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Magnetic Susceptibility and Specific Heat of the One-Dimensional Conductor $(H_3O)_{1,6}Pt(C_2O_4)_2 \cdot n\,H_2O$ at Low Temperatures

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It has been shown recently that some transition metal complexes exhibit one-dimensional metallic properties. We report, in this context, susceptibility and specific heat measurements of polycrystalline $(H_3O)_{1,6}Pt(C_2O_4)_2 \cdot n\,H_2O$ in the low temperature range. We find that the susceptibility can be described by a non-uniform Curie law with a characteristic break in the slope. The specific heat reveals no linear temgerature contribution, which could be explained by a transition into a Peierls distorted state. Until 13°K, the heat capacity follows a T^3-law. Deviations at higher temperatures are possibly attributed to the anisotropy of the system.

Tem sido mostrado recentemente que alguns complexos de metais de transição apresentam propriedades metálicas unidimensionais. Neste texto nos referimos a medidas de susceptibilidade magnética e calor específico de $(H_3O)_{1,6}Pt(C_2O_4)_2 \cdot n\,H_2O$, um típico metal unidiniensional, a baixas temperaturas. Encontramos que a susceptibilidade pode ser descrita por uma lei de Curie não uniforme, com uma troca característica na inclinação. A baixas temperaturas o calor especifico não apresenta o termo linear, o que poderia ser explicado por uma transição para um estado de distorção de Peierls. Ate 13°K, a capacidade calorífica segue a lei T^3 e desvios a temperaturas mais altas são possivelmente atribuídos a anisotropia do sistema.

Introduction

The platinum-dioxalatocomplexes belong to a class of sqúare-planar, mixed valency complexes (MVP), whose structure has been investigated and elucidated mainly by Krogmann and co-workers in the middle of 1960 (Ref. 1). These compounds have received special attention recently because of their structural property, which allows an electrical conductivity along one crystallographic axis.

By means of x-ray and neutron diffraction methods, it has been shown that the crystal is built up from columns with the metal atoms in the

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centre of a square and the ligands at the corners, in a staggered position. The Pt-atoms of the compound we investigated, have a distance of 2.8 Å, which is very close to the value of the bulk metal (2.77 Å). This small distance gives rise to an overlapping of the d^8-orbitals, which results in the formation of a quasi one-dimensional (1-D) band. In the absence of strong electron acceptors or donators, this band is completely filled, the substance thus being an ordinary band gap insulator. By partial oxidation, however, one obtains stable compounds with formally mixed valencies of the metal atoms, which in our case results to 2.40. This is equivalent to a partial emptying of the band, resulting in a 1-D metallic state, with a high electrical conductivity along the metal chains. Since the chains are insiilated from each other by the presence of the ligands, the conductivity shows a considerable anisotropy which can amount to five orders of magnitude[2]. From Mössbauer[3,4], susceptibility[3,5], and optical measurements[6], one can conclude that at ordinary temperatures the electrons move freely along the chains and form a 1-D electron gas.

The properties of such a 1-D system are hitherto – despite of numerous experimental and theoretical work – only uncompletely understood. Mainly two models have been discussed in the light of the experimental findings. In the interrupted strand model (ISM), the properties are derived from the picture that perfectly insulating lattice defects separate the metallic chains into smaller segments and that, in the resulting 1-D boxes, a free electron gas exists[7,8]. More recently, a second model has found strong experimental support[9]. As shown by Peierls[10], a 1-D metal must be – when treated in the one particle approximation, where electron-electron interaction is neglected – an unstable structure, which below a typical transition temperature undergoes a spontaneous lattice distortion, hereby lowering the kinetic energy of the electrons. In this process, the partly filled conduction band will be split up into a number of smaller zones, some of which are filled and the rest empty. These bands are separated by a temperature dependent gap, transforming the 1-D metal into a bandgap semiconductor. However, calculations taking into account electron-electron interaction[11] indicate that these systems are not bound to undergo a Peierls transition.

