# Orientational phase transition and the intermediate state of the monoclinic antiferromagnet $NiWO_4$ in a longitudinal external field

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Magnetic anomalies in a sublattice-flipping transition in antiferromagnetic $NiWO_4$ sublattices are considered. Investigation methods previously developed for uniaxial antiferromagnets [Sov. Phys. JETP **34**, 362 (1972)] are extended to include the more general and more complicated case of an antiferromagnet with low symmetry. A method is proposed for exactly determining the direction of the spontaneous-ordering axis in a monoclinic crystal. It is shown that in an external magnetic field inclined along a definite plane the sublattice-flipping transition is described by the thermodynamic potential characteristic of the uniaxial antiferromagnet. Its constants are determined. It is shown that the phase transition is of first order. The phase diagram in an oblique magnetic field is reconstructed. Critical points that are magnetic analogs of the liquid-vapor critical points are observed. The existence, in a critical field, of an equilibrium domain structure analogous to the structure previously investigated in uniaxial crystals, is proved.

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## 1. INTRODUCTION

Orientational transitions in antiferromagnets can be induced by an external magnetic field applied along the magnetic-ordering axis. At a certain critical value of this field, a relatively abrupt change of the orientation of the antiferromagnet is observed and is accompanied by an increase of the magnetization. The present paper is devoted to an investigation of the magnetic anomalies accompanying such a transition in antiferromagnetic $NiWO_4$.

The nickel tungstate lattice has monoclinic symmetry. It is customary to separate in it the twofold-axis direction $b$, and also the directions $a$ and $c$, which lie in a symmetry plane perpendicular to the $b$ axis. Neutron-diffraction measurements have shown that $NiWO_4$ is at low temperatures a two-sublattice antiferromagnet. The Néel temperature is 67 K.[2] From the results of the measurements of the magnetic susceptibility[3] it became possible to determine the effective exchange field $H_E = 600$ kOe, and also the direction of the magnetic-ordering axis $z$, which lies in the $ac$ symmetry plane and makes an angle of approximately 15° with the $c$ axis. Observations of antiferromagnetic resonance[4] in the far infrared have made it possible to calculate the anisotropy energy of this antiferromagnet, $H_{A1} \approx 30$ kOe, and to estimate the critical field of sublattice flipping transition $H_c \approx 180$ kOe. An optical manifestation of this transition was soon observed in the light absorption spectrum.[5] Measurements of the anomalies of the magnetic properties of the flipping transition in $NiWO_4$ were first briefly reported in Ref. 6. Interest in their detailed investigation, which has led to the writing of this paper, is due to the following circumstances.

Orientational transitions in monoclinic antiferromagnets have been little investigated. These transitions are simplest to describe in the case when the external magnetic field is directed strictly along the spontaneous magnetization axis of the antiferromagnet.[7] In a field oriented at an angle to this axis, the picture of the transition becomes more complicated. For uniaxial antiferromagnets, however, when the result does not depend on the azimuthal angle of inclination of the external field to the axis, the orientational transition problem has been solved.[8,9]

In biaxial antiferromagnets, the character of the orientational transition depends substantially on the direction in which the external magnetic field is inclined to the antiferromagnetism axis. In the case of an arbitrary azimuthal inclination angle, the picture of the orientational transition is confused, and the interpretation of the experimental data is difficult. Only at two values of the azimuthal angle is a description by relatively simple mathematical means still possible.[10] These are the so called easy and difficult directions. It is precisely experiments in these two cases that can hopefully permit an interpretation of the measurement results.

The experimental problem of studying orientational transitions in monoclinic antiferromagnets, such as the investigated crystal, is even more complicated. The point is that the antiferromagnetism axis in these crystals is not connected with any particular crystallographic direction. Worse even, the direction of this axis can be altered by external conditions, for example with changing temperature. Therefore the required control of the angle between the external field and the magnetic-order axis becomes possible only after first determining the direction of this axis, and the accuracy of this determination will be shown to be quite high.

The first step in the study of orientational transitions in monoclinic antiferromagnets should be to produce conditions under which their behavior is relatively simple to interpret. Such conditions are the determination of the direction of the antiferromagnetism axis and the turning on of the magnetic field in the "light" plane. In this case, according to general considerations and in

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agreement with the exact theory,[10] the trajectory of the motion of the magnetization vector in an external field should be planar and should not differ in any way from the trajectory of the motion in a uniaxial antiferromagnet.

Orientational transitions can have different degrees of smearing with respect to the magnetic field, i.e., the principal changes in the angle of the orientation of the antiferromagnetism vector occur in different intervals of external magnetic fields. In the general case of an arbitrary inclination angle $\psi$ of the external field **H** to the spontaneous-ordering axis, this interval is most frequently not rigorously defined, i.e., the orientation transition takes place smoothly, without any singularities. Only in the case of fully defined angles $\psi$ can one expect the appearance of phase transitions of first or second order. The results of the existing experimental studies of $NiWO_4$ are not peculiar to any of these cases and admit of either interpretation. The detection of the phase transitions and the identification of their type is likewise a task undertaken in this paper.

In all cases when the orientational transitions occur jumpwise, i.e., a first-order phase transition takes place, it is accompanied by an interesting phenomenon. A sample of finite dimensions breaks up in the vicinity of the phase transition into domains—alternating regions of coexisting phases. The sample is then in a thermodynamically stable state, which has been called the intermediate state. This state was observed, in particular, in the uniaxial antiferromagnet $MnF_2$.[11] However, few such samples have so far been observed, and it would be of interest to increase their number by investigating a less symmetrical monoclinic antiferromagnet, revealing both the features and the differences of the intermediate state in antiferromagnets with different symmetries. The solution of these problems becomes possible because of the use of the following experimental procedure.

