The Heat Capacity and the Entropy of Transition of Würster's Blue Perchlorate

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Würster's Blue perchlorate

$[(CH_3)_2N\text{-}C_6H_4\text{-}N\text{-}(CH_3)_2]^+ ClO_4^-$

is one of the free radical crystals that are stable at room temperatures. Other similar crystals include those of diphenylpicryl hydrazyl (DPPH) and 1, 3-bisdiphenylene-2-phenyl allyl (BDPA), which are believed to become antiferromagnetic below 1.73 and 0.2°K respectively.[1] The heat capacity measurements of BDPA indicated the occurrence of linear antiferromagnetic chains below its Néel point; the heat capacity shows a sharp spike at 1.73°K and a broad maximum at higher temperatures, centering at about 3°K.[2] The magnetic properties of BDPA and DPPH are also consistent with the idea of spin ordering into an antiferromagnetic array at low temperatures.

Würster's Blue perchlorate, on the other hand, has a transition at a relatively high temperature (190°K), as is revealed by the magnetic susceptibility measurements.[3] This transition has sometimes been referred to as antiferromagnetic transition. McConnell's electron spin resonance studies[4] showed the existence of a triplet exciton state below the transition temperature and give support to Hausser's idea that the cation radicals are dimerized to give a singlet ground state and a triplet excited state.[5] Chesnut[6] presented a simple theory, based on these experimental facts, to account for the transition in terms of cooperative interaction between triplet excitons.

The present paper will describe some results of the measurements of the heat capacities of powdered Würster's Blue perchlorate, measurements conducted in an attempt to discriminate among various possible mechanisms of the transition.

Experimental

The calorimeter, the cryostat, and their operations were the same as have been described previously.[7]

Fine flakes of Würster's Blue perchlorate (WB) were a donation from Dr. K. Suzuki of Kwansei Gakuin University, who will describe their preparation elsewhere. The molar magnetic susceptibility of the specimen as received was 1.28×10^{-3} e.m.u./mol. at room temperature (12°C), which corresponded to that of about 100% free radical; it did not show any change after having been stored in dark, dry air for a year. As the amount of the specimen available was small, only 0.7079 g. or 0.002684 mol., of powdered WB was used in the measurement of the heat capacity; as a result, the error in the heat capacity values amounted to about 2% under the most unfavorable conditions, when the empty calorimeter contributed about 3/4 to the total heat capacity. The results of the measurements to be reported in the following section are for the fresh WB of a 100 ±3% free radical. After these measurements in the copper calorimeter with a few mmHg of helium exchange gas in it, the specimen was stored in situ for about half a year, during which time the apparata were moved to the North Campus of the University. The second series of runs which were then taken did not give consistent results in the phase transition region; however, the normal portion of the heat capacity agreed with that obtained in the first series of runs within the range of experimental error. The molar magnetic susceptibility after the second run was about 73% of the intial value for the fresh WB.

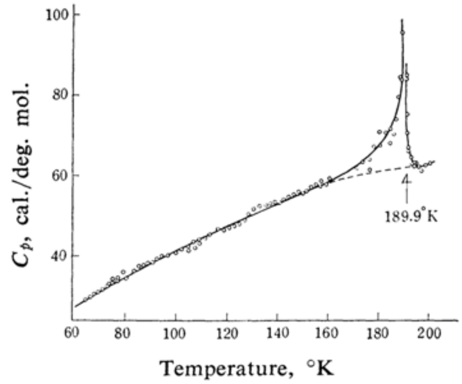

Fig. 1

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[1] A. S. Edelstein, *J. Chem. Phys.*, **40**, 488 (1964). This paper lists the earlier bibliography.

[2] J. P. Goldsborough, M. Mandel and G. E. Pake, Proc. VIIth Intern. Conf. Low Temp. Phys., Toronto, 702 (1961); A. S. Edelstein and M. Mandel, *J. Chem. Phys.*, **35**, 1130 (1961); W. O. Hamilton and G. E. Pake, ibid., **39**, 2694 (1963).

[3] K. Okumura, *J. Phys. Soc., Japan*, **18**, 69 (1963); see also W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

[4] a) H. M. McConnell and R. Lynden-Bell, ibid., **37**, 794 (1962); b) D. D. Thomas, H. Keller and H. M. McConnell, ibid., **39**, 2321 (1963).