Most of the experiments to study the properties of MVP-complexes have been performed on $K_2Pt(CN)_4Cl_{0,3} \cdot n\,H_2O$ (KCP), one of the solids which exhibit 1-*D* metallic properties[12]. To obtain further progress in the understanding of 1-*D* systems, we have investigated the magnetic and caloric properties of $(H_3O)_{1,6}Pt(C_2O_4)_2 \cdot n\,H_2O$ (HOP) – another 1-D system – which hitherto had not been studied.

Experimental

Samples

The partially oxidized dioxalatoplatinate complex was prepared at the Institiite for Inorganic Chemistry of the University of Heidelberg (Germany)* in a procedure described by Wahl[13]. The crystals had a deep blue colour with a coppery sheen, which still remained when the material was dehydrated at room temperature in a vacuum for some hours. The maximum loss of water achieved by this procedure amounted to about 10% of the original weight, corresponding to a loss of two water molecules per formula unit. Left at the open air at room temperature, after dehydration the material returned to its original weight without visible changes. Since dehydration is known to produce severe changes in the physical properties of the MVP complexes[14], we studied the properties of the crystal in the hydrated, as well as in the dehydrated state. However, in neither case the exact number n of the water molecules present in the complex was known. The unoxided potassium salt, $K_2Pt(C_2O_4)_2 \cdot n\,H_2O$, which does not exhibit 1-D metallic properties, was also prepared to allow for comparative measurements.

Susceptibility

Recently, two papers have been devoted to the magnetic susceptibility of the 1-D metals iridiumcarbonylchloride[3] and KCP[15]. In both cases, a peculiar magnetic behaviour was observed. The susceptibility of the materials investigated follows a non-uniform Curie law with a discontinuity in the slope at about 25°K. Neitheí the origin of the observed paramagnetism nor that of the characteristic break in the slope could be satisfactorily explained. The given explanations range from Pauli and van Vleck paramagnetism to impurities and ardering of ions in the crystal upon a temperature change.

To obtain more evidence about the controversy, we measured the magnetic susceptibility of the unoxidized and the partially oxidized dioxalatoplatinate complex from 1.5 – 300°K. We applied the Faradap method using a conventional helium cryostat[16] together with a zero

*We are particularly indebted to Prof. H. J. Keller for the preparation and provision of the crystals.

type electronic balance[17], having a resolution of 1 μg. The applied magnetic field of 7 000 *Oe:* was controlled by a Hall probe. The samples were placed in a quartz container suspended from a silver chain. The diamagnetic susceptibility of the empty system was constant over the whole temperature range. The temperature was measured using either a germanium resistor for low temperatures (.5 – 30°K) or a Au (+ 0.03 % Fe) and alumel thermocouple for higher temperatures (20 – 300°K). The calibration of the system was performed with $HgCo(SCN)_4$, whose susceptibility is well known[18]. In order to study the influence of crystal water on the susceptibility of HOP, some of the samples were dehydrated under vacuum at room temperature in the sample space of the cryostat. After, weight constancy dry helium gas serving as thermal contact was filled in and the sample cooled down to the desired temperature. In some other runs, the sample was introduced into the precooled cryostat and rapidly cooled down to 77°K in a helium atmosphere of 760 torr. Evacuation of the sample space and refill with helium contact gas of low pressure did not change the sample weight and served as an indication that the sample retained their original crystal water content.

