LOCAL MODES IN LOW-DIMENSIONAL MAGNETIC $NaFe(WO_4)_2$

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UDC 537.635:537.611.45,
537.621.4

The low-dimensional compound $NaFe(WO_4)_2$ is studied by the magnetoresonance methods in the frequency interval 25—142 GHz and in the temperature range 1.8—175 K. The frequency-field dependence of the AFMR spectrum along the easy axis of a crystal, and the characteristic parameters describing the antiferromagnetic absorption [ν_1=(141±1) GHz, ν_2=(168.7±1) GHz, H_{a1}=10.5 kOe, H_{a2}=15 kOe, H_{sf}=(50±0.1) kOe] are determined. The value of the interlayer exchange interaction is estimated, and the additional absorption related to the local modes, which are conditioned by the breaking of a translational order in the low-dimensional magnetic structure, is revealed. The dependence of the principal values of the magnetic susceptibility of $NaFe(WO_4)_2$ on temperature is studied. The effect of rotation of the magnetic susceptibility axes in the plane (*ac*) with a variation in temperature is discovered. The reason of the effect is a low symmetry of the crystal and a low dimensionality of the magnetic structure.

1. Introduction

The fundamental role in the formation of the physical properties of magnetically concentrated crystals is played by a low symmetry of crystal lattices and the dimensionality of magnetic systems. Such crystals are characterized by the sharply manifested anisotropy of magnetic, optical, and resonance properties. These compounds include both the family of double alkali-rare-earth molybdates and tungstates and the group of transition 3*d*-metals. They possess the strong anisotropy of the *g*-factor of a ground state and the anisotropy of the spin-spin interaction. The low symmetry of a crystal structure defines a number of particular thermodynamic and resonance properties in these compounds. For example, the effect of low symmetry in compound $KEr(Mo_4)_2$ is manifested in the EPR spectra and consists in the difference of the magnetic axes for the Kramers ground and excited doublets. With increase in the external magnetic field, the turn angle of the magnetic axes decreases [1]. Such a phenomenon was explained in the frame of the theory, where the crystal field potential includes the terms, whose symmetry is lower than the rhombic one. The experiments involving double alkali-rare-earth molybdates and tungstates showed that a part of monoclinic components in the crystal field potential is very large.

What else peculiarities of the physical properties can be caused by the monoclinic character of the symmetry and the low magnetic dimensionality of magnetically concentrated crystals in the paramagnetic and magnetically ordered phases? In our opinion, the answer to this question was derived upon the study of the resonance and magnetic properties of $NaFe(WO_4)_2$.

Iron-sodium double tungstate $NaFe(WO_4)_2$ is referred to the monoclinic syngony $P2/c$. The parameters of the elementary cell are: a=9.88 Å; b=5.72 Å; c=4.94 Å; β=(90±0.5)° [2]. As distinct from the other compounds of the double tungstates of transition elements, a monocrystal of $NaFe(WO_4)_2$ has layered crystal structure (Fig. 1,*a*). Its magnetic ion is the iron ion, Fe^{3+}, with the ground state $^6S_{5/2}$ (L=0, S=5/2). Ions Na^+ and Fe^{3+} form layers from identical ions in the planes parallel to the plane (*bc*), and the layers of Fe and Na alternate along the direction *a* (Fig. 1,*b*). Along the axis *c*, ions Fe^{3+} in a layer create the zigzag-like chains with the shortest Fe^{3+}—Fe^{3+} distance equal to 3.085 Å. The Fe^{3+}—Fe^{3+} distance in the plane (*bc*) along *b* is 5.72 Å which is almost twice greater than the shortest Fe^{3+}—Fe^{3+} distance in a chain. The distance between the closest magnetic ions along the direction *a* defines the two-dimensional crystallographic magnetic structure with chain structure in a layer (see Fig. 1). The search for the effects related to the manifestations of the low symmetry and the low dimensionality of a magnetic structure in the magnetic and resonance properties of this compound is the goal of our experimental studies presented in this work.

