

Shift of Curie temperature of the compound  $\text{Eu}_{0.96}\text{Gd}_{0.04}\text{O}$  with change of pressure.

the character of its pressure dependence agrees both qualitatively and quantitatively with that observed for  $\text{EuO}$ .

If we assume, in accord with the foregoing, that the magnetic state of single-crystal  $\text{Eu}_{0.96}\text{Gd}_{0.04}\text{O}$  is determined by the superposition of the ferromagnetic exchange interaction between the localized magnetic moments of the  $\text{Eu}^{2+}$  ions, which is not connected with the conduction electrons, and the indirect exchange via the conduction electrons, then we can conclude that under hydrostatic compression up to 10 kbar only the energy of the former type of interaction changes appreciably. The indirect exchange interaction via the conduction electrons obviously makes no noticeable contribution to this effect.

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#### CONDUCTION MECHANISM OF HIGHLY-CONDUCTING ORGANIC COMPLEXES BASED ON TCNQ

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Organic complexes based on tetracyanquinodimethane (TCNQ) are of interest as possible objects permitting realization of Little's idea of a superconductivity of a non-phonon type [1]. Certain complexes of this class have at room temperature a high conductivity ( $\sim 10^2$   $\text{ohm}^{-1}\text{cm}^{-1}$ ) along the directions of the stacks of TCNQ molecules [2], and there are grounds for hoping that when a second easily-polarized component is introduced into the complex, an

conductivity and of the coefficient of the thermal emf of  $\text{Eu}_{0.96}\text{Gd}_{0.04}\text{O}$  corresponds in accordance with our data to metallic conductivity.

The procedure for measuring the ferromagnetic Curie temperature at a quasi-hydrostatic pressure up to 12 kbar was described by us in [3]. The Curie temperature of the compound  $\text{Eu}_{0.96}\text{Gd}_{0.04}\text{O}$  increases linearly with the pressure in this pressure range (see the figure), the baric coefficient being  $d\theta/dp = (4 \pm 0.5) \times 10^{-4}$  deg/bar. Comparison of this result with our data for  $\text{EuO}$  of stoichiometric composition [3] shows that although the Curie temperature of the  $\text{Eu}_{0.96}\text{Gd}_{0.04}\text{O}$  single crystals is almost double that of  $\text{EuO}$  crystals,

organic superconductor may be realized [3]. There is little known at present on the conduction mechanism of this class of compounds. The fact that the magnetic susceptibility of certain highly-conducting complexes changes little over a rather wide temperature range [4] gave grounds for stating [2, 4] that such complexes have a degenerate - metal-type - system of carriers with a concentration corresponding to one spin per molecule. It will be seen from our results, however, that this statement are apparently in error.

We investigated the electric, magnetic, and optical properties of the TCNQ complex with phenazine [5], whose single crystals have a room-temperature conductivity  $\sigma_{\text{room}} = (1.7 \pm 0.3) \times 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$ . Formally, each molecule of the complex contains an unpaired spin, but the paramagnetic susceptibility  $\chi_{\text{para}}$  at room temperature (the diamagnetism of the core was calculated here and below in accordance with Pascal's rules) is several times smaller than that calculated in accordance with the Curie law assuming one spin per molecule. This means that the main spin system of the sample is coupled by strong interaction. It is therefore most natural to ascribe the increase that takes place in  $\chi$  at low temperatures, as is seen from the lower part of Fig. 1, to the presence in the sample of a small amount of localized spins obeying the Curie or the Curie-Weiss law. However, the variation of the susceptibility in the entire temperature range (1.6 - 300°K) cannot be described by a formula of the Curie-Weiss type, since the decrease of  $\chi$  at  $T > 4 - 5^\circ\text{K}$  is slower than called for by this formula. This suggests that additional contributions, missing at helium temperatures, are made to the susceptibility with increasing temperature.