## 2. MEASUREMENT METHOD

The magnetic properties of $NiWO_4$ were investigated by an induction procedure.[11] The pulsed magnetic field was produced by discharging a bank of high-voltage capacitors through a multiturn solenoid, of length 100 mm and inside diameter 20 mm, cooled with liquid nitrogen. This ratio of dimensions ensures a sufficiently homogeneous field at the sample. The field pulse duration is $15\times10^{-3}$ sec. The measurements were made in fields up to 300 kOe.

The intensity of the magnetic field was measured with an induction coil located in the working part of the solenoid at a certain distance from the sample. The voltage induced in the coil was applied to an electronic integrating circuit. The integrated signal, proportional to the magnetic field intensity $H$, is applied to the horizontal deflecting plate of a two-beam oscilloscope. Since the investigated phase transitions occur in a field interval $\Delta H$ which is very narrow compared with the absolute value of the critical field $H_c$ ($\Delta H/H_c \sim 10^{-3}$), a delay circuit is provided for the oscilloscope sweep. Its action is such that the deflection of the beams, which is proportional to $H-H_0$, begins at a certain field value $H_0$ somewhat lower than the orientational-transition field $H_c$. This makes it possible to stretch out the scale of the magnetic field in the section of interest to us by a factor of 100 and more. All the oscillograms presented here were obtained with such a stretched-out scale.

The $NiWO_4$ single crystal was grown by the Czochralski method and was a cube with 2.2 mm edge, cut in such a way that one of its faces was perpendicular to the proposed direction of the antiferromagnetism axis,[3] while the other was parallel to the crystallographic symmetry plane. The difference between the form of the sample from ellipsoidal introduces certain distortions into the measurement results, but offers conveniences in the experiment. The sample was cooled with helium or hydrogen in a finger-like stub that extended from the cryostat into the interior of the solenoid.

The measurements of the three components of the magnetization vector of the sample were made with the aid of mutually perpendicular induction coils wound directly on the sample. The coils had 30 turns each of copper wire of 30 $\mu$m diameter. Their axes, in accordance with the faceting of the sample, were parallel to the $a$, $b$, and $c$ directions. The voltage induced in the coils by the external magnetic field was offset by the voltage induced in the coil intended for the measurement of the field and located far from the sample. Voltages proportional to $dM_i/dt$, also induced in the measuring coils, were applied directly or after integration to the vertical deflection plates of the oscilloscope. The values of the three components of the magnetic moment $M_i$, plotted as functions of the magnetic field intensity, yield the complete information on the behavior of the magnetic moment in the course of the orientational transition. In addition, while applying to the horizontal and vertical deflection plates of one of the beams integrated signals from two measuring coils respectively it is possible to obtain a clear picture of the change of the magnetization in the course of the transition in any particular plane.

It was necessary in the experiment to vary the angle $\psi$ between the magnetic field and the antiferromagnetism axis in a wide range, with relatively low accuracy at large angles $\psi$, and also with high accuracy at small $\psi$. The angle was therefore set by two methods. The inclinations of the field in one plane coinciding with the symmetry plane of the sample were effected by a rotary device, which located the sample in the cryostat in an angle range ±45°. The relative error in the setting of the angle was 1°. In addition, an accurate change of the orientation in an angle range ±3° in two mutually perpendicular planes was effected by inclining the solenoid with the aid of the micrometric screws on which the solenoid was secured. The relative error in setting the angle by this method did not exceed 5′.

## 3. MAGNETIC ANOMALIES AND CONTROL OF THE DIRECTION OF THE ANTIFERROMAGNETISM AXIS

Measurements of the magnetization and of the magnetic susceptibility in a field parallel to the antiferromagnetism axis at a temperature 4.2 K yielded the following results. In fields $H$ lower than the critical value $H_c = 175$ kOe the magnetization of $NiWO_4$ was negligibly small. In the narrow field interval $\Delta H$ near the critical field, the longitudinal component of the magnetization $M_\parallel$ increases sharply reaching a definite value $\Delta M_\parallel$. The section of the magnetization curve, with the scale stretched out near the critical field, is shown on the oscillogram of Fig. 1a. The transverse components of the magnetization $M_\perp$ in the critical region of the fields remained practically unchanged (Figs. 1b and 1c).

Figure 2 shows an oscillogram of the voltage induced in the coil whose axis was parallel to the external magnetic field. It is known that this voltage is produced by changes of the linkage of the coil with the magnetic flux

$$\Phi \sim \mathbf{H} + (4\pi - \beta)\mathbf{M}.$$

This expression consists of two terms. The first depends on the external field and is not connected with the properties of the sample. The second depends on the sample magnetization **M** and on its demagnetizing factor $\beta$. Accordingly, the voltage induced in the coil also contains two terms:

$$\mathscr{E} \sim d\Phi/dt, \quad \mathscr{E} = \mathscr{E}_0 + \mathscr{E}_1;$$

$$\mathscr{E}_0 \sim dH/dt, \quad \mathscr{E}_1 \sim (4\pi - \beta)\, dM/dt = (4\pi - \beta)\chi\, dH/dt.$$

The two terms are clearly seen in the oscillogram. The sections of the curve above and below the abscissa axis pertain respectively to the increasing ($dH/dt > 0$) and decreasing ($dH/dt < 0$) fronts of the field pulse.

The quantity $\mathscr{E}_0$ marked on the oscillogram is practically independent of the magnetic field intensity in that narrow field interval which is shown on the oscillogram. This makes it possible to separate it from the other term, $\mathscr{E}_1$, which occurs only following the orientational transition, and again practically vanishes after going through a maximum. The value of $\mathscr{E}_1$, apart from a factor, is proportional to the magnetic susceptibility of the sample. The sharp increase of the magnetization and the burst of magnetic susceptibility indicate that an orientational transition takes place in the antiferromagnetic $NiWO_4$ in the field $H_c$.

