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MAGNETIC SUSCEPTIBILITY MEASUREMENTS ON $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$ SINGLE CRYSTALS*

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ABSTRACT

Static magnetic susceptibilities of single crystals of the mixed-valence platinum compound $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$ (KCP) are reported exemplifying the difficulties encountered at the measurements. The measurements have been carried out by means of a vacuum microbalance following the Faraday method at temperatures between 4 and 148 K and at field strengths between 6 and 20 kOe. The difficulties relate to: (1) the possible contamination by ferromagnetic impurities; (2) the non-cylindrical symmetry of the field around the axis of rotation of the magnet and the off-axis location of the sample holder; (3) the occurrence of free radicals after degradation of the material; (4) the parasitic effect of microgram quantities of oxygen adsorbed on the samples below 50 K; (5) the determination of the weak Pauli paramagnetism of the "quasi one-dimensional metallic" conductor above 65 K; and (6) the need for more accurate susceptibility references for the determination of n, the water content, by susceptibility measurements.

The gram-susceptibility of KCP at 65 K, for which n is estimated to be 1.5, is analysed to be -3.60×10^{-7} emu g^{-1} and -3.83×10^{-7} emu g^{-1} for the magnetic field vector being respectively parallel and perpendicular to the c-axis of the crystals. The 6 percent anisotropy is mainly attributed to the triple bond in the CN group.

INTRODUCTION

The mixed-valence platinum compound $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$ (KCP), in which material the platina atoms form linear chains, is a "quasi one-dimensional metallic" conductor at room temperature. It undergoes a transition into an "insulating" state at low temperatures[1]. The compound has been actively investigated[2]. The importance of the investigation lies in the correlation of the relative ease with

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which one-dimensional (1-D) systems can be handled theoretically and the relative ease with which the calculated results should be detected experimentally when the results differ considerably from those of 3-D systems. The reduced dimensionality indeed, is expected to lead to effects which are called "dimension-specific". Peierls[1] showed that in the one-particle approximation the 1-D metallic state becomes unstable, so that the linear electron system should transform spontaneously into an insulator. The expectation that a 1-D system may behave in a peculiar way as compared to the 3-D systems, has given rise to speculation at the assignment of experimental facts to "intrinsic" effects. For KCP, there was room for speculation because difficulties arise when the static susceptibilities of $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$ single crystals are measured by means of a vacuum microbalance following the Faraday method. Conflicting results have been obtained by different groups. The aim of the present paper is to discuss our experimental data with relation to the experimental difficulties and to show that precise measurements allow for differentiation of effects.

EXPERIMENTS AND RESULTS

The present study on the static magnetic susceptibility of $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$ single crystals has been carried out by means of an apparatus which has been described previously[3]. The striking part of the set-up is a vacuum microbalance from which the sample holder hangs down in a Dewar[4] between the pole pieces of an electromagnet. A data acquisition and processing system[5] has been added to the instrument. The gram susceptibilities of the samples have been measured at different temperatures, between 4- and 148 K, for six different field strengths H. The nominal values of H are 20.6, 18.7, 14.7, 11.9, 9.0 and 6.1 kOe. They will be referred to, in what follows, by the subscript i numbered from 1 to 6.

The first experiment, exp. 1, concerns the crystal water of KCP. In the considered susceptibility apparatus, the sample holder hangs freely in the sample tube just above the thermometer. The heat exchange between the sample and the thermometer is performed by means of helium gas at a pressure of approximately 10^{-1} Torr[4]. The helium should be free from impurity gases in order to prevent condensation on the sample at low temperatures. Consequently, the water-vapour pressure is extremely low in the Dewar. A bare single crystal, which has been brought in such a dry atmosphere at room temperature, lost its metallic copper glare and became black. The experiment resulted in a search for a "box" in which the sample should match tightly in order to prevent macroscopic quantities of water to leave the crystal. Signal-to-noise considerations further suggest that the box should be as light as possible. In an attempt to meet the requirements, the next sample has been covered with a thin layer of paraffine. Paraffine has been chosen because it had been used before with success in a similar situation in which, however, the lower temperature was limited to 57 K. The reasons for using the material are (i) its plasticity at room temperature; (ii) its low melting point which allows for sealing the box; and (iii) its diamagnetism which is practically independent on temperature and on field strength.

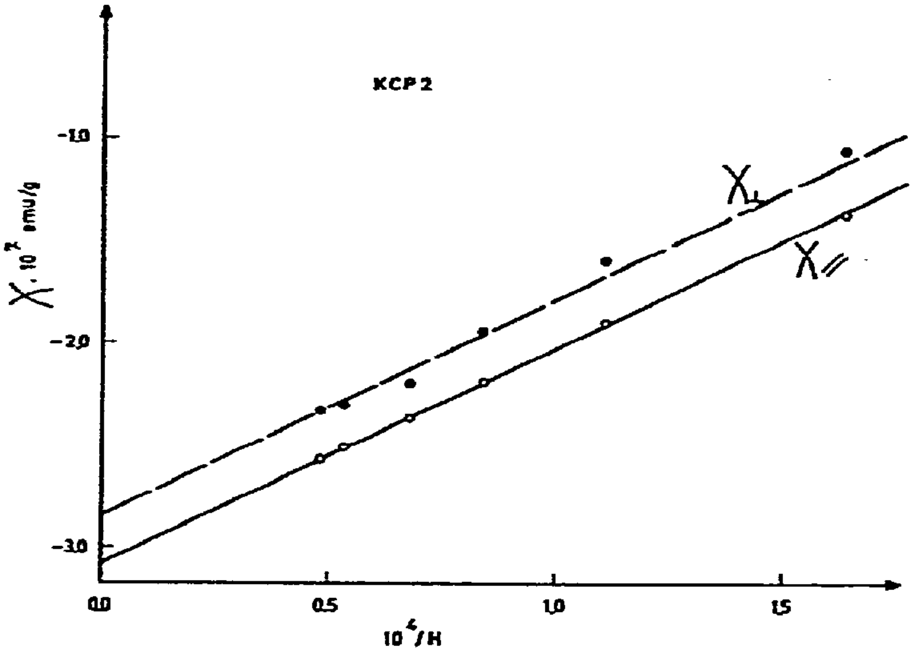

Fig. 1. The apparent susceptibility of KCP2 versus reciprocal field strength at 4.2 K for different orientation of the crystal $\bar{C}$-axis versus field direction $\bar{H}$ in exp. 2.1. The slope of the lines indicates the presence of ferromagnetic impurities.