2. Results of Experiments and their Discussion

The resonance studies of a monocrystal of $NaFe(WO_4)_2$ were carried out in the magnetically ordered state at a temperature of 1.8 K in the frequency interval 25—142 GHz. The example of the recording of the absorption spectrum along the axis of “easy” magnetization at a

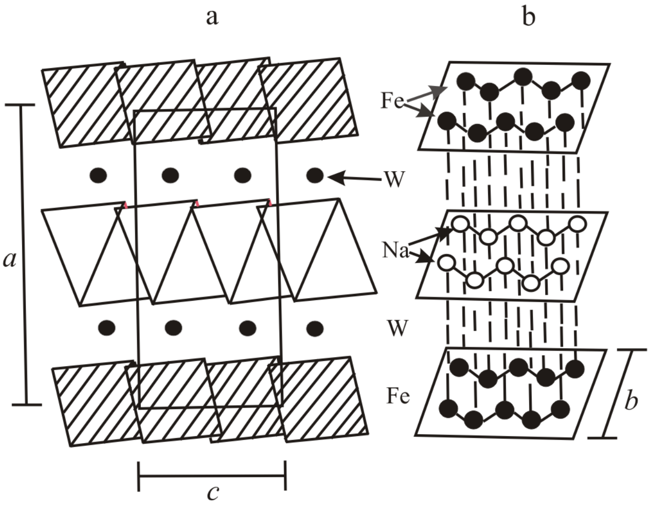

Fig. 1. Fragment of the crystal structure of NaFe(WO$_4$)$_2$: a — in the plane (ac), there are the octahedral chains of Fe (x=0) and Na (x=0.5); b — layers of magnetic ions Fe^{3+} separated by the layers of nonmagnetic ions Na$^+$

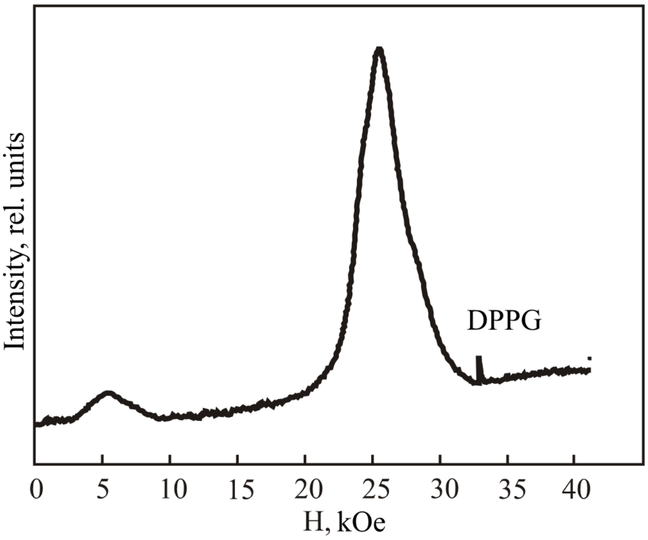

Fig. 2. AFMR spectrum of NaFe(WO$_4$)$_2$ at $\mathbf{H}\|\,\boldsymbol{l}$ and T=1.8 K at a frequency of 97.48 GHz. DPPG stands for the reference absorption line

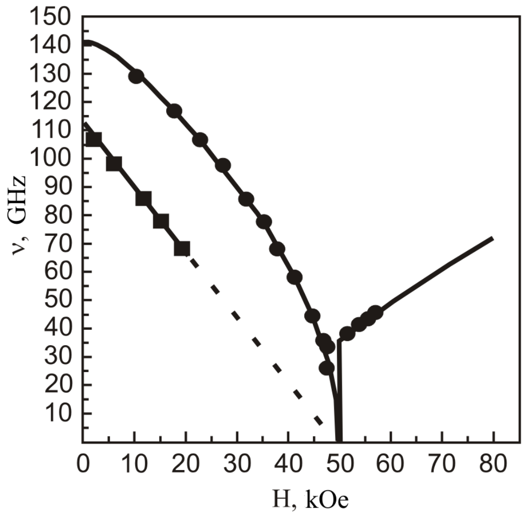

Fig. 3. Frequency-field diagram of the AFMR spectrum along the axis of "easy" magnetization at T=1.8 K: circles show the AFMR in the collinear and gauche phases, and squares correspond to the local mode. The continuous lines correspond to Eqs. (2), (3), and (5) with the parameters given in the text. The dashed line is the continuation of the curve by relation (5) drawn for convenience

