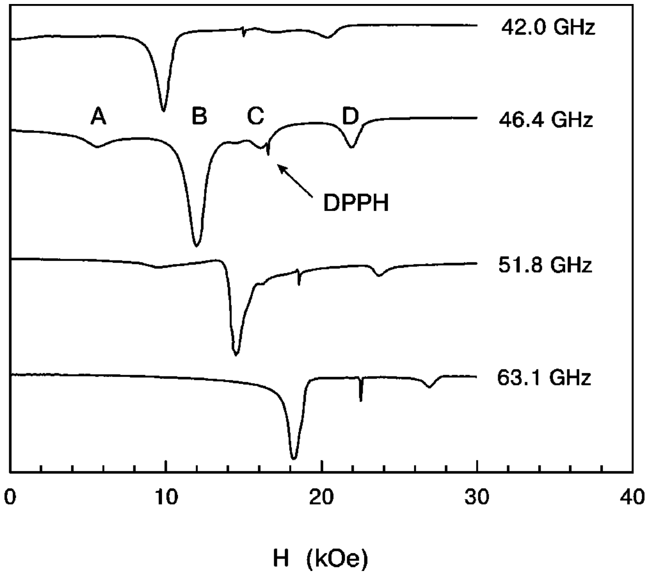

FIG. 5. The ESR lines at different frequencies at $T=4.2$ K ($\mathbf{H}\|b$).

temperature range below T_N and thus, should be of an antiferromagnetic type.

The magnetic resonance data at $T=4.2$ K are summarized in Figs. 6(a)–6(c), in which the frequencies of the resonant lines are plotted vs magnetic field oriented along the a', b, and c axes, respectively. The spectrum of the magnetic resonance in the ordered phase appears to be highly anisotropic. It consists of two branches with the gaps of 48 and 24 GHz. The falling branch of the magnetic resonance spectrum at $\mathbf{H}\|a'$ and the drop to zero of its resonance frequency at $H=6$ kOe clearly indicate the spin-reorientation process ended by a phase transition of the second kind. The characteristic feature of the field dependences of the resonance frequencies at $\mathbf{H}\|a'$ and $\mathbf{H}\|b$ is the nonzero slope of both branches. The smaller of these slopes reveals the existence of canting of sublattices.

III. DISCUSSION

The general form of the antiferromagnetic resonance spectra and the magnetization curves prove the appearance of the canted antiferromagnetic state in β-$Na_{0.33}V_2O_5$ below $T<T_N$. The detailed analysis given below will allow us to obtain its macroscopic parameters.

Using the phenomenological approach[14] we calculated the field dependences of the static magnetization and the resonance spectra of a canted antiferromagnet with two axes of anisotropy for the various orientations of the magnetic field. This macroscopic approach is based on the classical Lagrange formalism and is the most adequate for calculating the resonance frequencies of low lying acoustic modes in spin systems. It allows one to obtain analytical results for complicated magnetic systems (see, e.g., Refs. 15–17). The correspondence between the phenomenological parameters of the theory and the coefficients of the modeling spin Hamiltonian may be found in the molecular field approximation.[18]

