Anomalous diamagnetism (high-temperature Meissne effect?) in the compound CuCl

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Repeated transitions of CuCl from a weak-diamagnetism state with $\chi\sim-(10^{-5}-10^{-6})$ into a diamagnetic susceptibility close to $\chi=-1$ (the Meissner effect), accompanied in individual cases by an abrupt increase (by several orders of magnitude) of the electric conductivity, was observed when polycrystalline CuCl samples under a hydrostatic pressure $P\approx5$ kbar were cooled at a sufficiently rapid rate (>20 deg/min) from a temperature ~170 K. At temperatures below ~100 K, the CuCl goes over into a stationary or quasistationary state with $\chi\sim-1$, which is preserved in stable fashion in this temperature region for at least several hours.

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In theoretical investigations of high-temperature superconductivity as well as of the phase transition into the state of an excitonic dielectric, a special role is attributed to an electron-spectrum model with a large direct forbidden band E_D and a small indirect forbidden band E_g or with a small indirect overlap of the extrema of the valence and conduction bands. Under certain additional conditions, an instability to excitonic or superconducting pairing with high critical temperatures T_c is predicted for such systems (see, e.g.,[1]).

From this point of view, particular interest attaches to the compound CuCl, whose energy spectrum corresponds to the model indicated above.[2] The results of optical measurements, dilatometric and x-ray investigations, measurements of the magnetic, thermal, and electric properties at high pressures, all confirm the presence of a small indirect gap in CuCl, smaller than the binding energy E^d of the excitons. Under the condition $E^d\gtrsim E_g\ll E_D$, the CuCl crystal is in the state of an excitonic dielectric already at room temperature, with a hole/electron effective-mass ratio $m_h/m_e\gg1$.[1,3]

The parameters of the energy spectrum of CuCl, and in particular the size of the gap in the spectrum of the single-particle excitations, are most sensitive to the sample preparation method, to the presence of inhomogeneous stresses, impurities, charged defects, to the applied pressure, and others.[2,3]

Inasmuch as the onset of superconductivity requires that the spectrum parameters satisfy very stringent requirements[1] and the appearance of superconductivity can be expected only in a narrow range of these parameters, we have investigated in this study the temperature dependences of the magnetic susceptibility and of the electric conductivity of CuCl samples prepared in acccordance with various technological schemes, under hydrostatic pressures up to 10 kbar and under equilibrium and nonequilibrium conditions in the temperature interval 4.2–350 K.

