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Low Frequency Excitations in Antiferromagnetic Tungstates ($NiWO_4$, $CoWO_4$)

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***Abstract*—Absorption spectra of biaxial antiferromagnets have been studied from 7.5 to 500 cm^{-1}. Ordering directions and the g tensor are determined. A new spin-wave branch and spin–phonon interaction will be described.**

I. INTRODUCTION—PROBLEM FORMULATION AND EXPERIMENTAL TECHNIQUE

THE transition metal tungstates have a low (monoclinic) symmetry crystalline lattice. They belong to the C_{2h}^4 space group [1], [2]. Under magnetic ordering they become biaxial collinear antiferromagnets [3] and have the sufficiently high Néel temperature (T_N = 67 K for $NiWO_4$ [4] and T_N = 55 K for $CoWO_4$ [4], [5]). It is important to remember that the ground state of Ni^{2+} is $^3F_4$, and that of Co^{2+} is $^4F_{9/2}$.

According to the results of measuring magnetic, resonance, and optic properties of $NiWO_4$ [6], [10], $CoWO_4$ [5], [7], and isostructural $ZnWO_4$ containing cobalt or nickel [6], [8], [9], the crystal field potential at the magnetic ion site possesses considerable axial and orthorhombic components. This along with the fact that magnetic ion spin exceeds 1/2 (S = 1 for Ni^{2+} and S = 3/2 for Co^{2+}) permits the excitation of both antiferromagnetic resonance (AFMR) modes and a higher frequency spin branch. This follows from the recent theoretical work [11].

The frequencies of AFMR modes and the new high frequency branch should lie within far IR since both the anisotropy energy and exchange interaction are high in this crystal. Thus the estimate of the effective exchange interaction field H_{eff} from the magnetic susceptibility $\chi_\perp$ which was measured along the direction perpendicular to the spontaneous ordering is ~600 kOe for $NiWO_4$ [10]. In this connection the absorption spectra of nickelous and cobaltous tungstates were studied in the far IR (7.5–500 cm^{-1}). The spectrometer [12] composed of an evacuated grating monochromator, cryostats for cooling the sample and detector, and an electric magnet or superconducting solenoid, permitted the measurement resolution of 0.1 cm^{-1} in the vicinity of the long wavelengths and of about 1 cm^{-1} near the short wavelengths, the magnetic field being $H_0 \leq 50$ kOe. The sample temperature could vary from 5 to 300 K.

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II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Antiferromagnetic Resonance

We identify the lowest frequency absorption bands in the $CoWO_4$ and $NiWO_4$ as AFMR modes [13], [14]. Their characteristics are listed in Table I and the spectrum type is shown (for $NiWO_4$) in Fig. 1. The bands observed are polarized, and the polarization character is indicative of their magnetic dipolar nature. In the external magnetic field the AFMR frequencies are shifted. The frequency shift in the external magnetic field is anisotropic [Fig. 2(a)]. When the field is oriented along the monoclinic twofold axis $b(Y)$ and along the direction

TABLE I
CHARACTERISTICS OF AFMR MODES (T = 5 K)

		ν_{max} (cm^{-1})	Polarization	Magnetic shift (cm^{-1}) at 18 kOe	Full width (cm^{-1})	Integrated intensity (cm^{-2})	Angle between c and z	g_{zz}	g_{xx}	g_{yy}
$CoWO_4$	High frequency mode	79.3	$h_\omega \parallel b$	+2	0.9	120 ± 15	40° ± 5°	6.3	3.15	4.8
T_N = 55 K	Low frequency mode	67	$h_\omega \parallel x$	−2.3	1.4	180 ± 20				
$NiWO_4$	High frequency mode	22.4	$h_\omega \parallel b$	+1	<0.15	~40	15° ± 3°	2.26	2.15	2.15
T_N = 67 K	Low frequency mode	17.9	$h_\omega \parallel x$	−1	<0.15	~80				

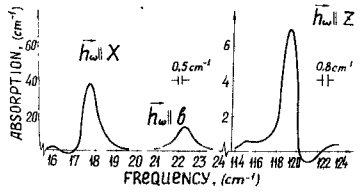
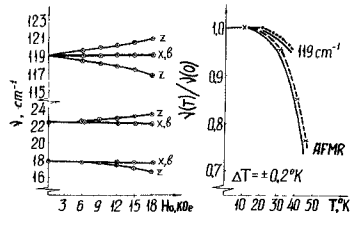


Fig. 1. Antiferromagnetic $NiWO_4$ absorption spectrum (observed contours); h_ω is the magnetic vector of the plane-polarized wave. X and Z are the magnetic axes.



(a) (b)

Fig. 2. Dependence of $NiWO_4$ absorption line frequency on the magnetic field strength (a) and temperature (b). —— — theory; —◎—; —·—; —×— — experiment.

