

not discuss further this effect, which is the special case of surface ordering.<sup>[5]</sup>

The possibility of the existence of surface superconductivity in dielectrics is very interesting. If the surface levels at  $T = 0$  are not filled under normal conditions,<sup>[6]</sup> they can be partly filled by charging the surface; under favorable conditions, the attainable surface-charge density  $\sigma \sim en \sim 10^4$  may be sufficient for this purpose (here  $n \sim 10^{14}$  is the number of filled surface levels per unit area). In general, the number of surface levels per unit area is of the order of the number of atoms, i.e.,  $n \sim a^{-2} \sim 10^{15}$ . Therefore, in the majority of cases, it is not possible to fill artificially the surface band.

The influence of a magnetic field and of a current on the surface superconductivity can be understood qualitatively by assuming that we are dealing with the usual superconducting film whose thickness is, however,  $l \sim a \sim 3 \times 10^{-8} \sim 10^{-7}$  cm. The critical field in the film<sup>[7]</sup> is  $H_C = (\sqrt{24} \delta_0 / l) H_{Cm} \sim 10^3 H_{Cm} \sim 10^{-5}$  Oe, if the "volume" values  $\delta_0 \sim 10^{-5}$  cm and  $H_{Cm} \sim 10^2$  Oe are used for the surface superconductivity.<sup>2)</sup> In the cylindrical geometry case<sup>[7]</sup>,  $H_C H_{Ic} = \frac{8}{3} H_{Cm}^2$ , where  $H_{Ic}$  is the field on the surface of a cylinder with radius  $r$  for a critical current  $I_c = \frac{1}{2} cr H_{Ic}$ . Under these conditions  $H_{Ic} \sim 10^{-3} H_{Cm} \sim 0.1$  Oe.

<sup>1)</sup>Here and later we assume, as usual, that the region of interaction is of width  $2\omega_D$  near the Fermi boundary ( $\omega_D$  is the Debye frequency). The field operators in Eq. (1) are two-dimensional and the symbol  $d^2$  represents a two-dimensional differential.

<sup>2)</sup>The film is assumed to be an open surface (we are considering a superconducting region of the crystal surface between two contacts). If the film is closed, its behavior in an external field is more complex (see<sup>[8]</sup>).

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## INVESTIGATION OF THE MAGNETIC PROPERTIES OF DIBENZENCHROMIUM AND DITOLUENCHROMIUM IODIDES AT VERY LOW TEMPERATURES

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IN an earlier work<sup>[1]</sup>, the present authors and Chibrikov investigated the hyperfine interaction of an unpaired electron with the protons in the molecules of paramagnetic cations of dibenzenechromium (DBC) and ditoluenechromium (DTC) and measured their magnetic susceptibility in the temperature range from 1.3 to 295°K. It was found that the unpaired electron in these compounds was localized mainly at the chromium atom and that the magnetic susceptibility of these compounds in the cited temperature range obeyed the Curie-Weiss law  $\chi = C/(T - \Theta)$ , where  $\Theta_{DBC} = -4.6 \pm 0.2$  deg K and  $\Theta_{DTC} = -2.0 \pm 0.2$  deg K, and the value of the constant  $C$  represents one electron spin per molecule.

It was of interest to extend these measurements to very low temperatures. For this purpose, we constructed a device which made it possible to investigate the proton resonance in the temperature range from 0.1 to 1.5°K. Very low temperatures were obtained by adiabatic demagnetization of iron-ammonium alum. The investigated powder sample was in a small glass ampoule; a copper cold duct entered the ampoule and its other end was pressed in the usual way into a pellet of the paramagnetic salt. Thermal contact between the sample and the cold duct was ensured by filling the ampoule containing the sample with carbon tetrachloride.