[5] K. H. Hausser and J. N. Murrell, ibid., **27**, 500 (1957).

[6] D. B. Chesnut, ibid., **40**, 405 (1964).

[7] T. Shinoda, H. Chihara and S. Seki, *J. Phys. Soc. Japan*, **19**, 1637 (1964).

Results and Discussion

The primary experimental results are plotted in Fig. 1. There is a sharp rise in the heat capacity at 189.9°K, with a tail extending down to about 160°K. Although the temperature did not exactly stop at the transition point, it is highly probable that the transition is of the first order. Two independent runs were performed for the determination of the enthalpy change of the transition; it was 408.6±4.5 cal./mol. The entropy of the transition was 2.19±0.02 cal./deg.mol. It should be noted that this entropy change is very close to $\boldsymbol{R}\ln 3$, which is 2.18 cal./deg.mol.

The temperature of the transition has been reported differently by different investigators: Duffy's susceptibility curve(3) shows a sudden decrease at 186°K, Okumura's one(3) at 189°K, Edelstein(1) gave 175±5°K, and Suzuki's differential thermal analysis(8) showed a peak at about 190°K. The present study agrees with Suzuki's probably because specimens from the same batch were used in both experiments. As has been mentioned in experimental section, the lowering of the transition temperature may be due to the partial dying of the free radicals.

We shall now compare our experimental results with several models hitherto presented to account for this transition.

a) The Paramagnetic-antiferromagnetic Scheme.—The shape of the curve showing the temperature dependence of the susceptibility near 190°K is similar to that in an antiferromagnetic, as has been pointed out by Elliot and Wolfsberg(9) and by Duffy(3). Edelstein(1) developed a theory for a linear Ising chain of half spins and applied it successfully to the cases of BDPA and PAC. Here inter-chain coupling was approximated by the molecular field treatment. However, although he estimated the intra-chain exchange intergral for WB as $J/k=-27\pm10$, he did not explicitly mention that WB was an antiferromagnetic. Also, Duffy and Okumura pointed out that the Curie temperature, $|\theta|=$ 23°K, derived from the high temperature susceptibilities is too small, compared to the transition temperature, for an antiferromagnetic transition. The entropy of the transition to be predicted for such a scheme is $\boldsymbol{R}\ln 2$; the experimental results can rule out such possibility if the transition arises solely from an order-disorder problem of the spin system. If an attempt is made to divide the total entropy of the transition into contributions from the latent heat portion and those from the low temperature tail of Fig. 1, the latter amounts to 1.36 cal./deg.mol. and is close to what one would expect for an antiferromagnetic transition. The rest of the entropy would then come from some structural changes. In fact, X-ray diffraction studies, cited by McConnell,(4b) show that the transition is accompanied with a small structural change from the room-temperature orthorhombic phase to the low temperature monoclinic phase. The X-ray density does not appear to change substantially, and the angular tilt is only 2.7°. A single crystal does not shatter in going through the transition. It is difficult to assess the entropy of a structural change, but it should come from a variation in the lattice frequency spectrum, which must also be seen in the normal part of the heat capacity below and above the transition point. As the smooth dash-line curve in Fig. 1 suggests, such a variation would appear to be small.

b) The Dimerization Scheme.—Hausser's study(5,10) of the electronic absorption spectra of WB in solution and in solid is believed to indicate the presence of dimerized species in solid WB at low temperatures. Suzuki's spectroscopic study also supports this view.(11) The idea of dimerization has, moreover, been indirectly substantiated by McConnell's electron spin resonance studies, in which the triplet exciton resonance, free from a nuclear hyperfine structure, was observed at low temperatures. The X-ray diffraction findings that the unit cell lengths become doubled in the directions of the a and b axes can also be regarded as showing that dimerization occurs at the transition temperature. From the temperature dependence of the ESR signal intensity, McConnell was able to derive the energy of exitation from the ground singlet state to the triplet exciton state of a dimer as 246 cm^{-1}. The heat capacity should see the consequence of this energy gap that a Schottky-type anomaly occurs, with the maximum of 1.02 cal./deg.mol. at 123°K. Unfortunately, no anomaly of this magnitude is discernible in Fig. 1 because of the lack of precision in the measurements. A simple calculation shows, however, that the total gain in entropy due to the Schottky anomaly is $(1/2)\ \boldsymbol{R}\ln 4$ and that about 69% of this would have been acquired when the crystal reaches the transition point. Therefore, the transition would be concerned only with the dissociation of the dimerized species and the rest of the spin disordering. The dissociation does not itself contribute to the entropy, except, of course,

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8) K. Suzuki, 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963, Abstract of Paper 2U12.