X perpendicular to this axis the shift does not occur. It is maximum along the Z direction in the ac plane which makes an angle α with the unit cell direction **c**. This direction is also characterized by the minimum static magnetic susceptibility [5], [7], [10]. Thus the Z direction is naturally considered the spontaneous magnetic ordering axis.

Although the magnetic ordering leads to an increased magnetic cell size, as compared to the crystallographic one [3], the spin moments are grouped in pairs and allow two collinear magnetic sublattices to be distinguished. Hence, we shall consider the crystals in question as collinear two-sublattice antiferromagnets with the ordering direction along the Z axis. Since the magnetic axes X, Y, and Z are mutually perpendicular, the magnetic properties of the monoclinic tungstates can roughly be described by the orthorhombic symmetry Hamiltonian. Earlier we employed the phenomenological model for describing magnetization and resonance in $CoWO_4$ [13]. This description is also valid for $NiWO_4$. The comparison between the theory and experiment provides the possibility of finding a number of parameters for the phenomenological Hamiltonian. In particular, the diagonal components of g tensor (Table I) have been calculated from the AFMR mode behavior in the external field [Fig. 2(a)].

B. Excitation of the New Spin-Wave Branch in $NiWO_4$ Spectrum

In addition to the two AFMR modes another magnetic dipolar band is observed in the $NiWO_4$ absorption spectrum (Fig. 1). The polarization ($h_\omega \parallel Z$ axis), considerable intensity, and the maximum frequency ν_{max} = 119 cm^{-1} close to the doubled exchange energy ($\nu_{exc} \simeq 60$ cm^{-1} [6]) serve as grounds for identifying the band observed as a new spin-wave resonance changing the magnetic quantum number to 2 ($\Delta M_s = 2$).

To establish the conditions allowing the transition to additional spin-wave branch, we shall consider a simple model for splitting the Ni^{2+} ground state level in effective exchange field H_{eff}. In doing so we shall take the account of the single ion anisotropy which was described by the Hamiltonian

$$\hat{\mathcal{H}} = \gamma \hat{S}_z^2 + \epsilon(\hat{S}_x^2 - \hat{S}_y^2).$$

Here, γ and ϵ are the single ion axial and orthorhombic anisotropy constants, respectively. Within the frameworks of this model the energy level of the Ni^{2+} ground state splits into three levels corresponding to the $S = 1$ spin projections ($M_s = 0, \pm 1$). In the absence of the single ion anisotropy ($\gamma = \epsilon = 0$) the $M_s = -1$ and $M_s = +1$ levels are situated above and below the $M_s = 0$ level, respectively; they are equally remoted from the central level by $g\mu_B H_{eff}$ (μ_B is the Bohr magneton), Fig. 3. In this energy scheme only magnetic dipolar transitions with $\Delta M_s = 1$ in the transverse polarization of a magnetic vector ($h_\omega \perp Z$) are allowed. The transition between the $M_s = +1$ and $M_s = -1$ levels at $\gamma = \epsilon = 0$ is forbidden for any polarization of an incident light. The single ion axial anisotropy cannot allow the $\Delta M_s = 2$ transition, though it changes the energy gaps between the $M_s = 1$ and $M_s = 0$ levels and $M_s = -1$ and $M_s = 0$ ones. However, the orthorhombic single ion anisotropy lifts the forbiddeness for the transition between the extreme levels ($M_s = 1$ and $M_s = -1$), since the term $\epsilon(\hat{S}_x^2 - \hat{S}_y^2)$ mixes the $M_s = +1$ and $M_s = -1$ states. The effect is analogous to the appearance of the "forbidden" transitions in the electron spin resonance (ESR) spectrum of

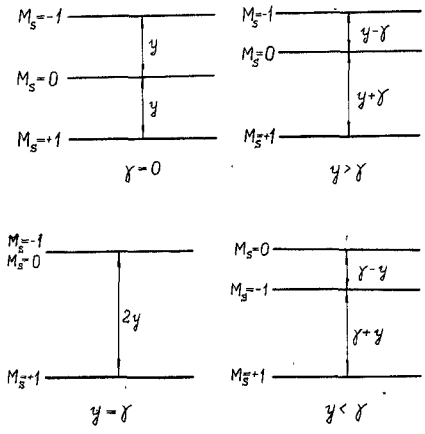


Fig. 3. Energy level scheme for an isolated spin S with different relations between the exchange interaction parameter y and axial single ion anisotropy γ.