frequency of 97.48 GHz is shown in Fig. 2. The frequency-field dependence of AFMR along the axis of "easy" magnetization z, which lies in the plane ac and is turned by (32±1)° relative to the axis c, is given in Fig. 3. The experimental measurements were performed in the following way. According to the study of the temperature dependence of the principal values of the magnetic susceptibility of the given crystal [3], the direction of the magnetic axis z in the basic plane ac depends on temperature and, at $T\approx 4\div 5$ K, was turned by an angle of (45±1)° relative to the crystallographic axes a and c. We oriented the specimen in this direction, decreased the temperature to 1.8 K ($T_{\rm N}$=3.8 K), and determined that the observed AFMR is not the low-field edge of the absorption spectrum. Only by the change of the angle to (32±1)°, we derived the resonance absorption in a minimum magnetic field and carried out the frequency-field measurements. At H=0, there exists a gap in the spectrum of spin waves equal to $\nu=\sqrt{2H_{a2}H_e}$=(141±1) GHz. We failed to observe the exchange branch along the axis of "hard" magnetization even upon the use of the pulse method (the maximum field $H\approx 220$ kOe). Therefore, the value of H_e was determined from magnetic measurements [3]. The estimates give the value H_e=121 kOe, which yields H_{a1}=10.5 kOe.

The frequency-field dependence of the AFMR spectrum, which was observed along the axis of "easy" magnetization z (see Fig. 3), corresponds to the theoretical description of the spectrum branches in the collinear and spin-flop phases of a two-axis antiferromagnetic upon the orientation of the external magnetic field $\mathbf{H}$ along the antiferromagnetism vector l.

When the external magnetic field $\mathbf{H}$ is less than the spin-flop transition field

$$H_{\rm sf}=\sqrt{2H_{a1}H_e}, \tag{1}$$

we observe AFMR in the collinear phase ($\mathbf{H}||\mathbf{l}, \mathbf{m}$=0) for the descending branch which is described by the formula [4]

$$\left(\frac{\nu}{\gamma}\right)^2 = \frac{1}{2}\big[H^2 + C_1 + C_2 -$$

$$-\sqrt{H^4 + 2H^2\left(C_1 + C_2\right) + \left(C_2 - C_1\right)^2}\big], \qquad (2)$$

where $\gamma = \mu_\mathrm{B} g$, $C_1 = 2H_{a_1}H_e$, $C_2 = 2H_{a_2}H_e$.

At the field $H = H_\mathrm{sf}$, the magnetic first-kind transition occurs, and the the antiferromagnetism vector is reoriented by a jump in the plane of the layer (ac) to the intermediate axis.

For the spin-flop transition field $H > H_\mathrm{sf}$, the dependence of the frequency on the field has the form

$$\left(\frac{\nu}{\gamma}\right)^2 = H^2 - H_\mathrm{sf}^2. \qquad (3)$$

Relations (2) and (3) allow us to determine the second anisotropy field H_{a2}=15 kOe and, hence, the high-frequency gap $\nu_2 = \sqrt{2H_{a2}H_e} = (168.7 \pm 1)$ GHz together with the spin-flop transition field H_{sf}=(50±0.1) kOe. Thus, at a temperature of 1.8 K, the experimental dependence $\nu(H)$ of the AFMR spectrum is characterized by the following parameters: ν_1=(141±1) GHz, ν_2=(168.7±1) GHz, H_{a1}=10.5 kOe, H_{a2}=15 kOe, H_sf=(50±0.1) kOe, and H_e=121 kOe. It is clear that, with our experimental resources (the maximum frequency $\nu \approx 140$ GHz, and the magnetic field of at most 80 kOe), we were unable to measure the frequency-field dependence of the AFMR spectrum for the orientation of the external magnetic field along the axis x or y and to determine the high-frequency gap. As seen from the experimental data for the crystal of NaFe(WO$_4$), there exists a weak correlation between a low value of the Néel temperature and the derived parameters of the AFMR spectrum. That is, the AFMR spectrum is observed as if from isolated ordered layers.

It is known that, upon the description of the magnetic and resonance properties of strongly anisotropic low-dimensional compounds, essential is the question on the ratio of the constants of the strong intralayer exchange interaction and the weak interlayer one which stabilizes the long-range magnetic order. In works [5,6], the relations between the critical temperature of the transition into an ordered state and the exchange constants were determined for a Heisenberg anisotropic low-dimensional magnetic. Let us try to estimate the value of the interlayer exchange interaction J'.

We use the relation [6]

$$1 \approx \frac{S^2 J'}{T_\mathrm{N}} \exp\left[4\pi\left(\frac{zS^2 J}{T_\mathrm{N}} - 1\right)\right], \qquad (4)$$

where J — exchange integral in a layer, and J' — interlayer exchange integral. The substitution of the relevant known parameters gives that J' is of the order of $10^{-6}J$. The estimates for low-dimensional magnetics [7] yield that J'/J is in the limits of 10^{-3} — 10^{-20}. Therefore, despite the sufficient smallness of the ratio J'/J, the above-presented estimate is reasonable.