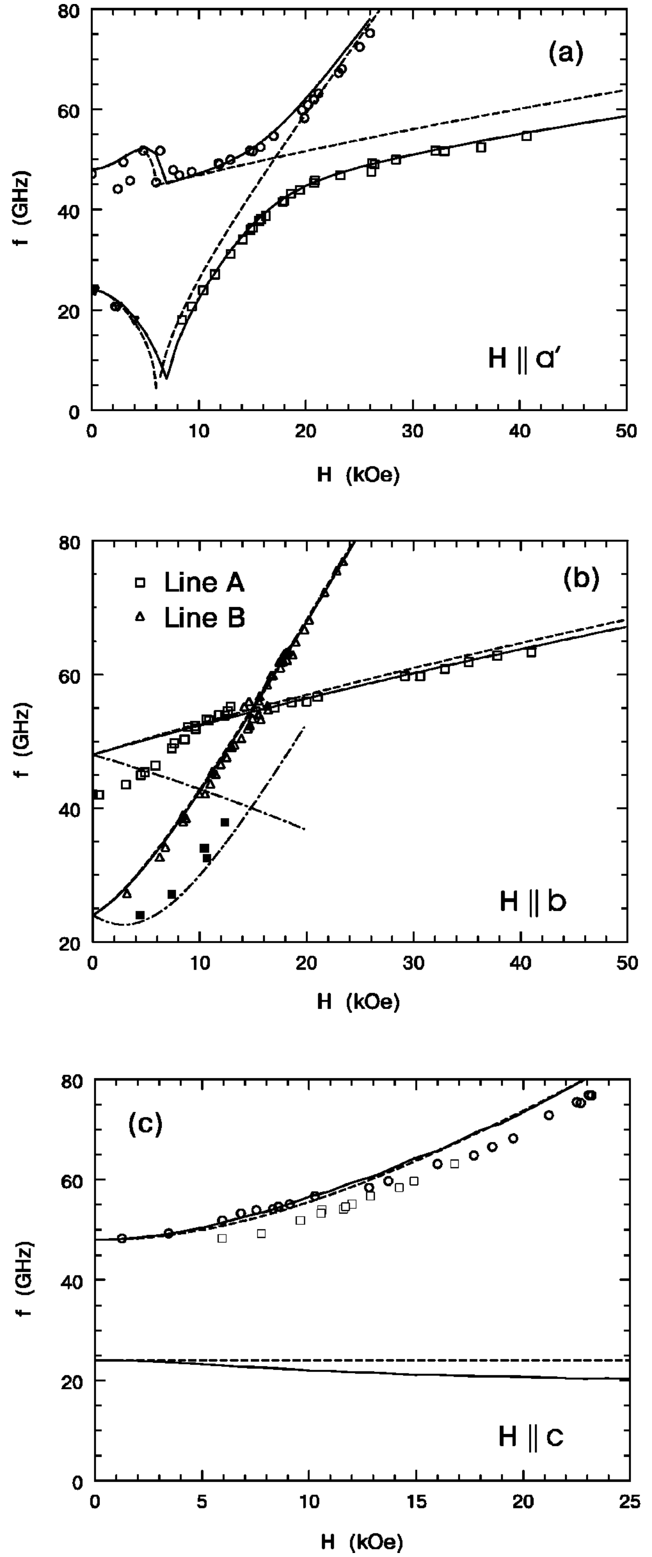

FIG. 6. The ESR spectra for three orientations of the magnetic field at $T=4.2$ K. Symbols are the experimental data (closed ones on the panel b represent the low intensity absorption ascribed to "negative" domains). The dashed lines are drawn by formulas (7)–(10) with $\Delta_1/(2\pi)=48$ GHz, $\Delta_2/(2\pi)=24$ GHz and $H_D=6$ kOe; solid lines are the result of theoretical calculations (see text) for "positive" domains, dashed-dotted lines are those for "negative" domains.

According to this approach the antiferromagnetic structure is considered to be collinear in the exchange approximation, while the canting of sublattices and the anisotropy (both resulting from relativistic spin-orbital and magnetic dipole-dipole interactions) are taken into account as perturbations. At low temperature the Lagrange function of a mole of such an antiferromagnet may be represented in the form

$$\mathcal{L}=\frac{\chi_{\perp}}{2\gamma^{2}}(\dot{\mathbf{l}}-\gamma\mathbf{l}\times\mathbf{H})^{2}-\frac{\chi_{\perp}}{\gamma}\mathbf{d}\cdot(\dot{\mathbf{l}}-\gamma\mathbf{l}\times\mathbf{H})-U_{a}, \qquad (1)$$

where $\mathbf{l}$ is the unit vector along the usual antiferromagnetic vector, $\chi_{\perp}$ is the antiferromagnetic perpendicular susceptibility (note, that the magnetic susceptibility parallel to the vector $\mathbf{l}$ vanishes at low temperatures in the exchange approximation,[14] see also Ref. 19), γ is the magnetomechanical ratio (suggested to be equal to that of a magnetic V ion $\gamma=g\mu_{B}/\hbar$), $\mathbf{d}$ is the Dzyaloshinsky vector giving rise to the spontaneous magnetization $\mathbf{M}_{sp}=\chi_{\perp}\mathbf{d}\times\mathbf{l}$, the vector $\mathbf{d}$ defines the direction of the spontaneous magnetization of an antiferromagnet with the weak ferromagnetism to be perpendicular to both vectors $\mathbf{l}$ and $\mathbf{d}$ and determines the canting angle of sublattices, the absolute value of vector $\mathbf{d}$ is equal to the value of Dzyaloshinsky field. U_{a} is the potential energy of the anisotropy taken as the quadratic form in the vector $\mathbf{l}$ components