The constant susceptibility greatly facilitates "background" corrections at the susceptibility calculations of the bare sample. The use of paraffine in the case of KCP was based on the assumption that its pleasant behaviour extrapolated to lower temperatures.

In experiment 2 the sample was taken small because only a very small quantity of KCP single crystals was available at the early stage of the investigation. Sample 2 weighed 2.89 mg and was covered with 0.79 mg paraffine. The tetragonal symmetry of KCP crystals[6] raises the question whether $\chi_\parallel$, the susceptibility measured with the field vector $\bar{H}$ parallel to the 1-D linear platina chains in the $\bar{C}$ axis of the crystal, differs from $\chi_\perp$, the susceptibility measured perpendicular to the $\bar{C}$ axis. To measure $\chi_\parallel$ the needle-shaped crystal has been put on the balance pan with its needle axis, the $\bar{C}$ axis, nearly parallel to the magnetic field vector, the orientation indicator of the magnet pointing to zero. To measure $\chi_\perp$ the magnet has been turned by 90°.

The apparent susceptibilities χ_i, as computed from the data taken at 4.2 K, are plotted in Fig. 1 versus reciprocal field strength. At constant temperature T and orientation 0, the apparent susceptibilities approximately fit the linear equation:

$$[\chi_i = \chi + K \cdot (1/H_i)]_{T,0} \tag{1}$$

with χ and K independent on field strength. The term containing K is proportional to the reciprocal field strength. This behaviour indicates the presence of saturated

TABLE I

SUSCEPTIBILITY OF KCP SAMPLE 2 VERSUS TIME t AT DIFFERENT TEMPERATURES

t(days)	T(K)	$\chi_\parallel \cdot 10^7$ (emu g^{-1})	$\Delta\chi \cdot 10^7$	$\sigma \cdot 10^7$
2	4.5	−3.24	−0.18	0.08
3	4.2	−3.08	−0.23	0.05
3	7.1	−3.06	—	—
7	4.3	+3.62	−0.5	[a]

[a] Single (— no) measurement.

ferromagnetic impurities[7]. It suggests that the susceptibility of sample 2 is 0.5×10^{-7} emu g^{-1} more diamagnetic than the apparent value measured at about 20 kOe.

For the two considered orientations, the apparent susceptibility difference is $\Delta\chi = \chi_\parallel - \chi_\perp \cong -0.2 \times 10^{-7}$ emu g^{-1}. On the same sample, more susceptibility measurements have been carried out. The results behave similarly to those reported in Fig. 1. It is observed that K is practically independent on temperature and orientation. Its value is 1.05×10^{-3} emu Oe g^{-1}.

The values of $\chi_\parallel$, as calculated by eqn (1) from low-temperature data, are given in Table I versus the time the sample spent on the balance pan in the apparatus.

The $\Delta\chi$ values and their standard deviation are given in the same table in columns 4 and 5 respectively.

For $t \leq 3$ days, the early stage of experiment 2 which is named exp. 2.1.1, sample 2 was clearly diamagnetic at temperatures as low as 4.2 K. No temperature-dependence has been revealed. A slight anisotropy seems to be present. Briefly, exp. 2.1.1, suggests that KCP is a slightly anisotropic, temperature-independent, diamagnetic material. Remains to explain the paramagnetism which is observed in exp. 2.1.2 after the sample spent seven days in the apparatus. The paramagnetic behaviour appeared after the crystal warmed up to room temperature during the week-end. It therefore is related with the degradation of the material in a dry atmosphere at reduced pressure. The paramagnetism is strongly correlated with reciprocal temperature. It is considered to consist of two components: a first one which is given by the Curie law, $\chi = C'/T$, which values fit the susceptibilities measured at the extreme temperatures; and a second component which is obtained by subtracting the values of the first one from the measured values. The second component appears in the temperature region between 50 and 5 K. It is paramagnetic and exhibits a maximum at about 40 K. This second component of the paramagnetic susceptibility has been studied in the following experiments. In exp. 2.2, sample 2 has been cooled slowly from 67 to 26 K at $t = 27$ days. The $\chi_{1\parallel}$ values then have been measured between 40 and 43 K in two runs. In the first one, the sample has been heated at a rate about 0.14 K per minute, exp. 2.2.1; and in the second run, exp. 2.2.2, it has been cooled at 0.12 K per minute. Just above the temperature at which the maximum of

$\chi_{1\parallel}$ occurs, the susceptibility strongly decreases with increasing temperature. The steep part of the slope $(\chi_{1\parallel}(T_1) - \chi_{1\parallel}(T_2))/(T_1 - T_2)$ is 0.8×10^{-7} emu g^{-1} K^{-1}, in both series, at the reference susceptibility 0.3×10^{-7} emu g^{-1} which is observed at 42.0 and 41.8 K for the heating- and the cooling-experiment, respectively. These data point to a rather reversible effect with practically no hysteresis. The maxima are about equal, i.e. $\simeq 1.2 \times 10^{-7}$ emu g^{-1} at 40 K. The orientational dependence of χ_1 has been checked by measuring the $\chi_{1\perp}$ values in the temperature region between 40 and 41 K immediately after cooling in exp. 2.2.2. The maximum of $\chi_{1\perp}$, 1.5×10^{-7} emu g^{-1} at 40.9 K, indicates the presence of a slight anisotropy, $\Delta\chi \cong -0.3 \times 10^{-7}$ emu g^{-1}. In exp. 2.3 at $t = 29$ $\chi_{1\perp}$ has been measured in two series for both of which the temperature increased with time. Before starting the experiment, the anisotropy is found to be $\Delta\chi = -0.1 \times 10^{-7}$ emu g^{-1} at 35 K. The first series, exp. 2.3.1, then has been measured in the temperature region between 35 and 44 K at a rather slow rate, about 0.034 K per minute in the neighbourhood of the peak temperature. The second series, exp. 2.3.2, covers temperatures between 9.8 and 50 K at a heating rate of 0.22 K min^{-1}. Although the heating rates are quite different, the peak susceptibilities again are about equal in both series, i.e. $\simeq 0.8 \times 10^{-7}$ emu g^{-1}. The peak temperatures differed slightly, 39.6 and 41.3 K for exp. 2.3.1 and exp. 2.3.2, respectively. Experimental $\chi_{1\perp}$ values of the "faster" series are plotted versus reciprocal temperature in Fig. 2 to show what is meant by a peak. Exp. 2.3