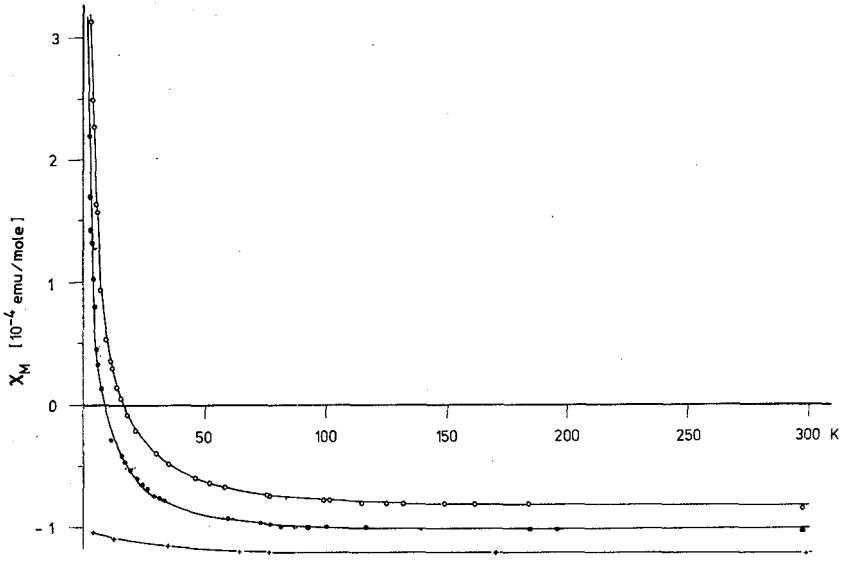

Fig. 1 – The molar magnetic susceptibility of polycrystalline HOP and the unoxidized potassium salt as functions of the temperature.
° HOP with low crystal water content (n ≈ 0).
● HOP with high crystal water content (n ≈ 2).
+ $K_2Pt(C_2O_4)_2 \cdot n\,H_2O$ (n ≈ 2).

The results of our susceptibility measurements on HOP with low (presumably n ≈ 0) and high crystal water content and on the unoxidized potassium salt $K_2Pt(C_2O_4)_2 . n H_2O$ as function of the temperature are shown in Fig. 1. The unoxidized material is seen to exhibit a temperature independent diamagnetism, except at the lowest temperatures, where, probably due to small impurities, a paramagnetic influence is observed. The oxidized products show a marked paramagnetism, which when plotted – as in Fig. 2 – as a function of $1/T$ displays the same fairly well defined discontinuity, as reported earlier for other 1-D compounds[3,15]. This similarity between various completely different compounds favours the conclusion that the observed unusual paramagnetism is a common property of the MVP complexes and is possibly associateti with the specific electronic structure.

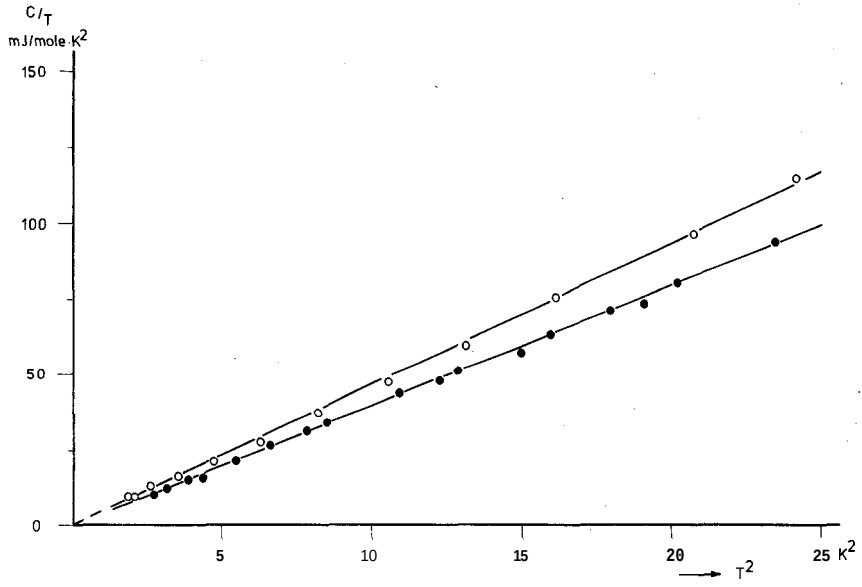

Fig. 2 – Molar susceptibility of HOP as function of the reciproca1 temperature.
o HOP with low crystal water content (n ≈ 0).
● HOP with high crystal water content (n ⊂ 2).