$$U_{a}=\frac{\beta_{1}}{2}(\mathbf{x}\cdot\mathbf{l})^{2}+\frac{\beta_{2}}{2}(\mathbf{y}\cdot\mathbf{l})^{2}, \qquad (2)$$

where β_{1},β_{2} are positive constants of anisotropy, unit vectors $\mathbf{x}$ and $\mathbf{y}$ determine two orthogonal directions in the crystal. One of these two directions (corresponding to the largest coefficient β_{i}) should be the hard direction for the spin structure, the other one should be the middle direction, the third orthogonal unit vector $\mathbf{z}$ will be an easy axis (the direction of the vector $\mathbf{l}$ at $\mathbf{H}=0$). The orientation of vectors $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$, and $\mathbf{d}$ with respect to the crystal axes *a*, *b*, and *c* is *a priori* not known, except for the condition that one of the vectors $\mathbf{x}$, $\mathbf{y}$, or $\mathbf{z}$ should be parallel to the twofold axis *b*.

The total static magnetization of this system is

$$\mathbf{M}=\frac{\partial\mathcal{L}}{\partial\mathbf{H}}=\chi_{\perp}[\mathbf{H}-\mathbf{l}(\mathbf{l}\cdot\mathbf{H})+\mathbf{d}\times\mathbf{l}]. \qquad (3)$$

The equilibrium value of the vector $\mathbf{l}$ is determined by minimizing the potential energy of the system $\mathcal{P}=-\mathcal{L}(\dot{\mathbf{l}}=0)$. The magnetic moment $M(H)$ measured in the experiment is the projection of $\mathbf{M}$ onto $\mathbf{H}$.

The crystal symmetry requires the spontaneous moment $\mathbf{M}_{sp}$ to be either parallel or perpendicular to the twofold *b* axis. The static magnetization measurements confirm the first orientation. At the same time the extrapolation of $M(H)$ at $\mathbf{H}\|c$ to $H=0$ gives no net magnetic moment. In accordance with formula (3) it means that the vector product $\mathbf{d}\times\mathbf{l}$ should be perpendicular to $\mathbf{H}$ in high fields. The only possibility to satisfy this condition is to align vector $\mathbf{d}$ with the *c* axis.

The easy direction $\mathbf{z}$ of a canted antiferromagnet should be perpendicular to $\mathbf{M}_{sp}$ and hence, lie in the *a*-*c* plane. Thus, either $\mathbf{x}$ or $\mathbf{y}$ should be parallel to the *b* axis. Taking this orientation for vector $\mathbf{y}$, we have also the vector $\mathbf{x}$ in the *a*-*c* plane. We shall denote the angle between the vectors $\mathbf{d}$ and $\mathbf{x}$ as α (see the inset to Fig. 3). This angle is not determined by the monoclinic symmetry and in principle may be arbitrary.

To describe the dynamical properties of the system one should find the variation of the Lagrange function (1) by $\mathbf{l}$:

$$\delta\mathcal{L}=\left(\frac{\partial\mathcal{L}}{\partial\mathbf{l}}-\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{\mathbf{l}}}\right)\delta\mathbf{l}. \qquad (4)$$

Taking $\delta\mathbf{l}=\delta\theta\times\mathbf{l}$, where $\delta\theta$ is the vector of a small rotation, we obtain the following system of nonlinear equations:

$$\mathbf{l}\times\{-\ddot{\mathbf{l}}+2\gamma\dot{\mathbf{l}}\times\mathbf{H}+\gamma^{2}[\mathbf{H}\times(\mathbf{l}\times\mathbf{H})]+\gamma^{2}\mathbf{H}\times\mathbf{d}-\Delta_{1}^{2}\mathbf{x}(\mathbf{x}\cdot\mathbf{l})$$
$$-\Delta_{2}^{2}\mathbf{y}(\mathbf{y}\cdot\mathbf{l})\}=0, \qquad (5)$$

where $\Delta_{1,2}^{2}=\gamma^{2}(\beta_{1,2}/\chi_{\perp})$ are two independent phenomenological parameters corresponding to two energy gaps of the spectrum. The linearized equations obtained from Eq. (5) by expanding $\mathbf{l}$ in the vicinity of equilibrium give the resonance spectrum of the system. The magnetic moment of a unit volume is much smaller than the magnetic field, therefore the demagnetization effects are negligible and will not be considered in the further analysis.

