High-frequency dielectric and magnetic anomaly at the phase transition in NaV$_2$O$_5$

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We found anomalies in the temperature dependence of the dielectric and magnetic susceptibility of NaV$_2$O$_5$ in the microwave and far-infrared frequency ranges. The anomalies occur at the phase transition temperature $T_c$, at which the spin gap opens. The real parts of the dielectric constants $\epsilon_a$ and $\epsilon_b$ decrease below $T_c$, while $\epsilon_e$ remains constant. The change in $\epsilon_a$ is proportional to the square of the ordering parameter below $T_c$. The dielectric anomalies found indicate a redistribution of charges at the phase transition. The character of the dielectric constant anomalies is of the antiferroelectric type, which is in agreement with the models assuming the zigzag charge ordering in the $ab$ plane below $T_c$. The anomaly of the microwave magnetic losses is probably related to the coupling between the spin and charge degrees of freedom in vanadium ladders.

I. INTRODUCTION

Two inorganic compounds, CuGeO$_3$ and NaV$_2$O$_5$, were extensively studied as quasi-one-dimensional (1D) magnets containing the chains of spins $S = \frac{1}{2}$ coupled by the antiferromagnetic Heisenberg exchange. Both materials show 1D behavior of magnetic susceptibility at high temperatures and the phase transition into the spin-gap state at low temperatures. Furthermore, the opening of the spin gap below $T_c$ is accompanied by lattice deformations and, in particular, by the doubling of the lattice period in the chain direction.

The phase transition in CuGeO$_3$ is generally considered to be a spin-Peierls transition. The driving force of this transition is the collective spin-lattice instability with the gain in the energy of the spin chains exceeding the loss in the lattice energy. The experimental data on CuGeO$_3$ are in a good agreement with theoretical results for antiferromagnetic spin-$\frac{1}{2}$ chains coupled to the lattice. Some deviations from the ideal spin-Peierls behavior found for CuGeO$_3$ are also well understood. They are related to considerable interchain interactions (the interchain exchange is about 0.1 of the intrachain exchange) and the strong next-nearest-neighbor exchange (about 0.3 of the nearest-neighbor exchange).

For some time NaV$_2$O$_5$ was considered as the second inorganic spin-Peierls system. The 1D-magnetic structure of NaV$_2$O$_5$ was first associated with the chains of V$^{4+}$ ions (spin $S = 1/2$) along the $b$ axis of the orthorombic crystal separated by the chains of nonmagnetic V$^{5+}$ ions. This structure with inequivalent vanadium sites was recently questioned in Refs. 7–10. On the basis of the structure refinement studies of the high-temperature phase of NaV$_2$O$_5$, the ladder-type structure with equivalent V sites was suggested. The ladders are oriented along the $b$ axes with the rungs along the $a$ axis. There is one electron per rung and the spin-$\frac{1}{2}$ chains are formed by the electrons localized on V-O-V molecular orbitals on rungs and coupled by the exchange interaction along the $b$ direction. In this structure the charge of V ions fluctuates, its average value being 4.5.

Recent experimental data, as well as the theoretical arguments, suggest that the phase transition in NaV$_2$O$_5$ can be a result of some charge ordering rather than the spin-Peierls instability. Two kinds of such an ordering were considered. In the model of Ref. 12 the electrons below $T_c$ become localized on one leg of each ladder, as in the initially proposed high-temperature structure. In this model one has to invoke an extra mechanism to account for the spin gap at low temperatures. In the second model the electrons (or the V$^{4+}$ ions) form zigzags on each ladder. The opening of the spin gap in this scenario is a direct consequence of the charge ordering. The optical spectra of NaV$_2$O$_5$ (Refs. 15, 16) were first interpreted as an indication of the presence of inequivalent V sites even at room temperature. However, these spectra could also be explained by the presence of only a short-range charge order with relatively slow charge fluctuations. An extra confirmation that the phase transition in NaV$_2$O$_5$ is not an ordinary spin-Peierls transition comes...
from the study of thermal conductivity: in contrast to the
spin-Peierls system CuGeO₃, the thermal conductivity of
NaV₂O₅ has a huge anomaly below Tₚ, which can be natu-
really explained by the charge ordering.¹⁷
Further information about the behavior of the charge sub-
system close to the phase transition point can be gained by
studying the dielectric constant. Measurements of the dielec-
tric constant at the frequency of 1 KHz along three principal
directions were performed in Ref. 18. An anomaly with a
strong anisotropy with respect to the electric field orientation
signifying the rearrangement of the charge in NaV₂O₅ has
been found.