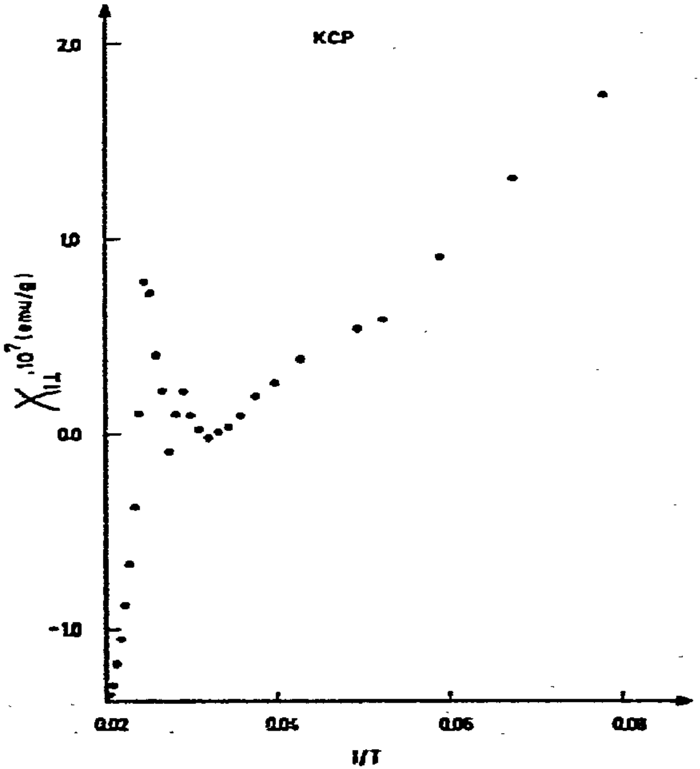

Fig. 2. The susceptibility of KCP 2 after degradation versus reciprocal temperature (exp. 2.3.2). The peak at $(1/T) \simeq 0.025$ is attributed to adsorbed oxygen.

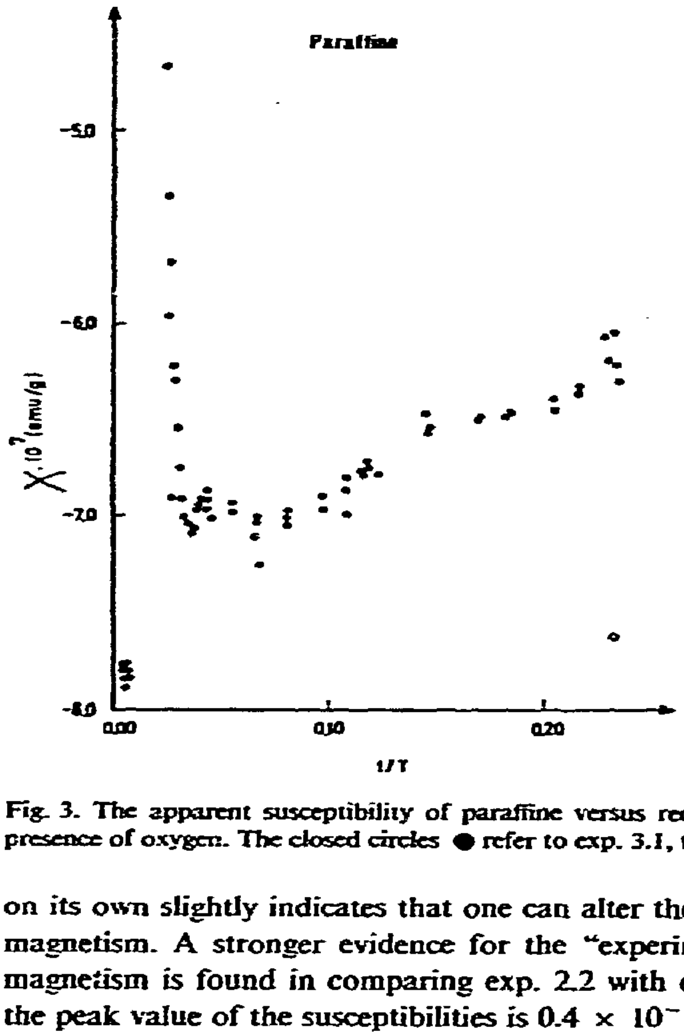

Fig. 3. The apparent susceptibility of paraffine versus reciprocal temperature, revealing also the presence of oxygen. The closed circles ● refer to exp. 3.1, the ○ to the fast cooling experiment 3.2.

on its own slightly indicates that one can alter the quantity of the considered paramagnetism. A stronger evidence for the "experimental dependency" of the paramagnetism is found in comparing exp. 2.2 with exp. 2.3. In the latter experiment, the peak value of the susceptibilities is 0.4 × 10^{-7} emu g^{-1} less paramagnetic than in the former experiment. The reduction of $\chi_{max.}$ is about 15 times the standard deviation on normal measurements, so that it becomes hard to explain the susceptibility difference in terms of scattering in the balance output. The "experimental dependency" suggests the idea that adsorption might cause the effect. When adsorption of oxygen causes the paramagnetism, then one might expect the effect to reproduce on bare paraffine. This is indeed the case, as shown by experiment number 3. Susceptibility measurements have been carried out on sample 3, a sheet of 2.40 mg paraffine, while it warmed up from 4.4 K in exp. 3.1. The results are shown in Fig. 3. The susceptibilities are in agreement with the hypothesis. At 4.4 K, the susceptibility is less diamagnetic than expected from the theory of the temperature-independent diamagnetism. The difference is attributed to a paramagnetic component. When the temperature is increased, then the paramagnetic part, at first, decreases obeying approximately the Curie law. Above 5 K the measured values deviate from the Curie law and become relatively more paramagnetic, although the total susceptibility still becomes more negative with increasing temperature up to about 15 K. The paramagnetic component of the susceptibility then starts to rise with temperature up to its peak value at about 40 K after which maximum, it quickly diminishes so that at 50 K the total susceptibility value equals the room temperature diamagnetism of paraffine. In experiment 3.2 the balance- and sample-space have been pumped for two days and nights with a cryopump consisting of zeolite adsorption material at 80 K. The sample has been cooled quickly to 4.4 K and measured at that temperature. The paramagnetic part of the susceptibility amounts only to 15 percent of the quantity found in exp. 3.1. On heating the sample afterwards in exp. 3.3 the peak in the susceptibility appears again at 40 K.