The underlying diamagnetism which emerges at higher temperatures is in accord with the calculated diamagnetic contributions of the platinum core and the ligands, when using Pascal's constants[19]. So, we find for the unoxidized $K_2Pt(C_2O_4)_2$ a molar susceptibility of 126.10^{-6} emu/mole, for HOP, a value of about 100.10^{-6} emu/mole and, for the dehydrated HOP, a somewhat lower figure, corresponding well with

the experimental findings. The Pauli temperature independent paramagnetism, which the 1-D metals might contain, is small in comparison with the above numbers. Using[7] $\chi_p = 2 . \mu_B^2 . g(\varepsilon_F)$ and for the electron state density $g(\varepsilon_F) = 2 . n_A/\pi . h . v_F$, we find $\chi_p = 7.10^{-6}$ emu/mole, when setting $n_A = 10^{14}$ strands/cm^2 and, for the Fermi-velocity, the approximate value $v_F = 10^8$ cm/s. Fig. 2 shows that the paramagnetism of HOP can be described in the $1/T$ diagram by two straight lines with different slopes. We use these slopes to calculate the effective magnetic moments of the complexes and find, for the sample with high water content, $\mu_{eff} = 0.097$ Bohr magnetons (BM) above 17°K and 0.079 BM below 17°K. The corresponding values for the dehydrated complex are 0.11 BM and 0.097 above and below 22°K respectively. These values are in good agreement with those reported for KCP and iridiumcarbonylchloride. Such a similarity for very different materials excludes magnetic impurities as possible sources for the observed paramagnetism. Whether this susceptibility can be ascribed to localized bonds of structural defects remains an open question[12]. The finding that the susceptibility of HOP increases with decreasing n indicates that lattice distortions generated by water deficiency may play a role. However, this model does not explain the peculiar break in the slope of the $1/T$ dependence. If the sample undergoes a Peierls distortion at low temperatures, a spin-paramagnetism from singly occupied states of localized electrons might also arise. Such a localization process would at least qualitatively describe the discontinuity in the slope of the Curie law. Nuclear magnetic resonance measurements on KCP (Ref. 20), however, seem to outrule such an interpretation.

It is evident, that more experimental and theoretical work is required for a full understanding of the magnetic properties of 1-D compounds. From the present investigation it is clear, however, that paramagnetic impurities cannot be respohsible for the observed effects.

Specific Heat

The specific heat has been calculated for 1-D metals in terms of the ISM in two quantum mechanical approaches. In the first model[7], a linear temperature term in the specific heat is predicted, as generally in a system containing free electrons. In the second calculation[8], the authors come to the conclusion that the heat capacity for a electron gas in a 1-D box is exponentially attenuated and thus exclude the presente of a linear term. The absence of such a linear contribution is

also expected if the system undergoes a Peierls distortion, transforming the material into a bandgap 'semiconductor.

So far, experimental results have been reported only for KCP[21] and (SN), Ref. 22. In the first case, no linear term has been observed, which is consistent with the Denton-Mühlschleger calculation, as well as a Peierls transition. However, in the more recent experiment on polysulfur nitride, a linear temperature contribution is found showing that – at least in this system – a Peierls transition is absent. This point of view is favoured by the ultimate finding that this system becomes superconducting at 0.26°K (Ref. 23).

Up to now, no experimental work on the specific heat of HOP has been communicated. Since our investigation of the magnetic susceptibility revealed a strong influence of the crystal water, we performed the specific heat measurements on samples with full and reduced water content. The procedure employed was designed specifically for small samples[24,25]. In this method, the sample is mounted onto a sample holder which consists of a thin (0.1 mm) sapphire slab. On one side of this sapphire disc, a heating film of about 1 000 Ohm is evaporated, and on the other, a germanium resistor (weight 0.5 mg) for temperature measurements is cemented. The sample is greased to the holder by means of approximately 0.5 mg Apiezon grease. Thin gold wires (0.25 μ) couple sample and holder thermically to a heat reservoir with variable temperature, which, in turn, is connected to the cryostat. Application of a small heating power P to the heating film gives rise to a temperature difference of about $\Delta T = 50$ m°K between sample and reservoir. Upon disconnecting P, the sample temperature decreases exponentially with a relaxation time τ. From the measured data P, AT, and τ, the heat capacity of the system sample and holder is evaluated[24]. The contribution of the sample holder had to be determined in a separate run and must be accounted for. In our case, it contributed with about 5% to the total heat capacity.