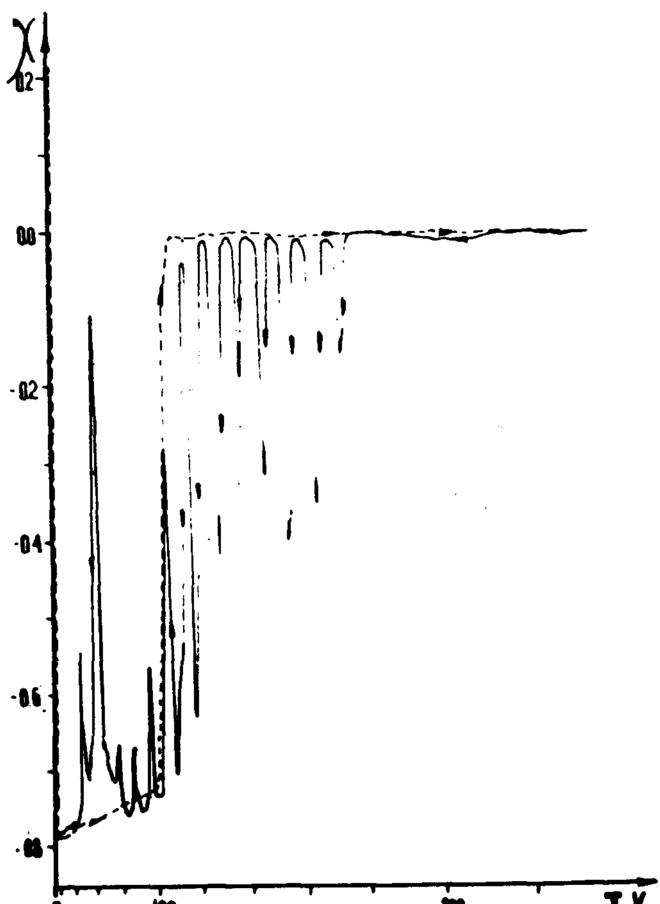

FIG. 1. Dependence of the magnetic susceptibility of CuCl on the temperature in the course of cooling (solid curve) and heating (dashed curve). At the origin is shown a calibration signal of the superconducting transition of a lead sensor. The temperature was measured with a copper-constantan thermocouple. $P \approx 5$ kbar.

The differential magnetic susceptibility χ was measured by a modulation method at a frequency ~20 Hz. The CuCl sample, pressed in the form of a cylinder (diameter ~1.4 mm, height ~3 mm) was placed in one of the measuring coils, and in the other was placed a lead or tin sensor of the same size, intended for the calibration of the absolute value of the sign of the susceptibility, and also to determine the pressure. The measuring coils were placed in the hydrostatic-pressure chamber. Two copper electrodes to measure the electric conductivity were pressed into the sample.

The temperature dependences of the differential magnetic susceptibility for one of the samples, at $P \approx 5$ kbar, are shown in Figs. 1 and 2. At zero pressure, the susceptibility of CuCl is[1] $\sim -5 \times 10^{-6}$ and it remains of the same order of magnitude at pressures up to ~8 kbar and temperatures ~300 K.

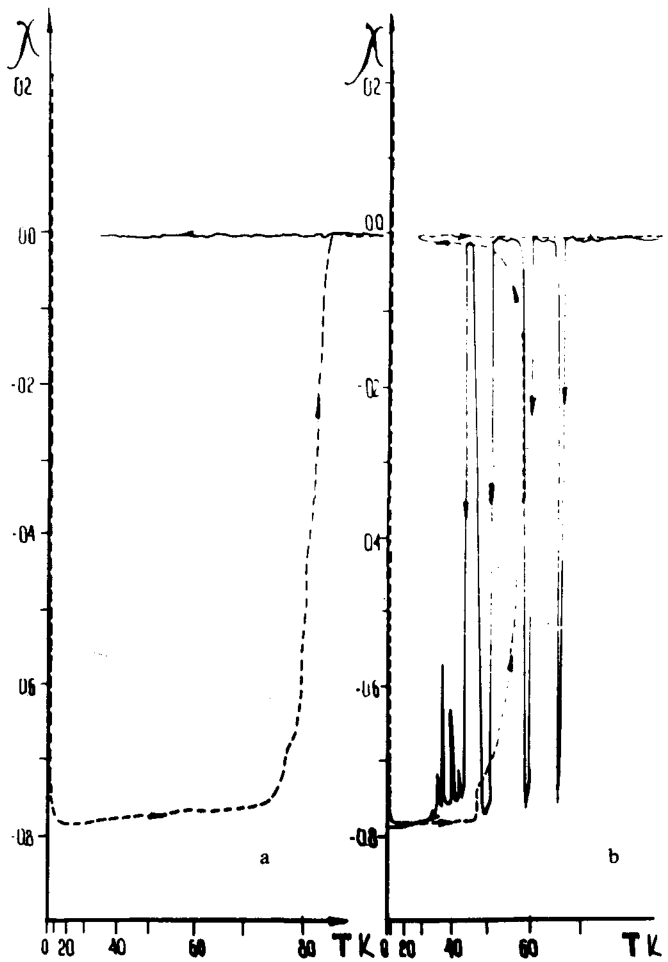

FIG. 2. Dependence of the magnetic susceptibility of CuCl on the temperature: a) Heating (dashed curve) and slow cooling (solid curve); b) rapid cooling from ~300 K (solid curve), heating and halt at the instant of transition, followed by cooling and heating (dashed line).

In the course of cooling from room temperature, diamagnetic jumps of the magnetic susceptibility, approximately periodic in the temperature, are observed in the region $\sim(170\text{–}100\ \mathrm{K})$.