Experiment 3 shows that paraffine is not a good protection material for KCP, as at temperatures below 50 K, it results in a temperature- and history-dependent part of the susceptibility for which it is difficult to correct.

Experiment 2 shows that (i) the degradation of KCP does not occur at tempera-

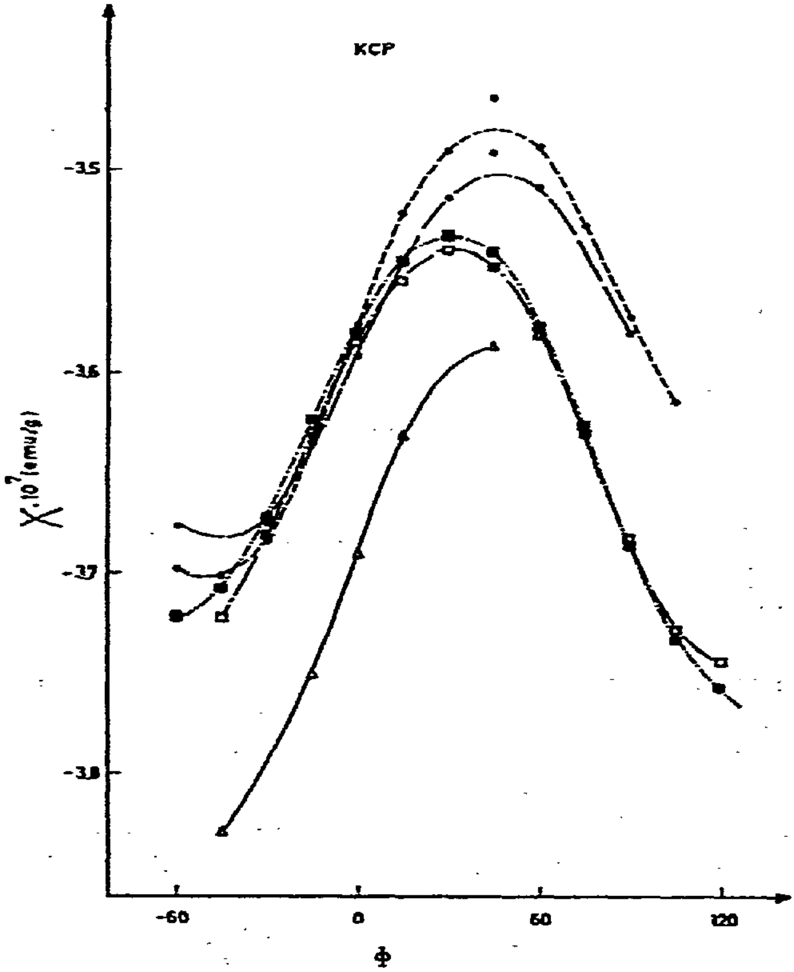

Fig. 4. Susceptibilities of KCP4 plotted versus ϕ the angle over which the magnet has been turned in exp. 4.1. The circles refer to 4.3 K, the squares to 130 K and the triangles to 65 K, ● to $t = 23$, ○ to $t = 30$, ■ to $t = 31$, □ to $t = 27$ and △ to $t = 24$.

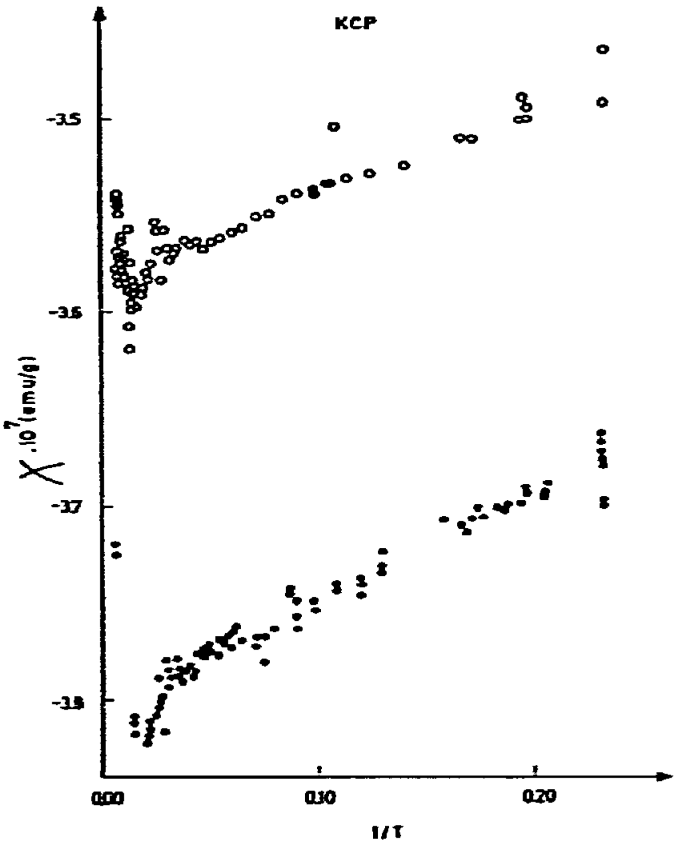

Fig. 5. The susceptibilities of KCP4 plotted versus reciprocal temperature. The open circles ○ refer to the measurements of exp. 4.2.1 carried out at $\phi = +45°$, i.e., for the $\bar{C}$-axis of the crystal about parallel with $\bar{H}$; the closed circles ● refer to $\phi = -60°$ in exp. 4.2.2.

tures below 150 K; and (ii) the undegraded crystal is diamagnetic and practically independent on temperature. The results of exp. 2 and 3 enable one to enhance the precision on the measurements on KCP in experiment 4 by choosing (i) the proper weight of the sample for maximum signal-to-noise ratio; (ii) single crystals with maximum volume to surface ratio for reducing the effect of adsorption; and (iii) an appropriate cooling scheme for bare crystals. In the final experiment, exp. 4, four single crystals of KCP were put on the balance pan with their c-axis parallel to each other. The materials were homogeneously distributed over the surface of the pan. The c-axis, however, in this case were not parallel to the field vector when the magnet orientation indicator pointed to zero. For orienting $\bar{c}$ parallel to $\bar{H}$, the magnet was turned with an angle $\phi = +45°$. The total mass of sample 4 was 32.39 mg. The Dewar tail, at room temperature, was filled with air at a pressure of one atmosphere. The Dewar then was fitted to the apparatus after which manipulation the sample space, together with the sample, were cooled quickly with liquid nitrogen to about 140 K. Then, the sample space was pumped and filled with the helium heat-exchange gas at a pressure of about 0.1 Torr. Each night the sample space, at ≃ 140 K, was connected to the cryopump to reduce the impurity gas concentration. During daytime, in exp. 4, the susceptibilities have been measured at temperatures between 4.3 and 148 K. A field strength dependency of χ has not been observed. The first series of χ_1 data, as obtained in exp. 4.1, is given in Fig. 4. The susceptibilities are plotted versus ϕ and the χ_1, ϕ correlation reveals an anisotropy $\Delta\chi = + 0.2 \times 10^{-7}$ emu g^{-1}.

