MAGNETIC ANISOTROPY OF Hg₂Cl₂ SINGLE CRYSTALS*

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The paper reports results of the measurement of the magnetic susceptibility in dependence upon the magnetic field, the temperature and the crystallographic orientation of Hg₂Cl₂ single crystals. The explanation is based on the assumption that the crystals contain molecules with the following bond structure: $Cl^-Hg^+ - Hg^+Cl^-$.

МАГНИТНАЯ АНИЗОТРОПИЯ МОНОКРИСТАЛЛОВ Hg₂Cl₂

В работе приводятся результаты измерений магнитной восприимчивости монокристаллов Hg₂Cl₂ в зависимости от магнитного поля, температуры и их кристаллографической ориентации. Объяснение полученных данных основано на предположении, что монокристаллы образованы молекулами со следующей структурой связы: $Cl^-Hg^+ - Hg^+Cl^-$.

I. INTRODUCTION

The single crystal of mercurous chloride have an important property, e.g. birefringence, which makes it possible to use this material in the construction of optical elements. Because of this useful property the single crystal of mercurous chloride is now intensively studied, both experimentally and theoretically. Up to now, negligible attention has been paid to their magnetic behaviour Farquharson et al. [1] reported that its material is diamagnetic and its magnetic susceptibility per gram at room temperature is -2.20×10^{-7} cm³ g⁻¹. Later Prasad et al. [2] and Kido [3] published similar results and for the susceptibility reported values of -2.45×10^{-7} cm³ g⁻¹ and -2.53×10^{-7} cm³ g⁻¹, respectively. Further results were published by Bhatnagar et. al. [4], Grillot [5] etc. and their susceptibility values were in the range of values quoted above. In the present paper the magnetic susceptibility of a pure and well defined single crystal of mercurous chloride was measured as a function of the magnetic field, temperature and crystallographic orientation at temperatures 77—300 K.

II. EXPERIMENTAL PART

Single crystals of mercurous chloride were grown from commercial calomel of spectroscopic purity which was several times recrystallized by sublimation in vacuum. The method published earlier [6, 7] was used with the following modifications: The distance between the growing crystal face and the evaporated material was diminished down to 3 cm and the temperature difference to 3 degrees. The crystal was grown at a temperature of 450 °C at a rate of 0.3 cm per 24 hours.
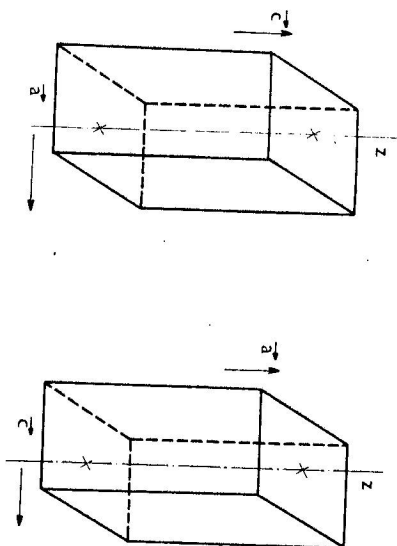

Fig. 1. Two different crystallographic orientations of the samples measured

The magnetic susceptibility was measured on single crystals of mercurous chloride of the shape of a parallelepiped $3 \times 3 \times 10$ mm attached to a quartz filament in the magnetic microbalance described earlier [8]. This material crystallizes in the tetragonal structure and the crystallographic orientation of samples is shown in Fig. 1. The magnetic field rotates perpendicularly to the longitudinal axis Z of the samples. The method makes possible to detect a change of susceptibility $\Delta \chi = 0.01 \times 10^{-7}$ cm^3 g^{-1}.

The measurement indicates that the magnetic susceptibility of mercurous chloride samples is independent of the magnetic field (up to 5 kG) and the temperature (77—300 K). From these results it is possible to conclude that this material is strictly diamagnetic and that it contains no measurable concentration of any paramagnetic component. Since the method permits to detect a susceptibility change $\Delta \chi = 0.01 \times 10^{-7}$ cm^3 g^{-1}, the concentration of any impurity having on the average the magnetic moment 5 μ_B must be lower than 1×10^{15} cm^{-3}.