The position of the susceptiblity peaks on the temperature scale, for several successive cycles of cooling, remains constant within the limits of the measurement accuracy. The period of the variation of χ is $\sim(8.8\pm0.3)$K (Fig. 3). At a temperature below ~ 100 K, the character of the variation of the magnetic susceptibility changes: whereas at $T > 100$ K the stong diamagnetism appears periodically against the background of weak diamagnetism, at $T < 100$ K the sample goes over into a state with almost ideal diamagnetism ($\chi \approx -0.8$), which is partially destroyed periodically in the course of cooling. Below ~ 45 K, the ideal-diamagnetism state is preserved unchanged.

When the sample is heated to ~ 100 K it remains in the diamagnetic state (dashed curve in Fig. 1), after which its susceptibility changes abruptly to a small value that prevails up to room temperature.

When the heating and cooling cycles (from 350 to 4.2 K) are repeated, the temperature T_c of the diamagnetic transition decreases gradually ($T_c \sim 50$ K after the tenth heating cycle). If the heating is halted during the time of the transition from the state of "ideal" diamagnetism into the weakly diamagnetic state, and the cooling is then started, then the diamagnetism continues to decrease and no reverse transition to a state with "ideal" diamagnetism takes place (Fig. 2b). Thus, the diamagnetic state is not stable near T_c. However, at temperatures below T_c the diamagnetic state is apparently stable and remains unchanged when the temperature is fixed, at least for several hours.

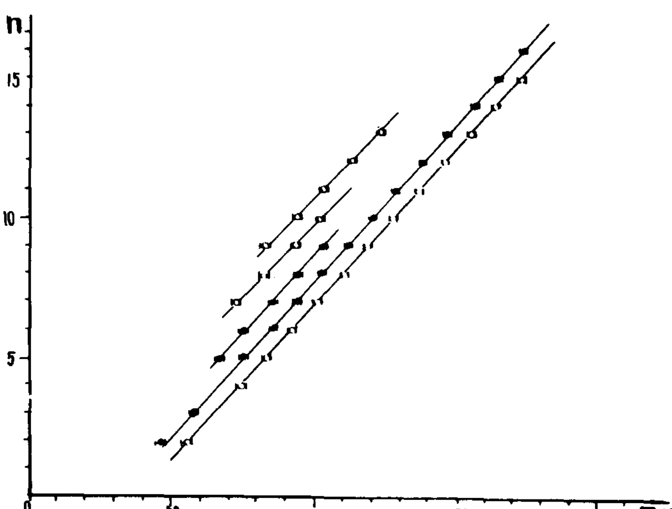

FIG. 3. Temperature dependence of the positions of the maxima (●) and minima (○) of the magnetic susceptibility at different cooling cycles (n is an arbitrary number of the maximum or minimum).

A characteristic feature of the temperature dependences is that the onset of a state with strong diamagnetism takes place only when the sample is cooled at a sufficiently high rate (more than ~20 deg/min). Slow cooling is not accompanied by any changes of the susceptibility whatever (solid curve on Fig. 2a). However, if the sample is heated after slow cooling to a temperature ~300 K and is then rapidly cooled, the character of the $\chi(T)$ curve, described above is fully duplicated (Fig. 2b).

The magnetic-susceptibility jumps that occur upon cooling are apparently subdivided into groups (4–5 peaks in each).

In the first high-temperature group the amplitude of the peaks first increases and then decreases, remaining less than -1 in all cases. When the heating and cooling cycles are repeated, the values of all peaks in this group first increases (they are seen most clearly in Fig. 1, in the region ~170–130 K, in the fifth cooling cycle), and then decreases practically to zero (this group is missing in Fig. 2(b), which shows a plot of χ against T for the ninth cooling). In the second group (in the region ~130–90 on Fig. 1), the amplitudes of the jumps of χ depends much more weakly on the number of the cooling cycle. In the third group (region ~90–45 K in Fig. 1) the directions of the jumps that occur when the sample is cooled are reversed (decrease of the diamagnetism).