When the vectors $\mathbf{d}$ and $\mathbf{z}$ are mutually perpendicular, i.e., at $\alpha=0$ the resonant frequencies may be presented by simple analytic expressions for three basic orientations of the magnetic field.

(1) $\mathbf{H}\|\mathbf{z}$: in this case the spin reorientation occurs under magnetic field. It is the continuous rotation of the vector $\mathbf{l}$ in the plane containing easy and middle axes. Two intervals of the magnetic field should be considered separately.

(a) $H<H_{c}$: the equilibrium angle ψ between $\mathbf{l}$ and $\mathbf{z}$ is determined by the condition

$$\sin\psi=\frac{H_{D}H}{\Delta_{j}^{2}/\gamma^{2}-H^{2}}, \qquad (6)$$

where $H_{D}=|\mathbf{d}|$, Δ_{j} is the smaller of the constants $\Delta_{1,2}$. The rotation terminates at $H=H_{c}$ determined by the relation $\sin\psi=1$, when $\mathbf{l}$ becomes perpendicular to $\mathbf{H}$.

The resonance frequencies ω_{1} and ω_{2} are the roots of the biquadratic equation

$$(\omega^{2}+A)(\omega^{2}+B)-4\gamma^{2}H^{2}\cos^{2}\psi\omega^{2}=0, \qquad (7)$$

where $A=\gamma^{2}(H^{2}\cos^{2}\psi+H_{D}H\sin\psi)-\Delta_{i}^{2}+\Delta_{j}^{2}\sin^{2}\psi$, $B=(\gamma^{2}H^{2}\Delta_{j}^{2})\cos2\psi+\gamma^{2}H_{D}H\sin\psi$, Δ_{i} is the largest of $\Delta_{1,2}$.

(b) $H>H_{c}$:

$$\omega_{1}^{2}=\Delta_{i}^{2}-\Delta_{j}^{2}+\gamma^{2}HH_{D}, \qquad \omega_{2}^{2}=\gamma^{2}H(H+H_{D})-\Delta_{j}^{2}. \qquad (8)$$

(2) $\mathbf{H}\|\mathbf{x}$:

$$\omega_{1}^{2}=\gamma^{2}H^{2}+\Delta_{1}^{2}, \qquad \omega_{2}=\Delta_{2}^{2}. \qquad (9)$$

(3) $\mathbf{H}\|\mathbf{y}$:

$$\omega_1^2 = \Delta_1^2 \pm \gamma^2 H H_D, \qquad \omega_2^2 = \Delta_2^2 \pm \gamma^2 H (H + H_D). \quad (10)$$

The signs ± correspond to the domains of positive and negative directions of the spontaneous magnetization with respect to the magnetic field. On increasing the field the negative domain disappears and the corresponding resonance line disappears too according to our observations.

The resonance frequencies calculated by formulas (7)–(10) are represented in Figs. 6(a)–6(c) by dashed lines. For an arbitrary value of α ($\alpha \neq 0$) the equilibrium orientation of **l** in magnetic field was found numerically (for three orientations $\mathbf{H} \| a'$, b, c) and then substituted to the expression for the magnetization and to the appropriate linearized equations of motion.

