At higher pressures, the sample consists apparently of a mixture of two or three superconducting modifications with larger values of $\partial H_c/\partial T$. The presumed existence of several superconducting modifications of P agrees with the notion that among the crystalline modifications that are stable at high pressures there should also be modifications with a structure analogous to the structure of the superconducting modifications of Bi and Sb [6] *.

Additional detailed investigations are necessary to clarify this question.

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LONG-WAVE INFRARED ABSORPTION IN ANTIFERROMAGNETIC CoWO4

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Cobalt tungstate $CoWO_4$ has a rhombic structure. Below $T_N = 55°K$ it goes over into an antiferromagnetic state [1]. Since the exchange energy ($\gamma H_E \sim kT_N$) is large, and apparently the magnetic-anisotropy energy is large (this is usual for antiferromagnetic compounds containing the ion Co^{2+}), we can expect both antiferromagnetic resonance and two-magnon absorption to lie in the far infrared [2-4,7,8]. If this is the case, then it becomes possible to determine in a single experiment the extremal frequencies of the spin-wave spectrum, both at the center of the Brillouin zone ($|\vec{k}| = 0$) and on its boundary ($|\vec{k}| = \pi/\alpha$).

In this paper we report the results of an investigation of the absorption spectrum of $CoWO_4$ in the frequency region 20 - 200 cm^{-1} and in the temperature range from 10 to 100°K. The experiment was performed with a previously described setup [5] that makes it possible to carry out low-temperature investigations in polarized radiation in stationary magnetic fields up to 25 kOe.

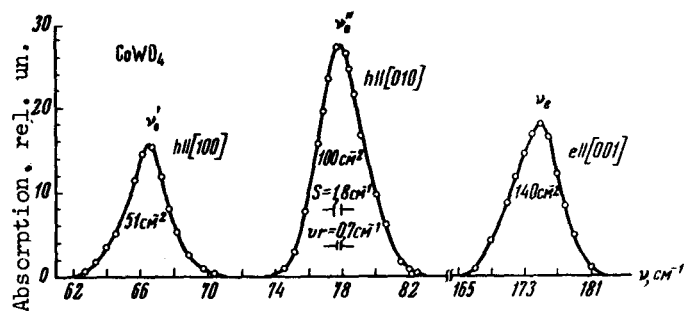Figure 1 shows the absorption bands observed only for the magnetically ordered $CoWO_4$.

Fig. 1. Absorption spectra of antiferromagnetic $CoWO_4$ in the far infrared region. $T = 22 \pm 3°K$, $T_N = 55°K$. The frequencies of the absorption peaks are corrected for $v\tau$.

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* Unfortunately, the phase diagram of phosphorus was investigated only up to a pressure of 150 kbar.

The use of polarized light and single-crystal samples with different orientations has made it possible to establish that the bands ν_0' and ν_0'' have a magnetic-dipole character, and the band ν_e has an electric-dipole character. The orientations of the magnetic or the electric vector of the light wave, at which the corresponding bands have a maximum density, are indicated in Fig. 1. The same figure indicates the tentative integral intensities in cm^{-2}. The spectra take into account the spectral distribution of the spectrometer intensity, and also the lattice absorption of the crystal.

In addition to investigating the dichroism of the observed bands, we investigated the influence exerted on these bands by an external magnetic field and by the temperature. The results of these investigations will be published in detail later. We note here that in an external field the bands ν_0' and ν_0'' shift in such a way that the interval between them increases by 4.2 cm^{-1} in a field $H = 20$ kOe, and the band ν_e does not respond to a field $H \leq 20$ kOe. All three bands shift to the long-wave side and broaden greatly when heated above $30 - 35°K$, so that at $45°K$ they are hardly distinguishable from the background.

The experimental results enable us to identify the bands ν_0' and ν_0'' with excitation of antiferromagnetic resonance, and the band ν_e with two-magnon absorption.