The jumps of the magnetic susceptibility in the course of cooling are apparently a characteristic feature observed for all samples that go over into the state with strong

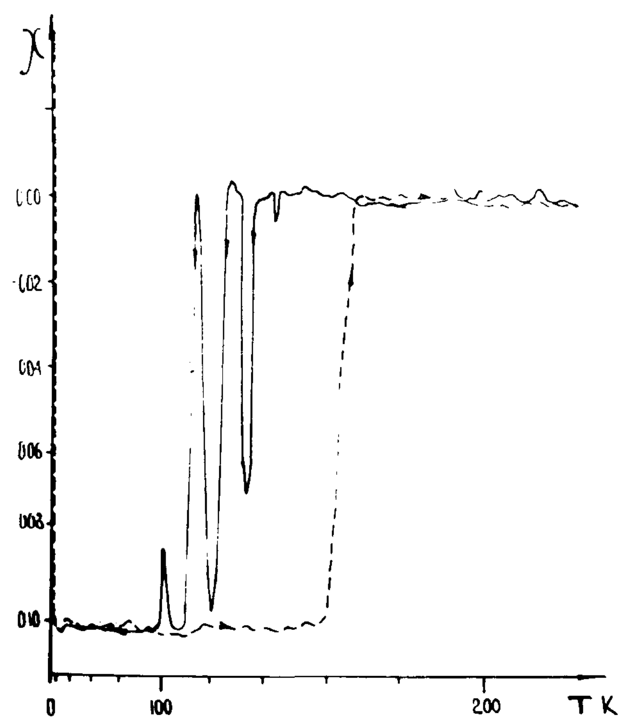

FIG. 4.

diamagnetism. The value of χ fluctuated for the various samples between ~ -0.01 and $-(0.8–0.9)$. The transition temperature in the course of heating varied from sample to sample; the maximum observed value of T_c is ~ 165 K (see Fig. 4, which shows the measured dependence of χ on T for a CuCl sample with $\chi \approx -0.1$).

The transitions of the samples into a state with "ideal" diamagnetism were accompanied by a synchronous increase of the electric conductivity. The increase of σ, however, varied strongly from sample to sample. In individual cases, the electric conductivity increased simultaneously by 4–6 orders of magnitude with increasing χ.

It must be emphasized that the described effects are extremely sensitive to the technology used to grow the crystals and to their subsequent heat treatment, and were observed only for samples obtained in a manner similar to that used in[3].

Thus, a transition from a state with weak diamagnetism ($\chi \sim -5\times 10^{-6}$) into a state with $\chi \sim -1$, which is close to "ideal" diamagnetism (Meissner effect) takes place in some of the investigated CuCl samples under the conditions indicated above. It is natural to assume that the crowding out of the magnetic field from the sample and the simultaneous strong increase of the electric conductivity of the sample are a consequence of the transition of the crystals into the superconducting state. It is most probable that it is the crystallites that make up the sample which go over into the superconducting state, while the intercrystallite boundaries, with the strongly disturbed structure, remain in the dielectric state. This assumption explains, on the one hand, the somewhat lower than $\chi = -1$ value of the diamagnetic susceptibility of the investigated samples, and on the other, the strong difference between the change of the electric conductivity in the Meissner effect for different samples: the change of the electric conductivity when the crystallites go over into the superconducting state is determined by the structure of the sample between the electrodes, and also by the ratio of the distance between them to the crystallite dimensions.

It seems obvious that the onset of the Meissner effect (and of superconductivity?) at such high temperatures cannot be explained within the framework of the traditional model of the phonon mechanism, and its explanation calls for consideration of other mechanisms (such as the excitonic mechanism[1]), that admit of the possibility of high-temperature carrier pairing.

[1)]All the quantities in the article are given in the c.m.s., in which "ideal" diamagnetism corresponds to $\chi = -1$.

[1]Problema vysokotemperaturnoĭ sverkhprovodnimosti (The Problem of High-Temperature Superconductivity), ed. by V.L. Ginzburg and D.A. Kirzhnits, Nauka, 1977.

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