9) N. Elliot and M. Wolfsberg, *Phys. Rev.*, **91**, 435A (1953).

10) K. H. Hausser, *Z. Naturforsch.*, **11a**, 20 (1956).

11) Private communication.

for the structural change which accompanies it.

The entropy of spin disordering at the transition is, thus, no larger than 31% of (1/2) $\boldsymbol{R}$ ln 4, or 0.42 cal./deg.mol., even if it is assumed that the rest of the Schottky anomaly is replaced by the cooperative disordering of spins.

c) Exciton Interaction.—Since the formation of cation dimers in WB at low temperatures and the excitation transfer of the triplet level of the dimers have been well established, another possible approach to the mechanism of the transition would be to incorporate the cooperative interaction between the excitons. Chesnut[6] showed that a type of order-disorder transition does occur if one includes in the interaction a term which is quadratic in the excitation density, ρ, and writes the Helmholtz energy for the N cations as:

$$F=\frac{1}{2}N\left[\varepsilon_0\rho+\frac{1}{2}\varepsilon_1\rho^2-\boldsymbol{k}T\{\rho\ln g-\rho\ln\rho-(1-\rho)\ln(1-\rho)\}\right]$$

where g is the multiplicity ($g=3$), ε_0 is the singlet-triplet excitation energy, and ε_1 is the inter-exciton energy. The justification for the quadratic energy term has already been discussed.[12,13] A diffuse first-order transition stems from the Helmholtz energy expression, and the entropy change will be:

$$\Delta S=\frac{1}{2}\boldsymbol{R}\Delta\rho\ln g$$

where $\Delta\rho$ is the change in the excitation density at the transition. The total entropy of the transition will now be:

$$\Delta S=\frac{1}{2}\times\frac{3}{4}\boldsymbol{R}\ln 3=0.82\ \text{cal./deg.mol.}$$

at the maximum since, in the limit of high temperature, the population in the triplet state would be $(3/4)N$.

We have now evaluated three possible interpretations of the transition and have found that no single mechanism can satisfactorily account for the observed change in entropy by the transition, 2.19 cal./deg.mol. Actually, if one considers only the spin system as the source of entropy creation at the transition, it is almost hopeless to get a larger value than $\boldsymbol{R}$ln 2 out of it. One of the recourses in such a situation is to assume some disordering in the orientation of perchlorate ions; this, however, has not been substantiated in WB experimentally. If this tetrahedral ion can assume one of two equally probable orientations in the high temperature phase and can then become frozen in either one of them at low temperatures, an entropy of $\boldsymbol{R}$ ln 2 would appear at the transition point. In fact, the combination of this type of disorder with the mechanism c, or the exciton cooperation, gives the total entropy of 2.20 cal./deg.mol., a value which is very close to what has been found by experiment. A refined X-ray diffraction study will give us some direct clue to the answer of this problem.

Summary

The heat capacity of Würster's Blue perchlorate (*N, N, N', N'*-tetramethyl-*p*-phenylenediamine perchlorate) has been measured between 66 and 200°K. A phase transition occurs at 189.9°K with its tail extending down to about 160°K. The transition is probably of the first order. The heat and the entropy of the transition are 408.6±4.5 cal./mol. and 2.19±0.02 cal./deg.mol. respectively. The magnetic susceptibility of the specimen at room temperature indicates that the paramagnetic spin density is 100±3%. The experimental results have been compared with current theories, and it has been inferred that some unknown structural changes are involved in the phase transition.

The authors would like to thank Professor Keisuke Suzuki of Kwansei Gakuin University, who gave us a sample of Würster's Blue perchlorate; the discussions with him have been helpful. The measurements of the magnetic susceptibility made, at our request, by Dr. Shuichi Tazawa of Osaka University helped to solve inconsistencies in the primary heat capacity results; to him the authors' deep gratitude is extended. Thanks are also due to Dr. Takako Shinoda, who helped us in part of the measurements.

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[12] H. M. McConnell and Z. Soos, *J. Chem. Phys.*, **40**, 586 (1964).

[13] D. B. Chesnut, ibid., **41**, 472 (1964).