The pellet and the sample were in an hermetically sealed glass jacket, into which a small amount of helium was admitted at room temperature; at very low temperatures, the helium was sorbed by the alum, which ensured thermal insulation between the sample assembly and the helium bath. The coil of a Pound-type oscillator, used to measure the resonance, was wound on the outside of the glass jacket. The temperature was determined from the susceptibility of the paramagnetic salt. A control experiment showed that the sample temperature did not differ, within the experimental error ( $\pm 5\%$ ), from the temperature

of the salt. In the control experiment, the sample was a powder of metallic  $Tl^{205}$ , the temperature of which could be easily determined from the intensity of the nuclear resonance absorption.

On cooling from 1.5 to 0.75°K, the proton absorption line of the DBC cation did not exhibit any anomalies but at a temperature  $T_{cDBC} = 0.75 \pm 0.03^\circ K$  the resonance line suddenly disappeared. The accuracy of the measurement of the temperature interval in which the line disappeared was limited by the fact that the sample temperature after demagnetization was rising continuously and a certain time was needed to record the line. Nevertheless, we can say that this temperature interval did not exceed 0.06 deg K. A similar disappearance of the proton line of the DTC cation was observed at  $T_{cDTC} = 0.33 \pm 0.03^\circ K$ .

The negative sign of the constant  $\Theta$  in the Curie-Weiss law and the simple crystal structure of the two compounds<sup>[2]</sup> make it natural to assume that the observed disappearance of the proton resonance absorption lines is due to the transition to the antiferromagnetic state. Knowing the values of the hyperfine interaction constants,<sup>[1]</sup> we can calculate quite accurately the value of the magnetic field which should appear at the protons below the transition temperature (see, for example, <sup>[3]</sup>). For DBC, this field is about 1.5 kOe at  $T = 0^\circ K$  and it vanishes at  $T = 0.75^\circ K$ . Since this field should have a definite orientation with respect to the crystallographic axes, the resonance line of a polycrystalline sample in an external field should be broadened so that it becomes practically unobservable.

Therefore, an attempt was made to observe the resonance signal in the absence of an external magnetic field. For this purpose, the frequency of the threshold oscillator was modulated about a fixed value and the sample temperature slowly raised. At some temperature  $T < 0.75^\circ K$  a proton resonance signal should have been observed. However, in spite of a careful search, we did not observe such a signal between 2 and 6 Mc.

The absence of a signal in a zero field is strange but it does not prove conclusively that the antiferromagnetic state does not appear in DBC and DTC iodides at sufficiently low temperatures. Another effect characteristic of the antiferromagnetic transition is the dependence of the transition temperature on an external magnetic field. The critical field  $H_c$ , which destroys antiferromagnetism at  $T = 0^\circ K$ , is of the order of  $kT_N/\mu_{eff}$ , where  $T_N$  is the transition temperature in a zero field (see, for example, <sup>[4]</sup>). If  $T_N$  of DTC iodide is taken to be 0.33°K, then  $H_c \sim 3$  kOe. The measurements

carried out show, however, that the proton resonance signal disappears at the same temperature, within the experimental error, in fields of 1.5 and 5 kOe.

It is known also that on transition to the antiferromagnetic state the electron spin resonance frequency should change considerably (see, for example, <sup>[4]</sup>). Using the same method, we observed the electron resonance in the DBC cation at 45 Mc in the temperature range from 1.5 to 0.1°K. At temperatures above 0.75°K, the line was asymmetric, which is due to the g-factor anisotropy.<sup>[5]</sup> On cooling below 0.75°K, the line did not disappear but began to narrow; its asymmetry decreased, and at  $T < 0.2^\circ K$  the line became practically symmetrical with an isotropic g-factor equal to 2.

The experiments described here show that obviously the DBC and DTC cations at very low temperatures are not normal antiferromagnets. It is possible that below the transition temperature uncompensated antiferromagnetism appears in them, as observed in ferrites. Nonequivalent sublattices may be formed of, for example, chromium atoms and benzene rings, at which there is considerable spin density.<sup>[1]</sup> It is also possible that at these temperatures there is some change in the electron configuration of the molecules, which is responsible for the observed effects.

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