The results were obtained under experimental conditions such that the inclination of the external magnetic field to the antiferromagnetism axis was small. At a large inclination, the behavior of the magnetization vector in the orientational transition differs substantially from the described one. The abrupt angular dependence of the magnetic properties, on the one hand, leads to the need for a very accurate reading of the angles between the direction of the external magnetic field and the antiferromagnetism axis, and on the other hand this dependence is itself the basis of the method of the exact determination of the direction of this axis in the crystal.

A detailed study of the magnetization curves in the orientational transition has shown that they vary differently when the external magnetic field **H** is inclined away from the ordering axis in two mutually perpendicular directions. In particular, an inclination by an angle $\psi_c \sim 1°$ in the "light" plane leads to a broadening and vanishing of the orientational transition. This property, just as in the case of uniaxial antiferromagnets,[11] has made it possible to determine the direction of the antiferromagnetism axis accurate to 5′. The same monitoring accuracy is necessary also for the angle in the other plane, which coincides in this case with the symmetry plane of the crystal.

However, when the field is inclined in the "difficult" plane, the orientational transition is preserved in a wide angle interval, so that in this case the changes of the magnetic susceptibility cannot serve as a criterion for the determination of the inclination angle between the field and the direction of the spontaneous-magnetization axis. One of the possible methods of orientation is to use the dependence of the critical field $H_c$ of the

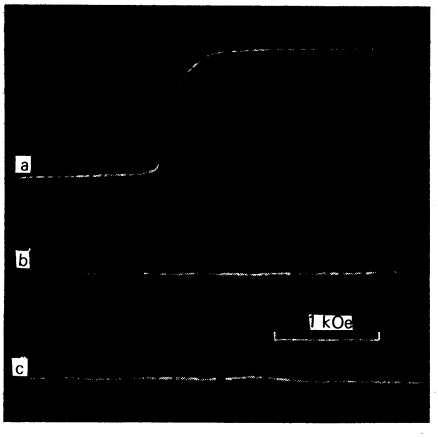


FIG. 1. Oscillograms of the longitudinal $M_\parallel$ (a) and transverse $M_\perp$ (b, c) components of the magnetization as functions of the magnetic field intensity in the region of the orientational transition ($H_c = 175$ kOe). The magnetic field direction is close to that of the magnetic axis.

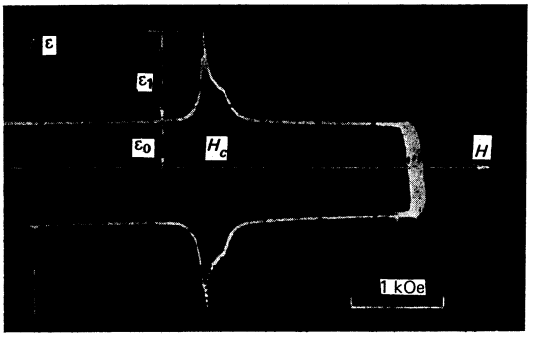


FIG. 2. Dependence of the voltages induced by the change of the external field ($\mathscr{E}_0$) and of the magnetic moment of the crystal ($\mathscr{E}_1$) in a longitudinal induction coil on the magnetic field intensity $H$. The upper and lower parts of the curve correspond to the increasing and decreasing sections of the magnetic-field pulse.

orientational transition on the angle $\psi$. This dependence is hyperbolic. However, the minimum of the function $H_c(\psi)$ is not distinct enough to determine the direction of the spontaneous-magnetization axis with the ±5′ accuracy needed to register a 0.0003% increase of the critical field. In practice we were able to register reliably a 0.1% change of the critical field and establish the angle $\psi$ by this method with accuracy of only ±1.6°.

Success was attained with the other orientation, applied for the first time ever to the study of phase transitions of this type and based on their distinctive features. It is based on the following hypothesis: the direction of the jump of the moment $\Delta\mathbf{M}$ in the orientational transition coincides with the direction of the external magnetic field $\mathbf{H}$ if and only if the direction of the external field coincides with the direction of the spontaneous-magnetization axis. Otherwise the angle between the vectors $\mathbf{H}$ and $\Delta\mathbf{M}$ differs from zero. Measurement of this angle turned out in fact to be the most sensitive method of determining the angle of inclination of the external magnetic field to the magnetic-ordering axis.

We consider now the vectors $\Delta\mathbf{M}$ and $\mathbf{H}$ in a coordinate system connected with the measuring coils. One of these coils is tentatively directed parallel to the expected ordering axis, while the other is perpendicular to this axis in the difficult plane. Because of the inevitable error in the preliminary setting of the direction of the transverse coil, even in case of the exact orientation of the magnetic field relative to the ordering axis, the coil registers transverse components of the magnetic field ($H_\perp$) and of the jump of the magnetization ($\Delta M_\perp$). Then the parallelism of the vectors $\Delta\mathbf{M}$ and $\mathbf{H}$ can be expressed by the proportionality of their components measured by the corresponding coils:

$$\Delta M_\parallel/H_\parallel=\Delta M_\perp/H_\perp.$$

In the measurements we are dealing with voltages proportional to the values of these projections. The latter differ from each other by almost three orders of magnitude. It is therefore convenient to change over to a comparison of the voltages induced in the corresponding coils, which have the same order of magnitude and are proportional to the derivatives of the projections with respect to time. Indeed, since the proportion written out above is valid at any instant of time it is valid also for the time derivatives. Therefore the condition

$$\mathscr{E}_{1\parallel}/\mathscr{E}_{0\parallel}=\mathscr{E}_{1\perp}/\mathscr{E}_{0\perp}$$