The magnetic structure of such a compound is composed from very weakly coupled (almost independent) layers, whose structure is defined by the great [H_e=(121±0.1) kOe] intralayer exchange and the anisotropy (H_{a1}=10.5 kOe, H_{a2}=15 kOe). That is, the magnetic ordering at a relatively high temperature (T_N=3.8 K) is conditioned by the intralayer anisotropy, and the dynamic properties of the magnetic NaFe(WO$_4$)$_2$ are close to those in the static model of independent ordered layers, what is observed in experiments.

It is a rare case where a substance with extremely low interlayer exchange interaction ($H_a >> H_{e'}$) is homogeneous. Upon the transition into an ordered state, a domain structure arises, and the width of a domain wall in a low-dimensional structure, as distinct from a three-dimensional one, turns out to be of the order of interatomic distances. In this case, the domain boundaries can be considered as topological defects. Therefore, it is possible to observe metastable distortions of the ideal translational order of a magnetic structure, namely the magnetic translational defects, in one-dimensional antiferromagnets. In the low-temperature region (1.8 K) at a very small J' (it is practically equal to zero), the ground state of the layered magnetic system in such crystals is the orientationally disordered collection of magnetic layers due to the degeneration of the energies of different magnetic orientational states of a crystal (with any number of domain boundaries). A growth of the weak interlayer interaction increases the ordering degree of layers. But this ordering is hampered by the interactions related to the presence of real defects of the crystal structure which stabilize any orientational state. Therefore, as long as the energies of the competitive interactions are of the same order, one will observe the magnetic translational defects, on which resonance modes are localized, in a crystal. According to the theoretical consideration [8], the presence of translational defects leads to the appearance of the additional absorption lines, the so-called local modes of AFMR. They are related to a “wrong” orientation of the antiferromagnetism vector in one or several layers. The physical reason for the appearance of the local modes is the closeness of the energies of magnetic interactions which establish the mutual orientation of the magnetic moments of adjacent layers (or in a layer) and the energies of various imprfections, which fixes the antiferromagnetism vector. For a layered antiferromagnetic, the presence of translational defects leads to the additional absorption line with a frequency lower than the frequency of the main resonance.

Indeed, such lines were discovered experimentally in the region without magnon excitations. As seen from Fig. 3, in addition to the resonance, we interpreted the additional broad line as the acoustic mode (AM) of the antiferromagnetic resonance. Namely, a local mode was observed in magnetic fields less than the resonance field of the acoustic mode. According to the theoretical work [8], the account of the decay of spin waves indicates that a broad absorption band related to the disordering of the frequencies of all possible local modes should be really observed in experiments, rather than the isolated absorption lines of local modes. The integral intensity of an additional line is almost two orders weaker than that of the AM. The presence of such a line and its width depend on the quality of a specimen and the conditions of its cooling. The optimum polarization for the local AFMR mode turns out to be the polarization **h**||**H**. In the zero magnetic field at a temperature of 1.8 K, the additional absorption gap frequency is ν_{0L}=(113±1) GHz. Despite the fact that the curve of the angular dependence of the revealed additional line crosses nowhere the curve of the AFMR AM and practically repeats it, the frequency-field dependence of the former is described by the relation linear in field

$$\nu_L = \nu_{0L} - c, \tag{5}$$

as distinct from the case of the AM.

Figure 3 shows that the local mode frequency must becomes zero at the same field, as in the case of the AM. With decrease in the frequency, the intensity of this line decreases, and it is not observed at frequencies less than 60 GHz. We may assume that the number of magnetic defects decreases with increase in the external magnetic field.

In the general case, the presence of an additional line can be caused by the other reasons. It should be noted that, in layered antiferromagnets, magnetic translational defects can be conditioned not only by the smallness of the interlayer exchange interaction in the direction normal to layers, but by the mutual compensation of exchange interactions between adjacent atoms. In [9,10], such a breaking of the magnetic translational order in layered low-dimensional antiferromagnets was experimentally discovered.