The dependence of the susceptibility upon the crystallographic orientation indicates anisotropy. Because the susceptibility is temperature independent, the measured dependences are the same, both at 77 K and 300 K. In Fig. 2 the

dependence of the susceptibility per gram upon the angle between the magnetic field B and the crystal axis c is shown for two samples (Fig. 1). We see that the diamagnetic susceptibility measured for the orientation $B \parallel c$ is lower than for the orientation $B \perp c$. The corresponding susceptibility values are $\chi_{a \parallel c} = -2.45 \times 10^{-7}$ cm^3 g^{-1} and $\chi_{a' \perp c} = -2.56 \times 10^{-7}$ cm^3 g^{-1}. If we compare these values with those measured earlier [1—3] we see a good agreement in spite of the fact that we observe the anisotropy of the diamagnetic susceptibility.
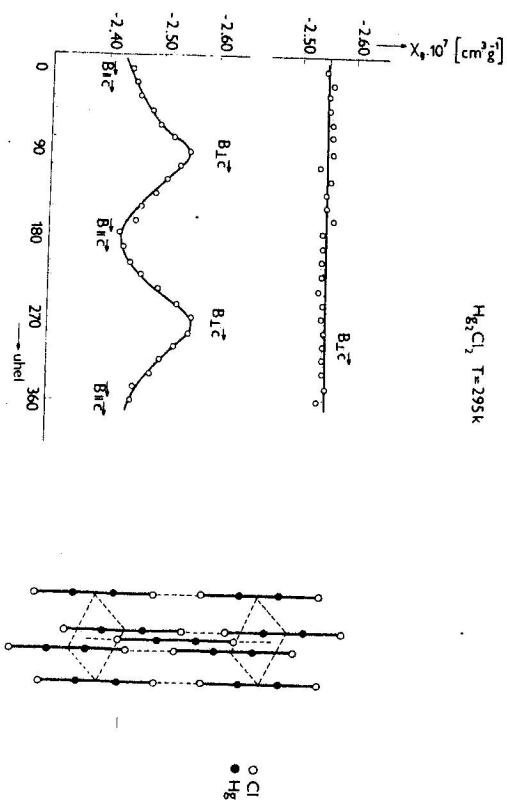

Fig. 2. Dependence of the magnetic susceptibility per gram upon the angle between the directions of the magnetic field and the c axis

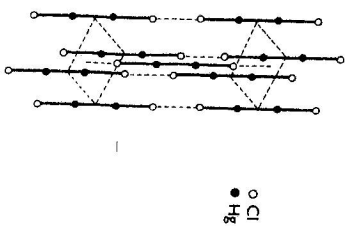Fig. 3. Structure of mercurous chloride

III. DISCUSSION OF RESULTS

The mercurous chloride crystalizes in a tetragonal structure which is shown in Fig. 3. We see that it contains Hg$_2$Cl$_2$ molecules. We suppose that the binding in these molecules can be described in the form Cl$^-$Hg$^+$—Hg$^+$Cl$^-$. This scheme is in agreement with the results obtained, indicating that this material is diamagnetic because Cl$^-$ ions as well as the complex Hg$^+$—Hg$^+$ are both diamagnetic. We supose that one s-electron from each mercury atom is transferred to the chlorine atoms to convert them into Cl$^-$ ions. The remaining s-electrons of the mercury atoms form a bond between the mercury atoms which is similar probably to a delocalized covalent bond ar a metallic bond. If we had a pure covalent bond in

the complex Hg^+—Hg^-, then the shared electron pair could be displaced along the bond. However, the anisotropy of the magnetic susceptibility indicates that its value is greater if the magnetic field is perpendicular to the c axis. Therefore we must suppose the delocalized covalent or metallic bond in the complex Hg^+—Hg^+.

This conclusion is supported further by the measurement of the dielectric permittivity of the mercurous chloride reported recently by Kočka [9]. He obtained the anisotropy $\varepsilon_{\|c} = 10.06$ and $\varepsilon_{\perp c} = 13.33$. If we used theory of diamagnetic susceptibility developed by Kirkwood [10], we can write $\lambda = k[(\varepsilon - 1)/(\varepsilon - 2)]^{1/2}$. For the ratio $\chi_{a,\perp c}/\chi_{a,\|c}$ we obtain then 1.04 which is in good agreement with the experiment giving the value 1.045.

Finally we checked the absolute values of susceptibility. Corresponding molar susceptibilities are $\chi_{m,\|c} = -115 \times 10^{-6}$ cm³mol⁻¹ and $\chi_{m,\perp c} = -120 \times 10^{-6}$ cm³mol⁻¹. According to the Pascal rule [11] we take $\Delta\chi_a = -23.3 \times 10^{-6}$ cm³mol⁻¹ and $\Delta\chi_{Hg^+} = -45 \times 10^{-6}$ cm³mol⁻¹ giving the value $\chi_{m,Hg_2Cl_2} = -136.6 \times 10^{-6}$ cm³mol⁻¹. All these values $\Delta\chi$ correspond to atomic entities having a spherical distribution of the electron density around nuclei. The difference between the calculated and experimental values is due to the existence of the complex Hg^+—Hg^+ in which the mercury atoms share a delocalized electron pair responsible for certain, though small asymmetry in the electron distribution.

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