is also an indication of the parallelism of the varying vector quantities $\Delta\mathbf{M}$ and $\mathbf{H}$. We have written here the voltages defined above, induced in the longitudinal and transverse coils. The amplitudes of the voltages induced in the longitudinal coil amount in our case to about half a volt, and their ratio $\mathscr{E}_{1\parallel}/\mathscr{E}_{0\parallel}$ remains practically unchanged in the case of small inclinations of the crystal in its symmetry plane. On the contrary, the ratio $\mathscr{E}_{1\perp}/\mathscr{E}_{0\perp}$ obtained from the oscillograms of the voltages induced in the transverse coil depends on the angle of inclination, and the dependence is stronger the better the guessed perpendicularity of the coil axis to the ordering direction. We take the orientation of the external field at which the voltage ratios become equal as the direction of the antiferromagnetism axis. We note that the possible non-orthogonality of the measuring coil changes only the amplitude of the voltages induced in them, but not their ratio, and therefore does not affect the result of the orientation. At an initial error of several degrees in the orientation of the measuring coils relative to the ordering axis, this procedure of establishing the direction of the external magnetic field along the spontaneous-magnetization axis has enabled us to attain an accuracy of about 5 minutes of angle. The described orientation method is of incomparable accuracy and may turn out to be useful in the study of the influence of external actions on the position of the antiferromagnetic axis in monoclinic crystals.

## 4. EXPERIMENTAL RESULTS

The investigation of the observed anomalies of the magnetic properties in the orientational transition in $NiWO_4$ yielded the following results. Some of them (items 1–5 below) were obtained in a strictly parallel magnetic field because of the use of the above-described method of accurately orienting the field relative to the spontaneous-magnetization axis.

1) *The absolute value of the critical field* $H_c$ of the orientational transition was measured at a strictly parallel orientation at a temperature $T=4.2$ K. The scales of the magnetic field were calibrated against the critical field of the well investigated phase transition in the antiferromagnetic $MnF_2$.[11] The transition field in $NiWO_4$ is $H_c=(175\pm7)\times10^3$ Oe. When the external field deviates from the antiferromagnetism axis in a plane perpendicular to the symmetry plane of the sample by ±1°, the critical field changes by not more than 0.1%.

2) *The magnetic-field interval* $\Delta H$ in which the orientational transition took place was measured also in a strictly longitudinal magnetic field. This transition has no sharp boundaries. Therefore the very concept of the experimental value of the interval $\Delta H$ must be specified beforehand. It was determined by two methods. On the one hand, the magnetization curve of Fig. 1a is approximately replaced by an idealized curve made up of two horizontal lines and one inclined to them to fit best the initial curve. The abscissas of the points of intersection of these lines are taken to be the start and the end of the transition, while the ordinate difference is taken to be the relative value of the magnetization jump. On the other hand, the bell-shaped curve of the magnetic susceptibility in the transition, represented in Fig. 2 by the voltage $\mathscr{E}_1$, is replaced by a rectangular one. The area under the rectangular spike is equal to the area of the initial curve, and the ratio of its height to the width is chosen such as to minimize the unequal areas of the experimental and idealized spikes. The height of the rectangular spike constructed in this manner is taken to be the mean value of the magnetic susceptibility in the transition, and its width is taken to be the transition interval. The size of this interval, measured by both methods, was the same at $\Delta H=290\pm40$ Oe; the relative width of the transition was $\Delta H/H_c$

$=0.0016$.

3) *The value of the possible hysteresis* was estimated by comparing the magnetic-susceptibility curves plotted in an increasing and decreasing magnetic field. The fine structure of these curves turned out in general outlines to be similar and made it possible to compare the scales of the magnetic fields. It turned out that the hysteresis in the course of magnetization and demagnetization, if it does exist at all, does not exceed 20% of the width of the transition, i.e., 60 Oe.

4) *The absolute value of the differential magnetic susceptibility* $\chi = dM_{\parallel}/dH$ was measured in the region of the orientational transition. It is known that in the induction method absolute measurements are difficult. To calculate $\chi$ we used the components $\mathscr{E}_0$ and $\mathscr{E}_1$ of the voltage induced in the coil. They are comparable in magnitude, and their ratio can be calculated from a single oscillogram. Using the definitions given for these components in the preceding section, we can calculate the differential magnetic susceptibility:

$$\chi = \frac{\mathscr{E}_{1\parallel}}{\mathscr{E}_{0\parallel}} \frac{1}{4\pi - \beta}.$$

For a sample of rectangular shape, the concept of the demagnetizing factor cannot be introduced rigorously, since the demagnetizing fields in the sample are inhomogeneous. We consider therefore approximately, instead of the cubic sample, a spherical sample of equal volume. If the centers of these samples are made to coincide, the non-congruent part of their volumes, which is source of the inhomogeneous field, amounts to approximately 30%. On this basis, we assign to the investigated cubic sample approximately the demagnetizing factor of the sphere $\beta = 4\pi/3$, recognizing that we introduce thereby an error of ~30% in the determination of the demagnetizing fields. Using the numerical values of $\mathscr{E}_1/\mathscr{E}_0$, we find that the largest differential magnetic susceptibility is 0.27. The average value of the magnetic susceptibility in the field interval in which the orientational transition takes place, determined by the method described in Sec. 2, is 0.15.

5) *The magnetization jump* in the orientational transition was determined from the area under the $\chi(H)$ curve, which was measured experimentally:

$$\Delta M = \int \chi(H)\, dH.$$

The integration is carried out in a field region including the interval $\Delta H$ in which the transition takes place. The same integral is calculated when $\chi$ and $\Delta H$ are determined (see Sec. 2), so that these quantities can be used to express the sought value: $\Delta M_{\parallel} = \chi \Delta H = 43.5$ G.