TABLE II
ABSORPTION BANDS OF $CoWO_4$ (T = 5 K)

Frequency (cm^{-1})	Polarization	Field effect $H_0 \| Z$	Full width at half maximum (cm^{-1})	Intensity
90	$e_\omega \| z$[a]	nonlinear shift (+4.5 cm^{-1} at 18 kOe)	0.75	weak (3.3 cm^{-2})
137.4	$e_\omega \| x$[a]	splitting 1.3 cm^{-1}/kOe	<1.6	weak
140.4	$e_\omega \| z$[a]	weak shift	<1.6	weak
160.4	$e_\omega \| c$	no reaction	0.9	average (21 cm^{-2})
167[b]	$h_\omega \| a$	no reaction	exists at $T \geq 35$ K T = 41 K 1.9	6 cm^{-2}
168.5	$e_\omega \| b$	splitting 0.9 cm^{-1}/kOe	0.9	12.5 cm^{-2}
173.4	$h_\omega \| a$	no reaction	0.6	strong (40 cm^{-2})
187.4	$h_\omega \| b$	no reaction	<1.6	strong
203.7	$e_\omega \| c$[a]	no reaction	<1.9	strong
218.3	$e_\omega \| c$[a]	no reaction	<1.6	strong

[a] Expected polarization; complete polarized radiation experiments cannot be done on the former due to the strong lattice absorption.
[b] All lines, 167 cm^{-1} excluded, disappear at $T < 40$ K.

the single Ni^{2+} in the low symmetry crystalline field. In the antiferromagnetic crystal this transition corresponds to the excitation of the spin-wave mode without preservation of the spin Z projection.

In terms of the perturbation theory one may show that the intensity of the $\Delta M_s = 2$ transition, whose frequency corresponds to the doubled exchange energy, is proportional to $(\epsilon/H_{eff})^2$, and has the longitudinal polarization $h_\omega \| Z$. Involving the external magnetic field $H_0 \| Z$ should lead to shifting the $M_s = +1$ and $M_s = -1$ levels to the opposite sides. As a result the new band with the frequency equal to the doubled exchange energy splits in the external field $H_0 \| Z$ into two components, the splitting value being twice as much as that for the $\Delta M_s = 1$ transition (i.e., AFMR). This was observed experimentally [Fig. 2(a)].

A more detailed theoretical calculation of the spin-wave spectrum for the antiferromagnet with $S = 1$ was carried out in [11] for $NiWO_4$. We shall omit the cumbersome calculation and note that a rigorous calculation gives a qualitative picture analogous to that Ni^{2+} described earlier in terms of the simple molecular field model taking into the account the orthorhombic single ion anisotropy. Using theoretical formulas [11] and experimental values of the AFMR and spin-wave branch frequencies one may estimate the axial and orthorhombic anisotropy constants $\gamma \simeq 3.4$ cm^{-1} and $\epsilon \simeq 0.75$ cm^{-1}. These are close to the values in the spin Hamiltonian $ZnWO_4 + Ni^{2+}$ which were found from the ESR measurements [9].

The experimental data and theoretical dependences [11] for temperature are shown in Fig. 2(b). The agreement is satisfactory.

C. Obscure Peculiarities of $CoWO_4$ Spectrum

In addition to the AFMR modes, the $CoWO_4$ absorption spectrum has a number of bands in the far IR. Their origin is still obscure. The band characteristics are listed in Table II. It is quite possible that some of them result from the impurity and defect presence in the crystals. One should bear in mind, however, that in the investigating frequency range optic Raman phonons are disposed [15], [16]. Their excitation under absorption is forbidden by

the parity selection rules. However, having the frequencies close to those of the electronic (magnon) transitions, the Raman phonons may mix up with the electronic excitations and become allowed even in the electric dipolar approximation. Just the results of the magnetic susceptibility studies [7] show that in addition to the magnon frequencies 67 and 79.3 cm^{-1}, this region of the $CoWO_4$ spectrum must contain electronic transitions at ~290 and ~300 cm^{-1}. The strong effect of the external field $H_0 \parallel Z$ on the frequencies of some of the bands requires special consideration.

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Far-Infrared Properties of Interacting Donors in Antimony-Doped Germanium

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***Abstract*—Absorption and photoconductivity of 337-μm radiation in Sb-doped Ge with excess donor concentrations ranging from 1.2×10^{16} to 3.6×10^{17} cm^{-3} have been investigated at liquid-He temperatures. The result suggests the existence of a "delocalized" excited state between the conduction band and the donor ground state which arises from the overlapping of donor wave functions.**

I. INTRODUCTION

ESSENTIAL PARTS of information about the impurity state in semiconductors can be obtained through studying their far-infrared properties. Investigations in this field on impurity centers in semiconductors have been restricted so far to the point where the impurity concentration is so low that the interaction between centers can be ignored.

The purpose of the present investigation is to study the far-infrared properties in semiconductors in which the impurity centers are interacting. One of the most interesting problems is impurity conduction in the intermediate impurity-concentration region where the resistivity is characterized by an activation energy ϵ_2 at low temperatures [1], as is shown in Fig. 1. The activation energy ϵ_2 depends strongly on the impurity concentration [1], magnetic field [2]–[6], deformation [7]–[10], and compensation [11], [12] in contrast to the donor ionization energy ϵ_1 and the activation energy ϵ_3 for hopping-type conduction. These behaviors of ϵ_2 have been understood in terms of the change in the overlapping of donor wave functions, and ϵ_2 has been supposed to be an energy needed to excite electrons from the donor ground state into the

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