With this method, we measured different samples weighing between 20 and 90 mg in the temperature range between 1.5 and 20°K. The results of our experiments are shown in Figs. 3 and 4, where C/T is plotted against T^2. Such a plot has the advantage that the measured values of substances following the general low temperature dependence $C = aT + bT^3$ form a straight line whose intercept at $T = 0$ gives the electronic contribution a. Fig. 3 shows that the specific heat of HOP follows the Debye T^3-law until 13°K. The departure from this law

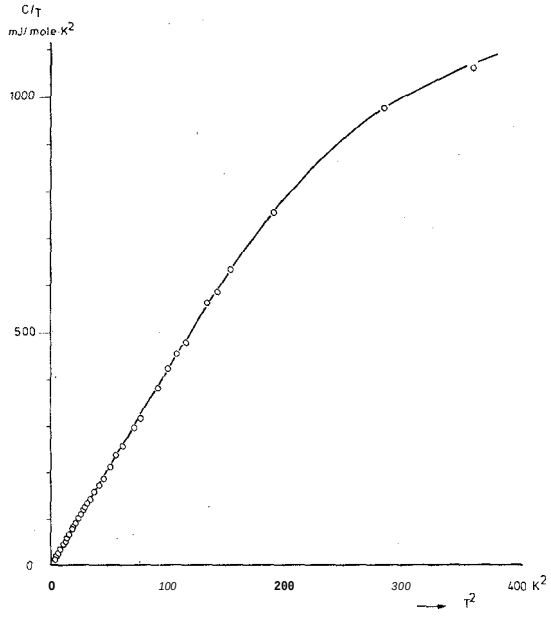

Fig. 3 – Specific heat of polycrystalline HOP Getween 1.5 and 20 K, plotted as C/T versus T^2.

above **13°K** indicates that the slope must be described by a smaller exponent. This observation is in accord with the results on another 1-D metal[22] and can be explained by the anisotropic force constants of these systems[26].

In Fig. 4, the results for both hydrated and dehydrated samples are presented for the range below 5°K. It is seen that the presence of crystal water does not change the general behaviour. The absolute values of the molar specific heat, however, differ by about 10%. Within experimental accuracy, no linear term in the temperature dependence is found. A least squares fit of the data gives for the hydrated sample the relation $C = (0 \pm 5.10^{-4}) . T + (4.5 \pm 0.1).10^{-3} . T^3$ J/mole.°K. The apparent absence of a linear term can be understood on the basis of either the quantum-mechanical ISM (Ref. 8) or could also be explained with a transition into a Peierls distorted state. Our specific heat data cannot make a distinction between these two proposed models. Investigation of the lattice dynamics and of structural changes by diffuse x-ray and neutron-scattering techniques[27], performed on KCP, are indications for a Peierls transition. Since specific heat and susceptibility

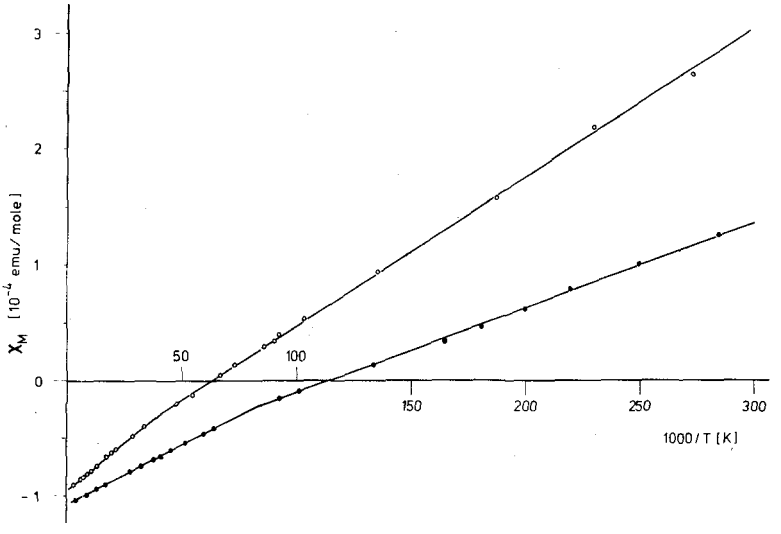

Fig. 4 – Details of the specific heat of HOP as given in Fig. 3 below 5°K. The open circles represent samples with full ($n \approx 2$) and the solid circles samples with reduced ($n \approx 0$) crystal water content. Assuming 25 atoms for the hydrated stacking unit, we calculate from the slope of the graph a Debye temperature of 221°K.