In this paper we present combined measurements of the
real and imaginary part of the dielectric and magnetic sus-
cceptibility of NaV₂O₅ at the microwave frequency of 36
GHz and of the refractive index in the far-infrared range. For
comparison the measurements of the same parameters were
performed also for CuGeO₃. Our results on NaV₂O₅ confirm
the presence of strong anomalies in the dielectric constant
along the a and c directions, although the type of the
anomaly for the c direction is different from the one found in
Ref. 18. The anomaly in εₐ is naturally explained by the
picture of the zigzag charge ordering suggested in Ref.
13,14. Possible reasons for the anomaly in εₐ are discussed
and further experiments to check this picture are suggested.

II. EXPERIMENT

We studied the complex microwave dielectric and mag-
netic susceptibilities by measuring the temperature depen-
dence of the resonance frequency and of the Q factor of the
microwave TE₁₀₄ cavity of the size 20×7.2×3.4 mm. The
resonance frequency f of the empty cavity is 36 GHz. The
presence of a sample shifts the resonance frequency of the
cavity. When the sample in the form of a thin plate is placed
at the maximum of the microwave electric field Eₘₜₑ, with
the plane of the plate parallel to the electric field, the reso-
nance frequency of the cavity should be shifted by the value
δf:

\[ \delta f = -2 \left( \frac{\epsilon' - 1}{V} \right) \nu. \]

Here ν, V are the volumes of the sample and of the cavity,
respectively, ε' is the real part of the dielectric constant.

When the sample plane is oriented perpendicularly to the
field Eₘₜₑ, the shift of the frequency is given by the relation:

\[ \delta f = -2 \left( \frac{\epsilon' - 1}{\epsilon' V} \right) \nu. \]

In this case the frequency shift is smaller due to the depolar-
ization factor effect. Formulas (1) and (2) are valid in the
quasistatic approximation when the sample is small in com-
parison with the length of the electromagnetic wave.

The imaginary part of the dielectric constant ε'' affects the
Q factor and results in a diminishing of the microwave
power U transmitted through the cavity. The relative change
of U is given by the relation:

\[ \frac{\delta U}{U} = -4Q \frac{\epsilon''}{V} \nu. \]

The analogous relations could be used to determine the
changes of relative magnetic permeability, \( \mu = \mu' + i\mu'' \), in
the case when the sample is placed at a maximum of the
microwave magnetic field.

The sample used for the microwave susceptibility mea-
surements had the dimensions 1×1×0.3 mm and, thus, was
much smaller than the half of the length of the standing
electromagnetic wave in the cavity (5 mm). This fact enables
us to separate the magnetic and dielectric susceptibilities by
positioning the sample at different points of the cavity. The a
and b directions were lying in the plane of the plate, the c
axis being perpendicular to the plate.

The change of the refractive index n with temperature was
measured in the frequency range between 1.2 and 3.0 THz
by registrating the interference pattern at different tempera-
tures in the transmittance spectra of thin (14–110 μm) plates
of NaV₂O₅ single crystals cleaved perpendicular to the c
direction. The spectra were measured using the BOMEM
DA3.002 Fourier transform spectrometer at a resolution of
0.2–2.0 cm⁻¹. The incident light was polarized either along
the a axis (E∥a) or along the b axis (E∥b). We have also
performed E∥c measurements at room temperature.

The position νₘ (in wave numbers) of the nth maximum
in the transmittance spectrum is given by the expression

\[ \nu_m = \frac{m}{2dn}, \]

where d is the thickness of the plate. We determined the
three principal values of the refractive index along the a, b,
and c axes by measuring the distance between the adjacent
maxima of the interference pattern.

The relative changes of the dielectric constant ε' were
found from the measured shifts of the interference maxima
according to the relation

\[ \frac{\delta \epsilon'}{\epsilon'} = 2 \frac{\delta n}{n} = -2 \frac{\delta \nu_m}{\nu_m}. \]

Single crystals of stoichiometric NaV₂O₅ used in our ex-
periments have been obtained by a melt growth method us-
ing NaVO₃ as a flux. The details of the growth procedure are
described in Ref. 19. Our samples were of the same growth
procedure as used in Ref. 20. The temperature Tₚ of the
phase transition obtained from the beginning of the magnetic
susceptibility drop is 36±0.5 K.