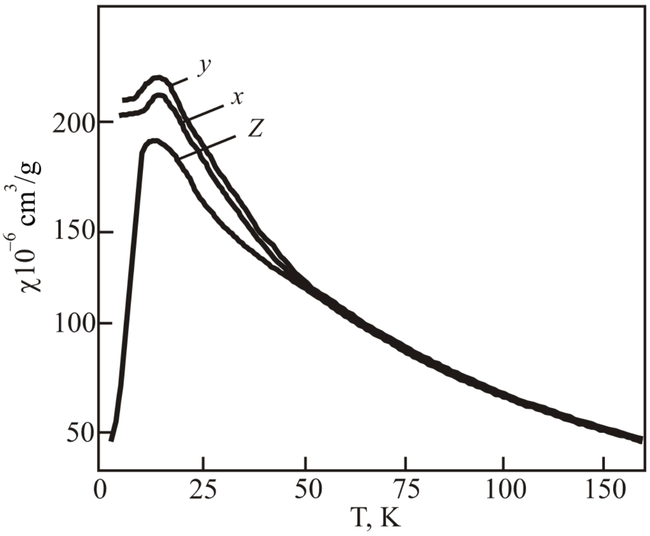

Fig. 4. Temperature dependences of the principal values of the magnetic susceptibility of NaFe(WO$_4$)$_2$ from 175 to 1.8 K

Because the studies of the antiferromagnetic resonance revealed some uncertainty as for the orientation of the antiferromagnetism vector and the minimum of the magnetic susceptibility in the plane (*ac*), we carried out the repeated temperature measurements of the magnetic susceptibility in the temperature range 1.8 — 175 K.

In Fig. 4, we present the temperature dependence of the magnetic susceptibility of NaFe(WO$_4$)$_2$ for three crystallographic directions. The high-temperature dependences are well described by the Curie—Weiss law with the Curie constant Θ=−19 K. However, as the temperature of NaFe(WO$_4$)$_2$ decreases, we observe the rotation of the axes of the magnetic susceptibility tensor (see Fig. 5). At high temperatures, the magnetic axis z coincides with the crystallographic axis a. At T=4÷5 K, the minimum of the magnetic susceptibility corresponds to the direction which lies at an angle of (45±1)° in the plane (*ac*). These results coincide with those in [3]. First of all, we note that the rotation of the magnetic axes does not contradict the monoclinic character of the crystal structure. The symmetry requires that only one principal axis of the susceptibility coincide with a single symmetry axis of the second order (b). At high

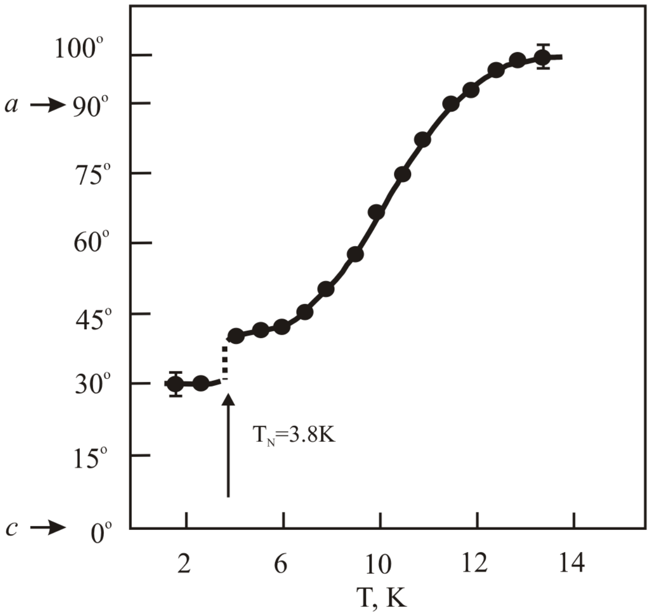

Fig. 5. Temperature dependence of the angle of the magnetic axis z in the plane (ac) of a monocrystal of NaFe(WO$_4$)$_2$

temperatures, when the population of all the levels is approximately the same, a minimum of the magnetic susceptibility must correspond to some value of the angle. In the low-temperature region, only the ground state is populated, and there occurs the turn of the magnetic axes. But such an effect is slight and characteristic of all the compounds of this family. Therefore, the reason for the turn is other. All the more, the minimum of the magnetic susceptibility at a temperature of T=1.8 K in the plane (ac) corresponds to the direction (35±1)° after the transition through the Néel temperature (3.8 K). This fact confirms our experimental studies of the antiferromagnetic resonance which showed that the antiferromagnetism vector $\boldsymbol{l}$ is oriented in the plane (ac) at an angle of (32±1)°. A small difference of the angles in two experiments can be explained by that AFMR is observed in very strong magnetic fields (to 50 kOe), and the action of the magnetic field is analogous, in this case, to the action of temperature. According to the theory developed in [11], the directions with extreme values of the magnetic susceptibility in a high-temperature region are defined by the joint contribution of the one-ion anisotropy, anisotropy of the dipole-dipole interaction, and the anisotropy of the exchange interaction which is conditioned by the crystallographic structure itself. At high temperatures, the direction of the anisotropy axis of the dipole-dipole interaction in the absence of one-ion anisotropy is defined by elements of the spatial symmetry and is practically coincides with the axes (a) and (c). We estimated the energy of the dipole-dipole interaction along these directions for the nearest neighbors in a chain which possesses the antiferromagnetic character by the formula