The results that follow (items 6–10) pertain to the angular dependence of the magnetic properties. In this case the external magnetic field is inclined to the spontaneous-magnetization axis in the easy plane by an angle $\psi$ up to $\pm 3°$, whereas in the "difficult" plane the inclination does not exceed 5′. We note that in an oblique magnetic field the orientational transition is accompanied not only by abrupt but also by smooth changes of the magnetization. These changes occur in a relatively wide range of magnetic fields and is not very well registered by the induction procedure. The results of items 6–10 pertain to the abrupt changes of the magnetization occurring in the narrow field interval $\Delta H$.

6) The oscillograms of the *trajectory of the motion of the magnetization vector* in the magnetic-moment space were obtained in the orientational transition with the aid of a "three-dimensional" procedure. It was observed that at all values of the angle $\psi$ this trajectory is planar, i.e., the relative value of the components of the magnetization in the "difficult" plane is negligibly small. This fact is a test of correct orientation of the magnetic field in this plane.

7) *The dependence of the amplitude of the magnetic susceptibility* in the orientation transition on the angle of inclination of the magnetic field to the ordering axis was reconstructed from a series of oscillograms (see Fig. 3). As seen from the plot of Fig. 4, the amplitude of the susceptibility spike changes little near $\psi = 0$, and then decreases sharply with increase of this angle.

8) *The dependence of the total jump of the magnetization* $\Delta \mathbf{M}$ in the orientation transition on the angle $\psi$ was also plotted by reducing a series of oscillograms (Fig. 5). The value of $\Delta \mathbf{M}$ was determined from each oscillogram by replacing it with an idealized one, as was done in item 2. As seen from Fig. 6, the jump of magnetization likewise decreases with increasing angle $\psi$.

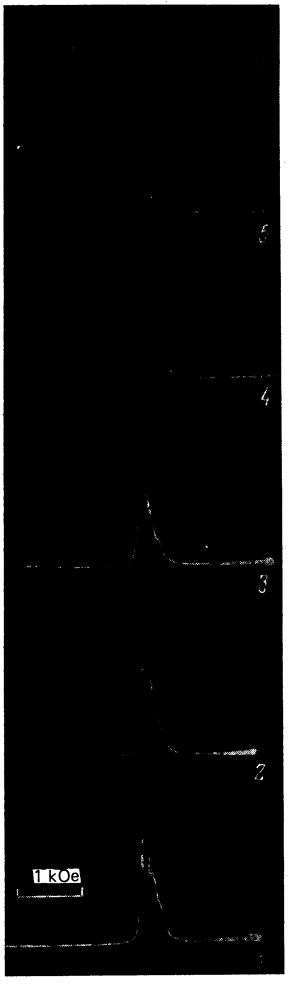


FIG. 3. Oscillograms of magnetic susceptibility, plotted at different angles $\psi$ of the inclination of the external field relative to the magnetic axis: 1—10′; 2—32′; 3—54′; 4—76′; 5—98′: 6—120′. The scales of the sections of the curves near $H_c$ are enlarged.

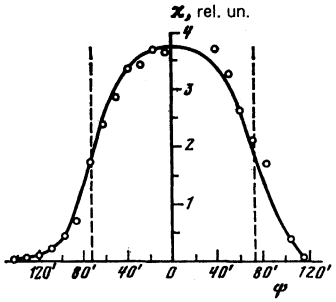


FIG. 4. Amplitude of the spike of the longitudinal component of the magnetic susceptibility in the orientational transition vs. the angle $\psi$.

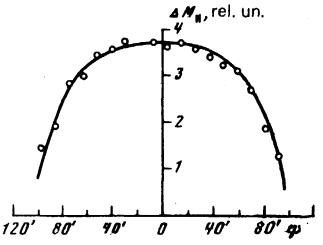


FIG. 6. Dependence of the jump of the longitudinal component of the magnetization in the orientational transition on the angle $\psi$.

9) *The value of the critical angle* $\psi_c$, which enters in the theory,[8,9] and at which the jump of the magnetization vanishes, was determined from the plot of Fig. 4. Theoretically, the magnetic susceptibility, remaining constant in the angle region $\psi < \psi_c$,[12] should decrease at $\psi \sim \psi_c$ so rapidly,[8,9] that in the scale of Fig. 4 the descent line should be practically vertical. Drawing vertical lines through the points at half the height of the smeared experimental curve, we obtain for the critical angle the value $\psi_c = 1.2°$.

The smearing of the $\chi(\psi)$ curve is apparently due to the inhomogeneities of the sample and possibly to the fact that the local direction of the crystallographic axis is not the same over the sample. A measure of such a deviation can be the decrease of the magnetic susceptibility $\chi$ averaged over the volume. The expected value of $\chi$ (see Sec. 5 below) differs from the observed ones (item 4) by 30%. This can be explained, on the one hand, to a block structure of the sample such that in 30% of its volume the angle deviates from the mean value by $\psi > 1.2°$. On the other hand, the same result can be interpreted by taking into consideration only the demagnetizing-field inhomogeniety due to the nonsphericity of the sample, and amounts according to our estimates to 30% (see Sec. 2). It is possible that a comparable role is played by both factors. Since the crystalline homogeneity of the sample is not monitored by us by other methods and we therefore are unable to take it into account, the error in the determination of $\psi_c$ increases to 30%.

10) *We investigated the transverse component of the magnetization of the sample* in the easy plane. It was observed that its jumplike changes in the orientational transition are negligibly small compared with the change of the longitudinal component. Thus, the magnetization-jump vector $\Delta\mathbf{M}$ is practically parallel to the magnetic-ordering axis at all values of the angle $\psi$.