Finding the antiferromagnetic susceptibility $\chi_\perp \approx 3.2 \times 10^{-3}$ emu/mol V^{4+} from the slope of $M(H)$ curve at $\mathbf{H} \| c$ and varying the other four parameters α, H_D, Δ_1, and Δ_2 one can fit the magnetization curves and the resonance spectra for all three orientations. The best fit to experimental data was obtained for $\alpha = 18°$, $\Delta_1/(2\pi) = 48$ GHz, $\Delta_2/(2\pi) = 24$ GHz, and $H_D = 6$ kOe. The values of energy gaps Δ_1, Δ_2 correspond to anisotropy constants $\beta_1 = 1.1 \times 10^{-2}$ K per V^{4+} ion and $\beta_2 = 2.7 \times 10^{-3}$ K per V^{4+} ion. The results of this fitting are shown in Figs. 3 and 6 by solid lines. The determined value of $\alpha = 18°$ means that the easy direction of the spin system **z** is near the crystallographic axis *a*. It should be noted that the resonance spectrum at $H \| a'$ is very sensitive to the value of α due to the effect of dynamic repulsion between two antiferromagnetic resonance branches.[20] The intersection of the two branches may be observed at the exact orientation of the field along the z or y directions [it was observed at $\mathbf{H} \| \mathbf{y}$, see Fig. 6(b)]. The "repulsion" is clearly seen in Fig. 6(a) at $\mathbf{H} \| a'$ when the magnetic field appeared to be tilted with respect to z. The relation $\Delta_1 > \Delta_2$ indicates that **x** is the hard axis and **y** is the middle axis of the ordered spin structure. The mismatch between the observed and calculated resonance frequencies for the first branch in low fields at $\mathbf{H} \| b$ remains unclear. This deviation may probably be associated with the coupling of the antiferromagnetic resonance mode with some impurity mode. As described in Sec. II several modes which cannot be attributed to the antiferromagnetic matrix are observed in our sample (see Fig. 5).

The magnetization is also described satisfactorily for $\mathbf{H} \| c$ and for $\mathbf{H} \| b$ (except for the small low field region associated with the poling). The agreement for the third orientation $\mathbf{H} \| a'$ appears to be only qualitative, but still covers the most remarkable feature—the low field nonlinear part (mentioned in Sec. II) appearing due to the process of the continuous spin reorientation.

The above approach to the description of the uniform magnetic properties of a spin system is self-consistent and does not require any suggestions except that the exchange structure of the system is not strongly distorted by relativistic interactions. To evaluate the exchange integral from our data we will for simplicity neglect for the effect of zero point fluctuations[18] on the susceptibility of quasi-one-dimensional system. In the molecular field approximation one can obtain the intrachain exchange integral $J = (g\mu_B)^2 N_A/(4k_B\chi_\perp) \simeq 120$ K which corresponds to the molecular field $H_e = 1700$ kOe. The approximate evaluation for the Neel temperature of a quasi-one-dimensional antiferromagnet $T_N \sim \sqrt{JJ_\perp}$ gives the value for the interchain exchange interaction $J_\perp \sim 1$ K.

For anisotropy fields H_{A1} and H_{A2} corresponding to the values $\beta_{1,2}$ we have the following estimations: $H_{A1} = 340$ Oe, $H_{A2} = 85$ Oe. From the value of Dzyaloshinsky field $H_D = 6$ kOe we obtain that the spontaneous magnetization $M_{sp} = \chi_\perp H_D = 3.4 \times 10^{-3}$ μ_B per V^{4+} ion which is in qualitative agreement with the data of Ref. 2.

IV. CONCLUSIONS

The magnetic resonance spectra and the magnetization curves obtained at low temperatures in the mixed valence charge ordered quasi-one-dimensional compound β-$Na_{0.33}V_2O_5$ confirm the transition into the canted antiferromagnetic state. The easy direction of the spin system and the vector of the spontaneous magnetization are found to be aligned with the *a* axis and *b* axis correspondingly. The Dzyaloshinsky vector was found to be directed along *c* axis. The hard axis of the spin structure lies in the *a*-*c* plane at an angle of 18° with respect to *c* axis, direction *b* is the middle axis of the spin anisotropy. The values of the intrachain and interchain exchange integrals as well as the anisotropy fields and the Dzyaloshinsky field are obtained.

ACKNOWLEDGMENTS

Authors thank H. Nojiri for cooperation in static magnetization measurements, L. A. Prozorova and V. D. Buchelnikov for valuable discussions. This work was supported by the Russian Fund for Basic Researches Grants Nos. 00-02-17317 and 99-02-17828, INTAS Grant No. 99-0155, NWO Grant No. 047-008-012, and CRDF Grant No. RP1-2097.

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