To separate these high-temperature contributions, we determined the parameters of the

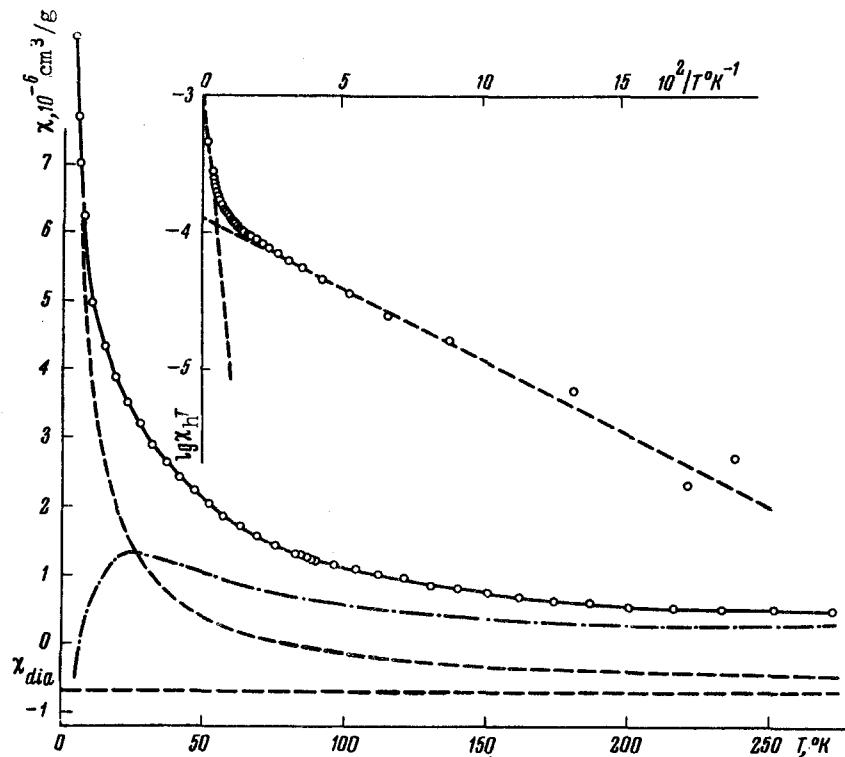


Fig. 1. Temperature dependence of susceptibility

Curie-Weiss law  $\chi_{loc} = C/(T + \theta)$ , which describes the temperature variation of  $\chi_{para}$  in the interval 1.68 - 4.22°K ( $\theta = 1.7^\circ\text{K}$ , and C corresponds to approximately 3% of the spins per mole). We then calculated the high-temperature part of the susceptibility  $\chi_h = \chi_{para} - \chi_{loc}$ . The results of such a resolution are shown dashed in the lower part of Fig. 1. It is seen from the plot in the upper part of Fig. 1 that the dependence of the quantity  $\chi_h T$  on  $1/T$  can be approximated by two exponentials. The activation energy of the low-temperature exponential, equal to  $25 \pm 5^\circ\text{K}$ , agrees well with the gap  $\Delta = 50^\circ\text{K}$ , observed in the optical-absorption spectrum of highly-conducting complexes of this type [6]. The increase of  $\chi_h T$  in this region of temperatures is therefore naturally connected with transitions of electrons to the conduction band, leading to an increase of the carrier density in accordance with the law  $n_e \sim \exp(-\Delta/2T)$ , inasmuch as there is so far no degeneracy  $\chi_h T = 2n_e \mu_B^2/K$ , where  $\mu_B$  is the Bohr magneton and K is Boltzmann's constant.

The increase of  $\chi_h T$  at high temperatures, which occurs with an activation energy  $400 \pm 100^\circ\text{K}$ , cannot be connected with the transition of the carriers from the valence into the conduction band, since the optical-absorption spectrum in the corresponding energy region has no singularities whatever. The intense interband transitions begin at energies higher than  $2000^\circ\text{K}$ . The increase of  $\chi_h T$  in this temperature region must therefore be ascribed either to incipient degeneracy or to the unfreezing of the main system of spins of the substance, or else to both jointly. In either way, however, we probably obtain approximately true values of the carrier density in the entire temperature range if we calculate them by means of the