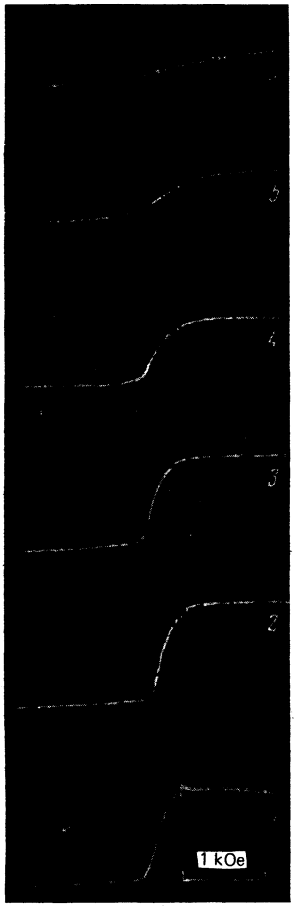


FIG. 5. Oscillograms of longitudinal component of magnetization, obtained at different angles $\psi$: 1—10′; 2—32′; 3—54′; 4—76′; 5—98′; 6—120′. The scales of the curves near $H$ are enlarged.

## 5. DISCUSSION

An analysis of the orientational transitions induced by a strong magnetic field in antiferromagnets is contained in a number of theoretical papers. The particular cases of a uniaxial antiferromagnet in a longitudinal[7] and inclined[8,9] fields, and also of a biaxial antiferromagnet[10] were considered. We used the results of these studies to interpret our experimental data.

The behavior of a monoclinic antiferromagnet in a magnetic field can be described by the thermodynamic potential of a biaxial antiferromagnet, if we confine ourselves to terms of second order in the magnetizations, and if the coordinate axes are directed along the magnetic axes:

$$\Phi = {}^1/_2 A\mathbf{m}^2 + {}^1/_2 a_1 m_x^2 + {}^1/_2 a_2 m_y^2 + {}^1/_2 b_1 l_x^2 + {}^1/_2 b_2 l_y^2 - 2M_0\mathbf{mH}.$$

We have introduced here the standard notation for the magnetization vector $\mathbf{m}$ and for the antiferromagnetism vector $\mathbf{l}$, which are connected with the sublattice magnetization vectors $\mathbf{M}_{01}$ and $\mathbf{M}_{02}$ by the relations

$$\mathbf{m} = \frac{\mathbf{M}_{01} + \mathbf{M}_{02}}{2M_0}, \quad \mathbf{l} = \frac{\mathbf{M}_{01} - \mathbf{M}_{02}}{2M_0};$$

$2M_0$ is the magnetization of the system in the case of total magnetic saturation. We have left out terms responsible for the Dzyaloshinskiĭ interaction in view of the absence of the experimental facts that point to their noticeable magnitude in $NiWO_4$.

We separate the axis of easiest magnetization $z$, assuming $b_1 > 0$ and $b_2 > 0$. In addition, we assume that $b_2 > b_1$. Then, in a field parallel to the $z$ axis, the antiferromagnetism turns out to be parallel to the $x$ axis

after the orientational transition. In this connection, the $zx$ plane will be called the easy magnetization plane.

The comparison of the results of a theoretical analysis[10] with the experimental data on $NiWO_4$ is best started with the following fact. According to the theory, if the external magnetic field lies in the "easy" plane, the sublattice magnetization vectors do not leave this plane at any value of the field, i.e., $m_y \equiv 0$ and $l_y \equiv 0$. The trajectory of their motion does not differ in this case from the trajectory in the uniaxial antiferromagnet. Our experimental result (item 6 of Sec. 4), confirms that this was precisely the case realized. Therefore we confine ourselves hereafter to the first, second, and fourth terms of the thermodynamic potential, recognizing that the third and fifth terms do not affect the behavior at the given field orientation. The investigated magnetic properties make it possible to determine all three unknown constants ($A$, $a_1$, and $b_1$) of the simplified thermodynamic potential.

First, the exchange interaction constant $A$ and the associated effective exchange potential $H_E$ can be easily calculated from the expression for the magnetic susceptibility, as was done, for example, in Ref. 3:

$$\chi_\perp \approx M_0^2/A = M_0/H_E.$$

The susceptibility in a magnetic field perpendicular to the antiferromagnetism vector can be calculated from the results of our measurements of the magnetization (items 1 and 5 in Sec. 4) in a field initially parallel to this vector, assuming that an orientational transition takes place: $\chi_\perp = \Delta M_\parallel / H_c = 0.25 \times 10^{-3}$. Using the numerical value of the sublattice magnetization $M_0 = 154$ G, we obtain an exchange constant $A = 380 \times 10^6$ erg/cm$^3$ and an exchange field $H_E = 620 \times 10^3$ Oe. We note that the value of $\chi_\perp$ determined by us, and consequently the constants $A$ and $H_E$, agrees well with the results of Ref. 3. This confirms the assumptions that in the field $H_c$ the orientational transition makes the antiferromagnetism vector perpendicular to the initial direction and to the external magnetic field.