The results of exp. 4.2 are given in Fig. 5 in which two sets of susceptibility values are plotted versus reciprocal temperature. The first set concerns data taken in exp. 4.2.1 at $\phi = + 45°$; and the second set concerns data taken in exp. 4.2.2 at $\phi = - 60°$. In each set, the temperature dependency of the susceptibility is small, so that the relative difference between the most extreme susceptibility values does not exceed 4.7 percent. The strong correlation between χ_1 and reciprocal temperature suggests that the reproducibility of the measurements is better than 0.6 percent. For both orientations a susceptibility minimum is observed at 65 K.

DISCUSSION

The static magnetic susceptibility data on $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$ single crystals, as measured by the Faraday method, are analysed now with relation to experimental difficulties. A first difficulty deals with the purity of the material. Indeed, the method is very sensitive to ferromagnetic contamination. Ferromagnetic saturated materials yield a linear dependency of the susceptibility versus reciprocal field strength. Such a behaviour is observed in Fig. 1 for sample 2. It stimulated the elimination of ferromagnetic tools at the preparation of new crystals. The susceptibility of sample 4 does not show this behaviour anymore. It is therefore concluded that in exp. 4 the measurements have been carried out on clean material. The sensitivity of the method for ferromagnetic impurities is demonstrated by the calculation of the mass concentration of iron which could cause the field dependency of sample 2. The slope of the straight lines in Fig. 1, the value of K in eqn (1), is the ratio, of the impurity — to the sample-mass, times the magnetic moment of 1 g of the ferromagnetic impurity. The moment of bulk iron is 221 emu Oe g^{-1} so that the experimental value $K = 1.05 \times 10^{-3}$ emu Oe g^{-1} results for sample 2 in 4.75 parts per million iron to be sufficient for explaining the observed effect. Consequently, it is assumed that in exp. 2 the ferromagnetic equivalence of 1.4×10^{-8} g of iron was present on the sample holder. Whether this amount was inside or outside the sample is not known. Another problem is related to the orientational dependency of the susceptibility. The result of exp. 2, $\Delta\chi_2 \cong - 0.2 \times 10^{-7}$ emu g^{-1}, is at variance with that of exp. 4, $\Delta\chi_4 \cong + 0.2 \times 10^{-7}$ emu g^{-1}. The difference in sign must be due to assumptions which do not hold. Our data were processed[5] without taking care of the angular dependency of the "background" on ϕ. The computer had been programmed with the assumption that, for symmetry reasons, the force acting on the balance can be expressed by:

$$F_z = m \cdot \chi \cdot \varphi_w \tag{2}$$

with:

$$\varphi_w = \left(H_x \cdot \frac{dH_x}{dz}\right)_w \tag{3}$$

being independent on ϕ because the sample is assumed to remain always at the position w on the centre-axis in the z direction of the magnet. Experiment 4.1, however, contains an element which shows that this assumption holds only approximately. The apparent susceptibility of sample 4, as measured at $t = 31$, can be formulated as follows:

$$\chi_\phi = -3.625 \times 10^{-7} + 0.103 \times 10^{-7} \cdot \cos(2[\phi - 32]) - 2.0 \times 10^{-11} \cdot \phi \tag{4}$$

The first term in the right-hand side of eqn (4) is attributed to the mean diamagnetic susceptibility of sample 4 at $T = 130$ K. The second term indicates that the susceptibility can be represented by an ellipsoid, with one semi-axis slightly different from the others, as expected[8] from the tetragonal symmetry of the KCP crystal structure. From a structural point of view, therefore, one does not expect χ to change when ϕ changes by 180 degrees. In exp. 4.1, however, χ does change. The fact is expressed by $\chi_{\phi 3}$, the third term in the right-hand side of eqn (4). The effect is attributed to a slight excentricity of the sample-holder position and the non-cylindrical symmetry of the values of φ about the centre-axis of the magnet. The uncertainty on the force is of the order of $|\Delta F_z| \cong m_4 \cdot \chi_{\phi 3} \cdot \varphi_w \cong 5 \times 10^{-3}$ dn. Such an uncertainty, when considered to exist for sample 2, yields an uncertainty on the susceptibility about 0.4×10^{-7} emu g^{-1}. The value is larger than the observed effect and consequently allows for explaining the wrong sign in $\Delta\chi_2$. On the other hand, as the mass of sample 4 is 11.2 times that of sample 2 the uncertainty on the measured anisotropy is less than 18 percent. The anisotropy $\Delta\chi_4$, as observed in exp. 4.1, therefore, has a very high probability to be a real effect. To account quantitatively for $\chi_{\phi 3}$ the sample-holder, centered at room temperature, should deviate out of centre by 0.24 cm at 130 K. The deviation is attributed to stresses which are induced on cooling in the two, 70 cm long, thin copper wires suspending the sample holder. Once the stresses and deviations are accepted, it becomes plausible to assume that the two wires not necessarily deviate in the same direction. A rotation of the sample holder is therefore expected. In agreement with this assumption, the maximum of χ_1 in Fig. 4 is observed to change the angle ϕ from 30 to 45° for a decrease of the sample temperature from 130 to 4.3 K. The change in orientation is rather well reproducible when the balance is kept continuously in equilibrium and the susceptibility apparatus is not disturbed. Consequently, the anisotropy of KCP is believed not to change direction with temperature. Systematic errors in the position of the suspension wires are assumed to change the orientation of the sample.