III. EXPERIMENTAL RESULTS

A. Microwave measurements

The shift of the resonant frequency of the cavity produced
by the sample at T = 40 K was of about 400 MHz both for
Eₘₜₑ∥b and Eₘₜₑ∥a. It corresponds to the dielectric constant
values \( \epsilon'_{a,b} = 12 \pm 1 \).

For Eₘₜₑ∥c, when the microwave electric field is perpen-
dicular to the plate, the shift of the resonator frequency was
only 40±15 MHz. Either the small value of ε' or the depo-
larization effect could result in this frequency shift which is
much smaller than in the case of Eₘₜₑ∥a or Eₘₜₑ∥b. Thus, the
FIG. 1. Temperature dependence of the real and imaginary parts of the dielectric constant at the frequency 36 GHz. The inset demonstrates the comparison of the measurements of $\epsilon'_a$ (present work) and of the intensity $I$ of the x-ray reflexes (Ref. 25): $\alpha = 1 - \delta \epsilon'_a(T)/\delta \epsilon'_a(45 K)$.

absolute value of $\epsilon'_c$ could not be estimated accurately enough: following the formula (2) we obtain the value $\epsilon'_c$ between 4 and infinity.

However, the frequency shift of the resonator at changing temperature can be measured with the accuracy of about 1 MHz and hence the relative change of $\epsilon_c$ at the phase transition was measured quite accurately. We used the value $\epsilon'_c = 8$ obtained in quasistatic measurements and in the far-infrared experiments described below, for the calculations of $\delta \epsilon_c$ according to the formula (2).

The temperature dependence of the change of the dielectric function was derived from the dependence of the resonator frequency shift with respect to the frequency at $T = 1.5 \text{ K}$. The value of the change of the imaginary part was derived from the temperature dependence of the transmitted signal relative to the reference value of this signal at 40 K.

The temperature dependence of the change of the dielectric susceptibility is shown in Fig. 1. The real part of the dielectric constants $\epsilon''_b$ decreases below the phase transition temperature, while the real part of $\epsilon_b$ does not show any observable change. The imaginary part of $\epsilon_b$ exhibits a well-pronounced peak. The change of the imaginary part of $\epsilon_d$ and $\epsilon_c$ were found to be smaller than the apparatus noise level.

A change in the response of the sample to the microwave magnetic field was only found for the imaginary part of the magnetic susceptibility. These data are close to those for $\epsilon''_b$ at zero frequency found earlier from the fitting of the reflectivity spectra of NaV$_2$O$_5$ single crystals by the model of independent oscillators.

Figure 3 shows the temperature dependence of the relative change of the refractive index at different far infrared frequencies for the electric field polarized along the $a$ and $b$ axes. Simultaneously with the decrease of the refractive index $n_a$, the absorption present in the low-frequency region of the far-infrared spectrum of NaV$_2$O$_5$ above $T_c$ decreases markedly when temperature decreases below $T_c$ (see the inset of Fig. 3 and Ref. 16). We checked that despite these changes of the absorption coefficient, Eq. (5) allows us to determine the changes of $n_a$ with sufficiently good precision. The relative change of the refractive index is of about 0.05 and corresponds to the change of the dielectric constant that is approximately twice as large as the value found at the microwave frequency of 36 GHz.

We have not found any observable changes of $\epsilon'_b$ (or $n_b$). Unfortunately, we could not observe the interference pattern for $E||c$ polarization at low temperatures and, hence, to detect the possible changes of $\epsilon'_b$.

FIG. 2. Temperature dependence of the change of the imaginary part of the magnetic permeability at the frequency 36 GHz.

IV. DISCUSSION

The observed dielectric anomalies could, in principle, arise from (i) an anomalous thermal expansion of NaV$_2$O$_5$ at $T_c$, (ii) a change of the lattice polarizability, and (iii) a rearrangement of electrons below $T_c$.