The theory connects the critical field of this transition with the constant $b_1$ and the anisotropy field $H_{A1}$:

$$H_c = (2H_{A1}H_E)^{1/2} = (A|b_1|/4\pi M_0^2)^{1/2},$$

so that we can determine these constants from the experimental results (item 1 of Sec. 4): $H_{A1} = 25 \times 10^3$ Oe, $b = +7.7 \times 10^6$ erg/cm$^3$. We note the good agreement between the obtained anisotropy field and the experimentally determined antiferromagnetic resonance in the far infrared region.[4]

The paramagnetic anisotropy constant $a_1$ exerts a substantial influence on the orientational transition together with the constant $b_1$, by determining its smooth or jumplike character. We consider now the trajectory of the magnetization vector **M** of the sample in the course of the orientational transition, since the differences in its form for smooth and jumplike transitions makes it possible, using the experimental data, to give preference to one or the other model. This trajectory, as already noted, is in the $zx$ plane. In the former case, when the transition is smooth, the trajectory should be described, with sufficient accuracy, by a semicircle[11] (Fig. 7). The connection between the modulus of the vector **M** and the angle $\theta$ of its orientation relative to the easiest axis is expressed in the following manner:

$$M = \frac{2b_1}{H_e} \sin\theta.$$

At the initial instant of the orientational transition, at small values of the magnetization, the magnetization vector is perpendicular to the easiest axis and with increasing modulus is rotated through $\pi/2$. The magnetization component perpendicular to the easiest axis passes in this case through the maximum value $M/2$. A smooth trajectory of the motion of the vector **M** in the orientational transition should be observed at a positive sign of the sum of the anisotropy constants in the thermodynamic potential $4\rho = a_1 + b_1 < 0$. Then, in an arbitrarily oriented magnetic field there should be no singularities on the magnetization curves, with the exception of the case of strict coincidence of the direction of the field with the $z$ axis, when two first-order transitions occur. Such a trajectory was not realized in our experiment and the foregoing inequality is apparently not realized in $NiWO_4$.

The magnetization curves should have a different form when the inverse inequality $\rho > 0$ is satisfied. In this case the orientational transition is via a first-order phase transition, and the magnetization of the sample in the critical field changes jumpwise from $\mathbf{M} = 0$ to $\mathbf{M} = \mathbf{M}_2$ (Fig. 7). No transverse components of the magnetization arise in this case. In a magnetic field directed at an angle $\psi$ to the $z$ axis, the orientational transition proceeds in three stages. In fields weaker than the critical value, the vector **M** rotates smoothly until the critical value $\mathbf{M}_1$ is reached, and the end of this vector describes part of a circle (Fig. 7). In the critical field, the magnetization changes jumpwise by an amount $\Delta\mathbf{M} = M_2 - M_1$. This is followed by a continuation of the smooth rotation of the vector **M**. It is important to note two circumstances: first, only the longitudinal components $\Delta M_\parallel$ of the magnetization vector changes jumpwise, whereas the transverse component $\Delta M_\perp$ remains practically unchanged.[8] Second, with increasing angle $\psi$ of inclination of the external

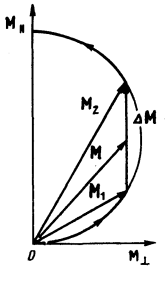


FIG. 7. Diagram of rotation of the magnetization vector **M** in the orientational transition. If the transition is smooth, the end of the vector **M** describes a semicircle. In the case of a phase transition the vector changes abruptly from $\mathbf{M}_1$ to $\mathbf{M}_2$. The state with the vector **M** terminating on the vertical straight straight line corresponds to stratification into domains.

magnetic field, the value of the jump decreases smoothly and vanishes at $\psi = \psi_c$.

This behavior, which was predicted theoretically, agrees well with the experimental observations. This pertains both to the absence of transverse components of the magnetization jump (item 10, Sec. 4) and to the smooth decrease of $\Delta M_{\parallel}$ (item 8, Sec. 4; Figs. 5 and 5). The agreement between theory and experiment confirms the fact that the orientational transition in the angle range $-1.2° < \psi < +1.2°$ in antiferromagnetic $NiWO_4$ proceeds via a first-order phase transition, and the inequality $a_1 + b_1 > 0$ is valid for the thermodynamic potential.

The phase diagram of an antiferromagnet for this case is shown in Fig. 8. The figure that bounds the region of metastable states is an astroid.[8] The almost horizontal line that divides it into two parts is the line of equilibrium first-order phase transitions. These transitions, in analogy with the liquid–vapor transition, are produced between phases with identical symmetry. The phases differ from each other only quantitatively, and therefore the transition from one to the other can proceed in principle smoothly, without jumps. On the phase diagram this manifests itself in the presence of critical points at which the phase-transition line terminates. The experimentally observed points with coordinates $H_c = 175$ kOe and $\psi_c = \pm 1.2°$ are in fact, apparently, such critical points (item 9 of Sec. 4). At these points the magnetization jump vanishes, and at $\psi \geq \psi_c$ the orientational transition proceeds smoothly, without any phase transitions whatever.

The constant $\rho$ in the theory is connected with the critical angle $\psi_c = \rho/A$, so that it can be calculated by starting from the experimental data (item 9 of Sec. 4). The quantity $\rho = +4.0 \times 10^6$ erg/cm$^3$ obtained in this manner at a known critical field $H_c$ determines the region of the possible hysteresis:

$$H_2 - H_1 = \frac{a_1 + b_1}{A} H_c = 7.4 \text{ kOe}$$

and specifies the vertical dimensions of the astroid (Fig. 8). Thus, the phase diagram of antiferromagnetic $NiWO_4$ in an oblique field has been completely reconstructed from the experimental data.

We note that the calculated constant $\rho = (a_1 + b_1)/4$ determines the energy of the intrasublattice anisotropy. At the same time, the available data enable us to calculate the energy of the intersublattice anisotropy $\rho_1 = (a_1 - b_1)/4 = \rho - 2b_1 = 0.15 \times 10^6$ erg/cm$^3$, which turns out to be smaller by one order of magnitude. Therefore, despite the possible substantial error in the determination of the constant $\rho$, we can state that the intrasublattice anisotropic interaction predominates.