measurements on KCP reveal the same low temperature behaviour as found in this work, we may conclude that such a transition occurs in our system also. In view of the experimental[2] and theoretical results, which show that a Peierls transition can be suppressed in substances with very weakly coupled chains, this would indicate that in both systems a strong interchain exists. This conclusion is supported by our observation that a deviation from Debye's T^3-law starts at a relatively high temperature of 13°K. Unfortunately, we cannot compare this finding with that of KCP, since these measurements have been performed only until 6°K. Up to this value, no departure from T^3 was found, indicating that this may start at some higher temperature, as observed by us. On the other hand, $(SN)_x$, the only system so far known to undergo no Peierls distortion because of its weak interchain interaction, the departure from T^3 behaviour starts already at 3.2°K. The correctness of this speculative idea would signify that specific heat measurements could give some information about the anisotropy of the lattice forces between the chains in 1-D systems.

References

1. K. Krogmann, Angew. Chemie 81, 10 (1969).
2. H. R. Zeller, A. Beck, J. Phys. Chem. Solids **35,** 77 (1974).
3. A. P. Ginsberg, R. L. Cohen, F. J. di Salvo, K. W. West, J. Chem. Phys. 60,2657 (1974).
4. W. Ruegg, D. Kuse, H. R. Zeller, Phys. Rev. B **8,** 952 (1973).
5. D. Heitkamp, H. S. Rade, H. J. Keller, H. H. Rupp, J. Solid State Chem. (in press).
6. H. R. Zeller, P. Bruesch, Phys. Stat. Solidi (b) **65,** 537 (1974).
7. M. J. Rice, J. Bernasconi, J. Phys. F **3,** 55 (1973).
8. R. Denton, B. Mühlschlegel, Solid State Commun. 11, 1637 (1972).
9. R. Comes, M. Lambert, H. Launois, H R. Zeller, Phys Rev B 8,571 (1973).
10. R. E. Peierls, *Quantum Theory of Solids,* Clarendon Press, Oxford, p. 108 (1955).
11. I. E. Dzyaloshinskii, A. I. Larkin, Sov. Phys. JETP **34,** 422 (1972).
12. H. R. Zeller, Festkorperprobleme **XIII**, 31 (1973).
13. H. Wahl, Chem. News **62,** 35 (1895); see also K. Krogmann, P. Dodel, Chem. Berichte **99,** 3416 (1966).
14. D. Kuse, H. R. Zeller, Solid State Commun. **11,** 355 (1972).
15. A. Menth, M. J. Rice, Solid State Commun. 11, 1025 (1972).
16. Oxford Instruments, Oxford, England.
17. Sartorius Werke A. G., Göttingen, W. Germany.
18. H. S. Rade, J. Chem. Phys. **77,** 424 (1973).
19. See for instance: W. Haberditzl, *Magnetochemie,* Vieweg Verlag, Braunschweig.
20. H. Niedoba, H. Launois, D. Brinkmann, R. Brugger, H. R. Zeller, Phys. Stat. Solidi (b) **58,** 309 (1973).
21. R L. Greene, W. A. Little, Phys. Rev. Lett. 29, 718 (1972).
22. R. L. Greene, P. M. Grant, G. B. Street, Phys. Rev. Lett. **34,** 89 (1975).
23. R. L. Greene, G. B. Street, L. J. Sutter, personal communication, to be published.
24. H. S. Rade, Messtechnik. **83,** 230 (1975).
25. H. S. Rade, Ber. dt. Bunsenges. Phys. Chemie (to be published).
26. S. M. Genensky, G. F. Newell, J. Chem. Phys. 26, 486 (1957).
27. W. Glaser, Festkorperprobleme **XIV**, 205 (1974).
28. G. Beni, Solid State Commun. 15, 269 (1974).