The change of the sample size at the phase transition was observed by studying the thermal expansion. The relative change of the sample size as temperature passes through the

FIG. 3. Temperature dependence of the relative change of the refractive index $n_a$ at the frequency 1.1 THz (□), 1.4 THz (△), 1.9 THz (▼), 2.2 THz (○), 2.6 THz (●), 2.8 THz (×), 3.1 THz (+), and $n_b$ at 3.1 THz (●). Inset presents the temperature dependence of the integrated intensity of the far-infrared absorption $I = \int_{1.8}^{12} \text{THz} \beta(v)d\nu$, $\beta$ being the absorption coefficient.
The coupled spin and charge degrees of freedom in vanadium ladders were described in Ref. 13 using the spin-isospin Hamiltonian. The isospin concept is introduced for the description of a charge ordering: isospin $t_i$ responds to the electron localized on one end of the rung $i$.

As for (ii), the changes in the lattice polarizability should be accompanied by the corresponding changes in the phonon spectrum below $T_c$. Our estimates show that the new modes that appear below $T_c$ cannot account for the observed change of $\varepsilon'$ due to their relatively small oscillator strengths.

Our data show that the phase transition in NaV$_2$O$_5$ is marked not only by the opening of a spin gap and by the lattice period doubling, but also by a strong dielectric anomaly. This dielectric anomaly indicates that the charge subsystem plays an important role in the phase transition and agrees with the conclusion about the charge ordering at $T_c$. Therefore, we believe that the models of the structure[13,15] that do not consider a charge ordering and which explain the opening of the spin gap as a result of the spin-Peierls transition are not adequate. Note that the spin-gap opening in CuGeO$_3$, which seems to be a conventional spin-Peierls material, is not accompanied by changes in dielectric susceptibilities, as follows from our measurements.

Furthermore, analyzing the form of the temperature dependence of $\varepsilon$, one can choose an appropriate model of the charge ordering. The model with a localization of electrons on one leg of the ladder[13,15] (see Fig. 4, bottom) with a formation of chains of localized electrons corresponds to the ferroelectric ordering with the spontaneous electric polarization along the $a$ axis. In this case the peak in the temperature dependence of $\varepsilon_i$ should be observed. Since the anomalies found in the real part of the dielectric constant have the form of steps (typical for the antiferroelectric transition) rather than peaks, we conclude that the charge ordering occurs without generation of a macroscopic dipole moment. Thus the experimental data agree with the antiferroelectric charge ordering in the form of the zigzag distribution of V$^{4+}$ ions as described in Refs. 13,14 (see Fig. 4, top).

The zigzag models developed in Refs. 13,14 result in the identical type of the charge ordering but differ in the mechanism of a spin-gap opening. In Ref. 13 the spin-gap opening is related to the alternation of the exchange integral along the ladder that results from the charge ordering, while in Ref. 14 the spin gap is explained by the formation of singlet pairs in the ordered phase due to interladder interactions. The present experimental data cannot provide arguments to choose between these two interpretations.

The concept of the zigzag charge ordering enables one to explain most general features of the observed data. The decrease of the dielectric constant $\varepsilon'$ can be attributed to the shrinking of the electron clouds along the $a$ direction due to the localization of electrons on the distinct V sites, instead of being smeared along the V-O-V orbitals. The observed diminishing of the optical absorption coefficient in the frequency range studied (1.2–3.0 THz) below $T_c$ is probably also connected with the above-mentioned shrinking of the electron clouds, the absorption itself being of an electronic origin (see, in particular, Ref. 23).

Using the Landau mean-field approach near $T_c$, one can show that the decrease of the dielectric susceptibility is proportional to the square of the charge order parameter, i.e., the value of $\delta\varepsilon'_a$ is proportional to the intensity of the additional x-ray reflections that appear at $T_c$. As shown in the inset of Fig. 1, there is, indeed, a good correlation below $T_c$ between $\delta\varepsilon'_a$ and the x-ray intensity measured in Ref. 25. There is some deviation of the data close to and above $T_c$—the value of $\delta\varepsilon'_a$ does not vanish at $T_c$ and shows a tail up to $T_\text{a} \approx 8$ K. This deviation above $T_c$ can naturally be ascribed to the existence of short-range charge ordered areas which are fluctuating in some frequency range. These fluctuations give rise to the dynamic dielectric susceptibility above $T_c$, but are averaged out and vanish when the susceptibility is measured on a large time scale as it was observed at 1 KHz in Ref. 18.