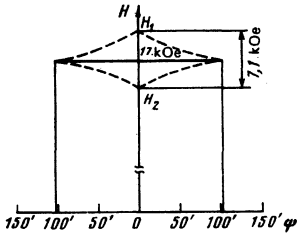


FIG. 8. Phase diagram of antiferromagnetic $NiWO_4$ in an oblique magnetic field lying in the $zx$ plane.

The intrasublattice interaction makes the main contribution to the constant $a_1$, which can be calculated from the experimental results: $a_1 = 4\rho - b_1 = 8.3 \times 10^6$ erg/cm$^3$. This constant determines the anisotropy of the magnetic susceptibility in the paramagnetic region: $(\chi_z - \chi_x)/\chi_x = a_1/A = +0.02$, which can be compared with that observed in Ref. 3. The reduction of the results, which are represented in that reference graphically, shows that the experimentally observed anisotropy of the magnetic susceptibility agrees with the calculated one in sign and is close to it in absolute value. From a comparative analysis of the values of the contributions of the single-ion crystallographic anisotropy and the anisotropy of the spin–spin interactions to the total energy of the magnetic anisotropy of $NiWO_4$ in Ref. 3 it was concluded that the predominant role is played here by the single-ion anisotropy. At the same time, the contribution of the anisotropy of the exchange interaction could not be excluded, since according to the estimates of Ref. 3 it is commensurate with that obtained in the experiment. On the basis of our results, the total energy of the anisotropy can hardly be connected with the exchange-interaction anisotropy, since the latter would more readily manifest itself in a stronger intersublattice exchange interaction in the first coordination sphere. The same can be said also of the dipole–dipole interaction. The predominance of the intrasublattice anisotropy energy compared with the intersublattice energy favors more readily a one-ion mechanism rather than a relatively weak interaction between the remaining ions located in the second coordination sphere.

We have considered above the explanation of the observed picture of the first-order phase transition, calculated for $NiWO_4$ the corresponding interaction constants with which the transition is described, and drew conclusions concerning the nature of these interactions. It was assumed that the transition from one phase, characterized by the vector $\mathbf{M}_1$ on Fig. 7, to another phase with vector $\mathbf{M}_2$ occurs jumpwise, i.e., no states with intermediate vector $\mathbf{M}$ are realized. This is true in practice only for an infinitesimally small region of the crystal. In experiment we measure the vector $\mathbf{M}$ of the sample as a whole and observe arbitrary intermediate positions of this vector. These positions correspond to crystal states wherein it loses its magnetic homogeneity and breaks up into two phases with relative concentrations $\rho$ and $1 - \rho$. Then the sample magnetization vector as a whole can occupy arbitrary intermediate positions: $\mathbf{M} = \rho\mathbf{M}_1 + (1 - \rho)\mathbf{M}_2$. We note that in this case, in the field interval $\Delta H$, the end of the vector $\mathbf{M}$ on Fig. 7 should be on a straight line joining the ends of the vectors $\mathbf{M}_2$ and $\mathbf{M}_1$, whereas in the case of homogeneous rotation it should lie on a semicircle. The presence of states with vector $\mathbf{M}$ on the vertical section of the diagram of Fig. 7 point to the appearance of magnetic stratification of the sample into coexisting phases. The observed stratification is practically at equilibrium. This is indicated by the absence of hysteresis of the phase transition (accurate to 60 Oe, item 3 of Sec.

4, at a width 7 kOe of the region of metastable states).

The nature of the magnetic inhomogeneities existing in the magnetic-field interval $\Delta H$ is most clearly illustrated by the correspondence of this interval (item 2 of Sec. 4) to the demagnetizing field of the sample $H_d = \beta \Delta M \approx 0.2$ kOe. Some excess of the observed value of $\Delta H$ can be understood by taking into account the inhomogeneity of the demagnetizing field in a sample of cubic shape, an inhomogeneity estimated in Sec. 4. According to the theory,[12] the demagnetizing field of the sample is the cause of the onset of an intermediate state in the sample during the first-order phase transition. It appears that in monoclinic $NiWO_4$, just as in the uniaxial antiferromagnet $MnF_2$,[11] a domain structure is also realized in the magnetic-field interval $\Delta H$, consisting of an alternation of regions of coexisting phases that are in statistical equilibrium with one another.

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# Spin-phonon interaction in a trigonal crystal

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The spin-phonon interaction (SPI) of $Ni^{2+}$ ions in a trigonal zinc fluorosilicate ($ZnSiF_6 \cdot 6H_2O$) crystal is investigated. The complete set of the SPI tensor elements obtained from experiments on the effect of axial compression on the electron paramagnetic resonance (EPR) spectrum at 4.2 K is used to calculate the spin-lattice relaxation (SLR) time of the direct processes in the investigated system. A comparison of the calculated and experimental values shows good agreement when the phonon bottleneck effect is taken into account. The contribution of the crystal-lattice dynamics and of the temperature compressibility of the crystal to the initial splitting parameter $D$ is calculated. It is established that the temperature compressibility and the SPI of the single-phonon processes do not describe the observed temperature dependence of $D$, while the SPI of two-phonon processes can describe this dependence.

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## INTRODUCTION

The possibility of observing magnetic-resonance spectra and of practical utilization of diamagnetic crystals doped with paramagnetic ions in quantum-electronics devices is due greatly to the speed of the relaxation processes between the sublevels of the spin system. Numerous experimental and theoretical investigations have shown that when the paramagnetic crystals are diluted the principal role can be assumed by the relaxation processes connected with energy transfer from the paramagnetic system to the phonon reservoir of the crystal lattice.

Theoretical calculations of the elements of the spin-phonon interaction (SPI) tensor[1] for cubic crystals lead to values that agree well with the experimental results. When the symmetry is lowered, however, the calcula-

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