A third difficulty to surmount, when measuring susceptibilities at low temperatures by the Faraday method, deals with the adsorption of oxygen. In a certain way, the difficulty reminds that formerly discussed for ferromagnetic impurities. Indeed, in the oxygen case too the magnetic moment of the contaminant is relatively large and its peculiar behaviour allows for the analysis of the magnetic data. Therefore, it is assumed that the susceptibility of adsorbed oxygen is comparable to that of the bulk material. The bulk pure solid oxygen is known to crystallize in three phases[9]: (1) the monoclinic α- for $T < 24$ K; (2) the rhombohedral β- for $24 \leq T \leq 44$ K; and (3) the cubic γ-phase for $44 < T < 54$ K. The susceptibility of α-, β- and γ-oxygen is about 0.4-, 1- and 3- $\times$ 10^{-4} emu g^{-1}, respectively. That of β-oxygen, $\chi_0 = 1 \times 10^{-4}$ emu g^{-1}, is compared to the parasitic paramagnetic component of the susceptibility, χ_p, which is estimated for experiments 2, 3 and 4 at a temperature of about 35 K. The force on the balance is:

$$F_x = m_s \cdot \chi_s \cdot \varphi_w + m_0 \cdot \chi_0 \cdot \varphi_w = m_s \cdot \chi_a \cdot \varphi_w \tag{5}$$

in which the subscripts s refer to the sample, o to oxygen and a to an apparent value. The apparent susceptibility is assumed to be:

$$\chi_a = \chi_s + \chi_p \tag{6}$$

Introducing eqn (6) into (5) yields for the adsorbed oxygen mass:

$$m_0 \cong m_s \cdot \chi_p / \chi_0 \tag{7}$$

In Table 2 are given: (1) the sample number; (2) the mass of the sample; (3) the estimated value for χ_p in the related experiment; (4) the corresponding mass of adsorbed oxygen as calculated using eqn (7); and (5) the pressure the oxygen would exert if the mass m_0 were released in the sample-plus balance-space at $T = 273.15$ K. The pressure is calculated using the ideal gas law, $p(O_2) = (m_0/32) \cdot RT/V$, with the space volume $V = 10.6$ l. The resulting pressures, for the three experiments, are of the same order of magnitude indicating that experimental conditions remain rather unchanged. The deduction seems plausible when it is remembered that the balance cannot be baked for outgassing. Consequently, one should watch for systematic errors.

Some further comments on the parasitic paramagnetic component of the susceptibility are given next.

(1) The quantitative magnetic analysis is based on the assumption that the susceptibilities of the adsorbed- and the β-oxygen are about equal at $T \cong 35$ K. The assumption is plausible when the number of oxygen molecule layers on the sample surface becomes large. A number of 200 is the lower limit for sample 3 when

TABLE 2

THE CALCULATED MASS m_o OF OXYGEN ADSORBED ON THE SAMPLE AT ABOUT 35 K

Sample no.	m_s (10^{-3} g)	χ_p (10^{-7} emu g^{-1})	m_o (10^{-6} g)	$p(O_2)$ (10^{-4} Torr)
2	2.89	1.2	3.5	1.8
3	2.40	0.5	1.2	0.6
4	32.39	0.02	0.65	0.3

it is assumed that the surface of the paraffine sheet was smooth, its area being $\simeq 0.1$ cm^2.

(2) The sudden susceptibility decrease, which is observed at 24 K on cooling pure oxygen and which step is attributed to the β- to α-phase transition, does not appear in the parasitic susceptibility component. The step seems to be smeared out over a few degrees. The same effect is reported by Mori[10] et al. for oxygen diluted with a few percent of argon.

(3) The Curie-type low-temperature component of the parasitic paramagnetism of the paraffine sample 3 can be explained once more by the dilution of oxygen, e.g., with nitrogen. The weakening of the anti-ferromagnetic exchange interaction also has been discussed by Mori et al.[10] for the oxygen–argon mixtures.

(4) The relatively low amount of Curie-type paramagnetism in exp. 3.2 can be understood assuming that cooling to 44 K has been so fast that the major part of the oxygen condensed on the Dewar-tail wall before it reached the sample. Raising the temperature should enable the oxygen to move to the sample. This deduction is in agreement with exp. 3.3.

(5) In the higher temperature region, the sudden susceptibility increase, which is observed at 44 K on warming up pure oxygen and which is attributed to the β- to γ-phase transition, neither appears in the parasitic susceptibility component. The peak of this component, nevertheless, is attributed to this transition because Mori et al.[10] showed that the addition of a few percent of argon to the oxygen started the transition at 40 K. At the β–γ transition, the diffusion of the molecules is greatly enhanced. Consequently, it is plausible to accept the onset of desorption to occur at this temperature.

Taking care for possible systematic errors, the present static magnetic susceptibilities of KCP samples will be compared with data existing in the literature. The latter are briefly summarized at first.

(1) Shchegolev[2] reported in 1972 that $K_2Pt(CN)_4Br_{0.3} \cdot 2.3\ H_2O$ is diamagnetic at room temperature. The diamagnetism is slightly less than the diamagnetic contribution of the core calculated by using Pascal's rules. The susceptibility of the complex seems to remain constant down to about 50 K below which temperature some increase is observed. The origin of the paramagnetic contribution to the susceptibility was not clear to him.

(2) Menth and Rise[11] (MR) reported, also in 1972, that their measurements on $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ single crystals reveal an anisotropic temperature dependence. The susceptibility perpendicular to the linear platina chains is independent on temperature and equal to $\chi_{M\perp} = -160 \times 10^{-6}$ emu mol^{-1}. The susceptibility parallel to the chains, however, depends on temperature and exhibits a fairly well-defined discontinuity in the region of $T = 40$ K. The molar susceptibility $\chi_{M\parallel}$ is $160 \times 10^{-6} + 2.50 \times 10^{-3}/T$ emu/mol for $T \geq 40$ K and $100 \times 10^{-6} \pm 1.84 \times 10^{-3}/T$ emu/mol for $T < 40$ K.

(3) Kuindersma and Sawatzky[12] (KS) reported in 1973 that in the temperature region they considered, i.e., between 77 and 300 K, the temperature-dependence of

$K_2Pt(CN)_4Br_{0.3} \cdot 2.3H_2O$ was found to be similar to that reported by MR above under (2), with slightly different values: $\chi_{K\perp} = -171(\pm 5) \times 10^{-6}$ emu mol^{-1} and $\chi_{K\parallel} = -176 \times 10^{-6} + 9.2 \times 10^{-3}/T$ emu/mol. They interpreted their results by showing that the upper limit for a possible Pauli paramagnetism is $\leq 10 \times 10^{-6}$ emu mol^{-1}. The only paramagnetic contribution to $\chi_{K\parallel}$ is of the Curie type. They felt that the Curie contribution more likely should be attributed to some localized Pt impurity. For single-crystal samples, a small temperature-independent paramagnetic susceptibility was found when the measurements were made with the material in vacuum. Discoloration and loss of the coppery lustre of the crystals was observed.