The nature of the behavior of the dielectric constant $\varepsilon'_i$ is less clear, especially in view of the difference in the anomaly of $\varepsilon'_i$ obtained in our measurements (see Fig. 1) and in the

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**FIG. 4.** Schematic form of the chain-type (bottom) and zigzag-type (top) charge ordering in NaV$_2$O$_5$ according to Ref. 13. Solid lines represent the possible paths of the electron hopping in ladders, circles mark maxima of the electron density in the ordered state. The directions of the local dipole moments appearing on the rungs of the ladders are marked by arrows on the left from the rungs.
quasistatic measurements of Ref. 18, where the $\lambda$-type anomaly was observed for $\varepsilon'_c$ instead of the steplike behavior shown in Fig. 1.

Both these measurements show the appearance of local dipole moments along the $c$ direction at the transition temperature. The possible origin of such moments may be, e.g., the shifts of the V ions within $O_5$ pyramids along the $c$ direction. The charge ordering (localization of the electrons on particular V ions) accompanied by the shifts of these ions along the $c$ direction can modify the local dipole moments in the $c$ direction.

From the crystal structure of NaV$_2$O$_5$ one would then again expect an antiferroelectric ordering of such dipoles, which would give the behavior of $\varepsilon'_c$ consistent with the one observed in the present work (see Fig. 1). The reason for different type of the $\varepsilon'_c$ anomaly observed in our measurements and in quasistatic measurements of Ref. 18 is not clear at present. A possible explanation might be related to the small but measurable conductivity of NaV$_2$O$_5$ single crystals. The conductivity has a large peak at $T_c$: it is 1.5 times higher than the conductivity both below and above $T_c$. The conductivity contributes only to the imaginary part of the microwave dielectric constant and at 40 K the contribution is of the order of $10^{-7}$. Thus, the conductivity is too small to affect the results of the microwave measurements. However, the influence of this small conductivity on the results of the electric capacity measurements at 1 KHz (Ref. 18) could be significant, because the observed value of conductivity results in the capacitor discharge time of about $10^{-3}$ s. Therefore, the electric-field potential within the capacitor might be disturbed by a leakage current and this fact might result in an additional change of the capacity. Further experiments are needed to elucidate this point and also to check whether the anomalies in $\varepsilon'_c$ are indeed related to the shifts of V ions along the $c$ axis below $T_c$ as argued above.

The picture of the phase transition in NaV$_2$O$_5$ as being mainly of the charge-ordering type with some degree of a short-range order persisting above $T_c$ is also qualitatively consistent with the behavior of the dielectric losses $\varepsilon''$ shown in Fig. 1. There should definitely exist slow enough charge fluctuations close to $T_c$, which would give rise to the dielectric losses. Why the anomaly in $\varepsilon''$ is most pronounced for the electric field directed along the $b$ axis is not clear yet.

Correspondingly, a coupling of the charge (and lattice) degrees of freedom to spins, definitely present in this compound, should result in magnetic losses, which were indeed observed (see Fig. 2). This coupling originates from the Pauli principle, which relates the symmetry of the spatial and spin parts of the wave function of two exchange-coupled electrons from the neighboring rungs of the ladder. As a result, triplet excitations on the ladder rungs could carry a dipole moment.

Note that the peak in the imaginary part of the magnetic susceptibility is of significant value and exceeds several times the value of the real part of the susceptibility at $T_c$. Therefore, the fluctuations of the spin gap alone could not explain the peak of magnetic losses and such a peak is indeed not observed in CuGeO$_3$, where the charge ordering is absent.

V. CONCLUSIONS

The anomalies of the dielectric and magnetic susceptibility in the microwave and far-infrared frequency range were found in NaV$_2$O$_5$. The pronounced dielectric constant anomaly and the peak in magnetic losses at $T_c$ indicate that the nature of the spin-gap opening in NaV$_2$O$_5$ is different from that of CuGeO$_3$. These anomalies are in agreement with the zigzag charge-ordering scenario of the phase transition in this material, while the models that do not involve a charge ordering below $T_c$ (Refs. 7,8), as well as the models with the ferroelectric charge ordering can be rejected.

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