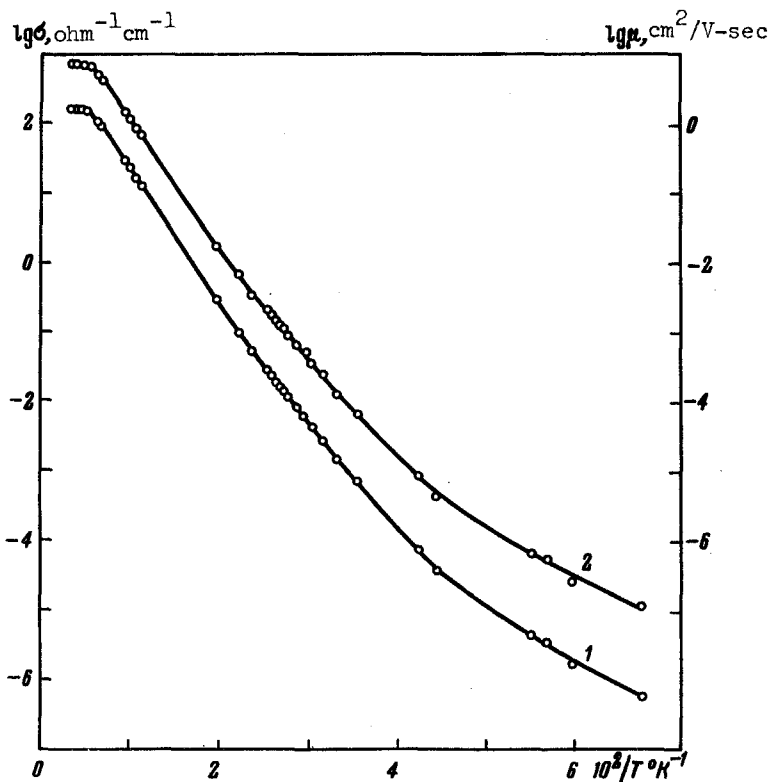


Fig. 2. Temperature dependence of the conductivity (1) and of the mobility (2).

formula  $n_c = \chi_h T \cdot K / 2\mu_B^2$ , taking for  $\chi_h T$  the values obtained by extrapolation of the low-temperature exponential into the region of higher temperatures.

Figure 2 shows the temperature dependence of the measured conductivity  $\sigma$  of the single crystals (curve 1) and the mobility  $\mu$  (curve 2) calculated using the concentration data obtained by the method described above ( $n_c = 1.4 \times 10^{20} \text{ cm}^{-3}$  at  $T = 300^\circ\text{K}$ ). The nearly exponential dependence of  $\mu$  on  $1/T$  does not demonstrate in this case a jump conductivity mechanism. The conductivity may be connected, for example, with the presence of potential barriers produced by defects in the linear conducting chain. The data at our disposal are not sufficient for a final answer to this question.

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#### OPTICAL PROPERTIES AND STIMULATED EMISSION OF $\text{Nd}^{3+}$ IN FLUOR-APATITE

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The optical properties and the stimulated emission of the ion  $\text{Nd}^{3+}$  were investigated in a large number of crystals of simple and complex fluorides and oxides. Fluor-apatite (FA)  $\text{Ca}_5(\text{PO}_4)_3\text{F}:\text{Nd}^{3+}$  is a new fluoride-oxide system containing both fluorine ions and oxygen ions. Information on the properties of FA crystals and their laser characteristics, which in certain respects are unique, are given in [1].

Crystals of this compound were recently synthesized and investigated in the Oscillation Laboratory of our institute. FA crystals, both pure and doped with  $\text{Nd}^{3+}$ , were grown from the melt by the Czochralski method from a platinum-rhodium crucible (30% Rh, 70% Pt). The initial substances were calcium orthophosphate and calcium fluoride. The crystals were grown in an atmosphere that prevented the reduction of the phosphorus or the loss of the fluorine. The linear growth rate was 9 mm/hr. We investigated the absorption and luminescence spectra of the grown crystals at 300, 77, and  $4.2^\circ\text{K}$ , and also the radiative lifetime  $\tau_{\text{rad}}$  of the  $^4\text{F}_{3/2}$  level at 300 and  $77^\circ\text{K}$ . The spectral measurements on the crystal with  $\text{Nd}^{3+}$  concentration 0.5% yielded the scheme of the crystalline splitting of the levels  $^4\text{I}_{9/2}$ ,  $^4\text{F}_{3/1}$ ,  $^4\text{F}_{5/2}$ ,  $^2\text{H}_{9/2}$ , and  $^4\text{F}_{7/2}$ ,  $^4\text{S}_{3/2}$ , as shown in Fig. 1. The level positions correspond to  $T = 77^\circ\text{K}$ . The scheme constructed in accordance with our data differs somewhat from the scheme constructed in [1]. The  $^4\text{I}_{9/2}$  level splits into five components, in agreement with the theory, making it unnecessary to interpret a number of levels in [1] as due to the