$$E_{dd} = \frac{m_1 m_2}{r^3}, \qquad (6)$$

where $m_{1,2}$ are magnetic moments of neighboring atoms, $m_{1,2} = gS\mu_{\rm B}$ (for the geometry of this structure).

The energy of the dipole-dipole interaction along the axis c (the distance between neighbor magnetic atoms is equal to 3.085 Å) is 0.52 K. The interaction energy in the direction of the axis a (the distance between neighbor magnetic atoms is 9.88 Å) is 0.0114 K. We mention a strong anisotropy of the dipole-dipole interaction. The direction of the one-ion anisotropy axes is defined by the local environment of a magnetic ion and does not coincide with the crystallographic axes for a low-symmetry crystal. With decrease in temperature, the ratio of the anisotropic contributions of different nature varies. Therefore, one must observe the rotation of the extreme directions of the magnetic susceptibility tensor of a monoclinic magnetic in the basic plane of the crystal. In our opinion, the critical fluctuations of a short-range magnetic order appear near the Néel temperature. At the Néel temperature, a strong instability arises, and the appeared spontaneous magnetic moment at a site is affected by the enhanced collective action of the above-mentioned anisotropies. This leads to the further rotation of the axis in the plane (ac).

We mention the single experimental work [12], where the authors reported on a similar temperature-induced rotation of the axes in the ordered antiferromagnetic phase, whose reason was considered to be the short-range magnetic order and the exchange interaction anisotropy conditioned by a low dimensionality of the magnetic structure.

3. Conclusions

Thus, the derived experimental results and their analysis allow us to draw the following conclusions.

1. We determined the characteristic parameters of the AFMR energy spectrum, the energy gaps ν_1=(141±1) GHz and ν_2=(168.7±1) GHz, the anisotropy fields H_{a1}=10.5 kOe and H_{a2}=15 kOe, the exchange field H_e=(121±0.1) kOe, and the values of the dipole-dipole interaction E_{ddc}=0.52 K and E_{dda}= 0.0114

K. We estimated the ratio of the values of the exchange interaction in layers and between them.

2. We established the additional absorption related to the local modes which are conditioned by breaking the translational order of a magnetic structure.

3. We found the rotation of the magnetic axis z in the plane (ac) of the magnetic $NaFe(WO_4)_2$ in the temperature interval (20—1.8 K).

4. The effects discovered by the magnetic and resonance studies are a consequence of the manifestation of both the monoclinic symmetry of the crystal and a low dimensionality of the magnetic structure.

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Received 06.07.05.
Translated from Ukrainian by V.V. Kukhtin

ЛОКАЛЬНІ МОДИ В НИЗЬКОВИМІРНОМУ МАГНЕТИКУ $NaFe(WO_4)_2$

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Резюме

Проведено магніторезонансні дослідження низьковимірної сполуки $NaFe(WO_4)_2$ в інтервалі частот 25—142 ГГц і температур 1,8—175 K. Виміряно частотно-польову залежність спектра АФМР вздовж легкої осі кристала і знайдено характерні параметри, які описують антиферомагнітне поглинання: $\nu_1 = (141 \pm 1)$ ГГц, $\nu_2 = (168,7 \pm 1)$ ГГц, H_{a1}=10,5 кЕ, H_{a2}=15 кЕ, $H_{\rm sf}$=(50±0,1) кЕ. Оцінено величину міжшарової обмінної взаємодії. Виявлено додаткове поглинання, пов'язане з локальними модами, які зумовлені порушенням трансляційного порядку у низьковимірній магнітній структурі. Досліджено температурну залежність головних значень магнітної сприйнятливості $NaFe(WO_4)_2$. Виявлено ефект кручення осей магнітної сприйнятливості в площині (ac) зі зміною температури, причиною якого є низька кристалічна симетрія та низька вимірність магнітної структури.