This identification is based on the following considerations. $CoWO_4$ has a crystallo-graphic structure of orthorhombic symmetry (D_{2h}). Each unit cell contains two magnetic ions Co^{2+}. Therefore $CoWO_4$ can be regarded as a biaxial orthorhombic antiferromagnet with two magnetic sublattices. The behavior of the antiferromagnetic-resonance frequencies of such an antiferromagnet in an external magnetic field (without allowance for the Dzyaloshinskii interaction) was investigated by Zarochentsev and Popov [6]. Our calculation shows that allowance for the Dzyaloshinskii interaction does not change the picture qualitatively. In a zero electric field the resonance should be observed at two frequencies; with increasing intensity of the external field, which is oriented along the ordering axis, the high-frequency and the low-frequency components of the antiferromagnetic resonance shift in opposite directions, and the interval between them increases. The character of the polarization of the AFMR bands should be magnetic-dipole, and if the magnetic vector h of the wave is polarized along a, b, and c (the axes of the rhombic $CoWO_4$), the ratio of the integral intensities (including both bands) should be proportional to the ratio of the static susceptibilities, measured along the same directions, i.e., $S_a : S_b : S_c = X_a : X_b : X_c$. This can be readily obtained from the Kramers-Kronig relation (see, e.g., [2]). Good agreement is observed for $CoWO_4$ if the data of [1] on the magnetic susceptibility are used. The behavior of the frequencies in an external magnetic field agrees with the results of the calculation [6]. Nor do the temperature dependences of the frequencies of these bands contradict the assumption that the bands ν_0' and ν_0'' are due to AFMR excitation. Both bands vanish near T_N.

Proceeding to the interpretation of the ν_e band, it should be recalled that the two-magnon absorption bands due to simultaneous excitation of two spin waves with oppositely directed wave vectors $\vec{k}_s$ have an electric dipole character and do not respond to an external magnetic field [3,4]. The ν_e band has precisely the same features. Its behavior with in-
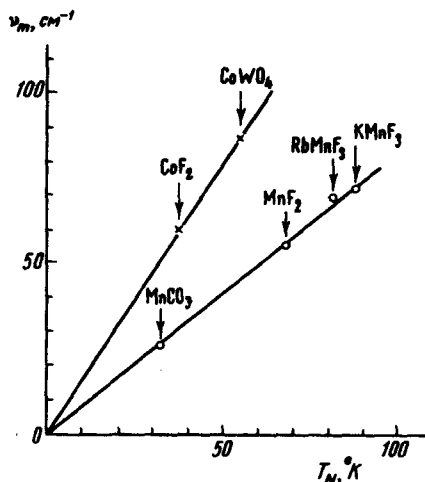
Fig. 2. Dependence of the max-
imum frequencies in the spin-
wave spectrum of the Neel tem-
perature T_N.

creasing temperature and the spectral position also agree with the proposed identification. Figure 2 shows the values of the frequencies of the two-magnon absorption of CoF_2 [3], MnF_2 [7], and $MnCO_3$ [8], decreased by one half, and the frequencies of the spin waves with maximum momentum $|\vec{k}| = \pi/\alpha$, determined in $RbMnF_3$ and $KMnF_3$ [9] with the aid of neutron scattering. The same figure shows the value, decreased by one half, of the frequency ν_e of the absorption band under consideration. It agrees well with the value expected by assuming that ν_e is due to two-magnon absorption and is equal to $2\nu_m$. The fact that the plot of the maximum magnon frequency ν_m against the magnetic-ordering temperature T_N is steeper for antiferromagnetic cobalt compounds than for manganese compounds is apparently due to the appreciable contribution of the magnetic-anisotropy energy to ν_m for the former case (i.e., Co^{2+}) *.

Thus, the aggregate of the experimental facts confirms the proposed identification of the observed absorption bands in $CoWO_4$: ν_0' and ν_0'' are AFMR bands and ν_e is a two-magnon absorption band. We note that no such bands were observed in the $ZnWO_4$ investigated by us, which is similar in structure to $CoWO_4$ but contains no magnetic ions.

Assuming such an identification, we determine directly the extremal values of the spin-wave spectrum of $CoWO_4$: the spectrum splits near $\vec{k} = 0$ into two branches with frequencies $\nu_{k=0}' = \nu_0' = 66.4$ cm^{-1} and $\nu_{k=0}'' = \nu_0'' = 77.7$ cm^{-1}, and the frequency on the edge of the Brillouin zone is $\nu_m = \nu_e/2 = 87.5$ cm^{-1}. The frequencies are accurate to ± 0.2 cm^{-1}.

In conclusion, we take the opportunity to thank B. I. Verkin for continuous interest in the work.

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* Thus, for example, in the case of fluorides with rutile structure, we have $\nu_m = \gamma(H_E + H_A)$ [3,4], where H_E and H_A are the effective fields of the exchange interaction and of the magnetic anisotropy, respectively.