(4) Ginsberg et al.[13] reported in 1974 that DiSalvo's measurements on $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ crystals, grown by Guggenheim, reveal no Curie term at low temperatures.

The present study in exp. 4.2 yields susceptibilities for KCP which are in good agreement with the qualitative results reported by Shchegolev. The compound is diamagnetic and nearly independent on temperature. Below 50 K, a paramagnetic contribution occurs which is shown to exhibit a maximum at 40 K. The general behaviour of the paramagnetism suggests that it is due to oxygen adsorbed on the sample. At variance with the results of Menth and Rice and of Kuindersma and Sawatzky, the present study, to within the limits of its precision, does not reveal an anisotropic temperature-dependence of the susceptibility of KCP. In agreement with all authors mentioned above, the $\chi_\perp$ values measured on a rather quickly cooled crystal, are observed to be nearly temperature-independent. In agreement with the results of MR and KS, the $\chi_\parallel$ values in exp. 2.1.2 are found to show a Curie-type paramagnetism. The present study, by the use of a turnable magnet, revealed that the difference in behaviour is not due to a difference in crystal orientation but must be attributed to a change in the susceptibility of the sample. The Curie-type paramagnetism, therefore, is attributed to degradation of KCP when slowly warmed up to room temperature under reduced pressure. The susceptibility change could give rise to a systematic error if one would not be aware of the degradation and if one would reorient the crystal after the warming-up period. In such a case, one might attribute the appearing paramagnetism to reorientation instead of degradation. It would be even worse if one could reach low temperatures in a less sensitive apparatus because then the peak in the parasitic paramagnetism of the adsorbed oxygen would be observed as a well-defined discontinuity in the temperature-dependence of the susceptibility at 40 K.

When it is accepted that the Curie-type paramagnetism is due to degradation of KCP, then the produced free radicals should no longer be felt to be attributed more likely to some platinum impurity as KS suggested, because the lack of anisotropy of the Curie magnetism, that results from the present work, reduces the arguments in favour of Pt. The degradation reaction is deduced not to proceed below 225 K as Menth and Rice measured a constant value for $\chi_{M\perp}$ up to that temperature. The deduction allows one to explain DiSalvo's experiments together with the present experiment 2.1.1 in which no Curie term at low temperatures has been revealed. In the other experiments of the present work, a Curie term does occur. The Curie constants are found to be $C_{g2} \cong 6 \times 10^{-6}$ emu K g^{-1} and $C_{g4} \cong 4.5 \times 10^{-8}$ emu K g^{-1} for exp. 2.3.2 and 4.2, respectively.

To compare these values with those of the literature, the latter are converted to the same units by the use of eqn (8):

$$\chi_g = \chi_m / M \tag{8}$$

that relates the gram- to the molar-susceptibility by dividing the latter by the molecular weight of the sample material. The conversion leads to the Curie constants $C_{MR} = 5.5 \times 10^{-6}$ emu K g^{-1} and $C_{KS} = 20.8 \times 10^{-6}$ emu K g^{-1} for the experiments of MR and KS, respectively. The difference in the Curie constants, $C_{MR} \neq C_{KS}$, allowed Kuindersma and Sawatzky to realize that the Curie paramagnetism should not be attributed to an intrinsic effect. In the present model, it means that the degradation of KCP may differ from crystal to crystal.

The next topic in the discussion of the magnetic data analysis deals with the determination of the intrinsic diamagnetic susceptibility of the undegraded KCP crystals. The general pattern of the low-temperature part of the correlation of the measured susceptibility versus reciprocal temperature, as revealed in Fig. 5, indicates the presence of adsorbed oxygen on sample 4 and a slight degradation of the material. The degradation might occur at the sample surface only. The effect of oxygen is negligible at temperatures above 50 K and below 5 K at fast cooling. The susceptibility values, measured at these temperatures, are used to determine the Curie-type paramagnetism so that the susceptibilities, measured at higher temperatures, can be corrected for the effect of degradation. At temperatures above 65 K, the susceptibility becomes less diamagnetic with increasing temperature. The effect is unexpected from the point of view of a constant diamagnetic susceptibility behaviour. The paramagnetic difference is attributed to the Pauli paramagnetism of the electronic conducting material. At $T \geq 130$ K it is about 0.1×10^{-7} emu g^{-1} and lower than 0.23×10^{-7} emu g^{-1}, the converted upper limit given by Kuindersma and Sawatzky. As the electronic conductivity decreases steeply with decreasing temperature in the region of about 100 K[1], the Pauli paramagnetism is assumed to be negligibly small at 65 K. The underlying diamagnetism of sample 4, therefore, is calculated by correcting the experimental susceptibility values for the Curie-type paramagnetism. The correction, $(C_{g4}/65) \cong 7 \times 10^{-10}$ emu g^{-1} leads to the diamagnetic susceptibilities of the KCP sample 4 at 65 K: $\chi_\perp = -3.83 \times 10^{-7}$ emu g^{-1} and $\chi_\parallel = -3.60 \times 10^{-7}$ emu g^{-1}. To compare numerically the present susceptibility results to those in the literature, in which the 6 percent anisotropy of the underlying diamagnetism of KCP is not mentioned, the orientational average of the susceptibility is considered. This is, for sample 4:

$$\chi_g = \frac{1}{3}(\chi_a + \chi_b + \chi_c) = -3.75 \times 10^{-7} \text{ emu g}^{-1} \tag{9}$$

with the principal susceptibilities $\chi_a = \chi_b = \chi_\perp$ and $\chi_c = \chi_\parallel$. The same treatment for the data of sample 2 yields $\chi_g = -3.2 \times 10^{-7}$ emu g^{-1}. These values are to be compared with $\chi_{gMR} = -3.51 \times 10^{-7}$ emu g^{-1} and $\chi_{gKS} = -3.90 \times 10^{-7}$ emu g^{-1}, the converted values of Menth and Rice and of Kuindersma and Sawatzky, respectively. The gram-susceptibilities of KCP seem to cover a large range, from -3.2 — to -3.90×10^{-7} emu g^{-1}. For single-crystal samples, Kuindersma and Sawatzky reported that a small temperature-independent paramagnetic susceptibility was found when the measurements were made with the material in vacuum. Their observation of the discoloration and the loss of the coppery lustre of this material has been repeated in the present exp. 1. The effect is attributed to the loss of water. Drosdziok and Engbrodt[14] showed that 3 of the water molecules of crystallization can be extracted and added again in KCP by varying the external water vapour pressure. In the present experiment, the water content of the KCP samples is not well known, as the humidity of the laboratory atmosphere in which the single crystals were stored for some time was not measured. It seems that other authors too had some difficulties with the determination of "n" in the $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$ of their single crystals. Indeed, two groups, which both reported quantitative values for the diamagnetism of KCP, agree that the susceptibility is understood on the addition of Pascal's constants. This means that:

$$\chi_m = \chi_a + n \cdot \chi_w \tag{10}$$

The χ's are molar susceptibilities and the subscript m refers to the material, a to the water-free part of it and w to water. For two different samples, which are characterized by (m, n) and (m', n') respectively, the equation (10) leads to:

$$\chi_m - \chi_{m'} = (n - n') \cdot \chi_w \tag{11}$$

expressing that for $n > n'$ the material m should be more diamagnetic than m'. The statement is at variance with the data in literature: (-160×10^{-6} emu mol^{-1}, 3) for MR and (-171×10^{-6} emu mol^{-1}, 2.3) for KS. The water content problem, therefore, is considered the other way round. The value of n is calculated from the experimental gram-susceptibility χ_g. Equation (10) is substituted in (8) which yields χ_g as a function of n:

$$\chi_g = \frac{\chi_a + n \cdot \chi_w}{M_a + nM_w} \tag{12}$$

in which the molecular weight of the material is expressed as the sum of its components. Equation (12) leads to:

$$n = \frac{\chi_a - \chi_g \cdot M_a}{\chi_g \cdot M_w - \chi_w} \tag{13}$$

With the most diamagnetic material data found in the literature, as reference, $\chi_{m'} = -171 \times 10^{-6}$ emu mol^{-1} and $n' = 2.3$, taking $\chi_w = -13 \times 10^{-6}$ emu mol^{-1},

$M_a = 401.5$ and $M_w = 18$, one obtains that for sample 4, for which $\chi_g = -3.75 \times 10^{-7}$ emu g^{-1},

$$n = \frac{-141.1 + 150.5}{-6.75 + 13.} = \frac{9.4}{6.5} \cong 1.5 \tag{14}$$

The precision on n is rather poor because the numerator in eqn (14) is the small difference of two relatively large values. In this case, the difference is 6.7 percent of the reference value. The reference value is deduced, with the use of Pascal's rule, from the experimental value χ_m, which is claimed by the authors KS to be precise to within 3 percent. The uncertainty on n in eqn (14) is at least 45 percent. When the same procedure is carried out for sample 2, it leads to the unrealistic negative value -1.7 for n. It means that χ_g is apparently less diamagnetic than can be accounted for by the reference data. From these data, a calculated minimum for the diamagnetic gram-susceptibility of KCP is:

$$\chi_{g\min} = \chi_a/M_a = -3.51 \times 10^{-7} \text{ emu g}^{-1} \tag{15}$$

The less diamagnetic apparent susceptibility of sample 2 can be explained on the assumption that, at the moment of the weighing of the sample, n was still 3 but that afterwards, at the sealing of the paraffine box, most of the water evaporated from the sample. The mass of the sample, at the susceptibility measurements could be lower by a factor $M_a/(M_a + nM_w)$ than the weighed mass. Correction for it results in $\chi_g' = -3.6 \times 10^{-7}$ emu g^{-1} yielding $n = +0.5$. The explanation for the low diamagnetic susceptibility value of sample 2, together with the result of exp. 2.1.1, which shows that the susceptibility of sample 2 was independent on temperature before it heated-up slowly, indicates that at about room temperature the water molecules of crystallization can be extracted from KCP without damaging the basic compound. The relatively small quantity of water left in sample 2 seems to be sufficient for generating degradation products at the slowly heating up of the apparatus in exp. 2.1.2.

CONCLUDING REMARKS

Static magnetic susceptibility data on $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$, as measured by means of a vacuum microbalance following the Faraday method at temperatures between 4 and 148 K and at field strengths between 6 and 20 kOe, have been presented. The experimental data have been discussed in a way showing the difficulties, encountered at the measurements, the effects of which may explain some of the rather divergent results obtained by various groups on this material.

The field dependence of the apparent susceptibility, observed in exp. 2, indicates that ferromagnetic impurities are sometimes present. The equivalence of one part per million of iron yields a paramagnetic contribution which is 2.8 percent of the diamagnetic susceptibility of pure KCP when measured at 20 kOe.

Paramagnetic centres which obey the Curie law appeared in sample 2 after heating it up slowly to room temperature under reduced pressure. The effect is attributed to free radicals created at the degradation of the sample. Degradation seems to occur only above 225 K. In extreme cases, the paramagnetism exceeds the diamagnetism of the sample.

A parasitic paramagnetic component of the susceptibility is observed below 50 K where it exhibits a maximum at 40 K. It is attributed to the effect of microgram quantities of oxygen adsorbed on the sample.

A small but systematic reduction of the diamagnetism is measured for increasing temperatures above 65 K. It is about 4×10^{-6} emu mol^{-1} at $T \geq 130$ K and is attributed to the Pauli paramagnetism of the conductor.

The analysis of the data of sample 4 yields -3.60 and -3.83×10^{-7} emu g^{-1} for the intrinsic static magnetic susceptibility of $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$ at 65 K when the magnetic field vector is respectively parallel and perpendicular to the c-axis of the crystals.

The comparison of the orientational average of these susceptibilities to data in literature, in principle, allows for the estimation of $n = 1.5$ for sample 4. The precision on n is very poor and its discussion suggests that the susceptibility references should be measured more accurately.

The 6 percent anisotropy of the susceptibility is attributed mainly to the π^2-bond in the CN groups. The bond configuration results in a relatively strong value for the diamagnetism in the direction of the CN bond and may produce a paramagnetic contribution perpendicular to this direction[15]. For structural reasons, on the average, the anisotropy of only one half of the CN groups is measured when a single crystal of KCP is turned from $\bar{C} \perp \bar{H}$ into $\bar{C} // \bar{H}$. Therefore, one can calculate that, if all CN groups as they exist in KCP were oriented parallel to each other, the maximum anisotropy would amount to 20×10^{-6} emu mol^{-1}.

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