ESR Spectrum of Triplet Species in Würster's Red Perchlorate

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Numerous investigations have been carried out on the electronic and magnetic properties of Würster's salts in both solution and solid. Thomas *et al.*[1] reported a triplet species in a single crystal of Würster's blue perchlorate (WBP) below the temperature of the phase transition (186°K), and suggested the dimerization of the cation through small molecular displacement in the crystal below transition point. Sakata and Nagakura[2] showed that the intensity of the charge transfer band between the cation in the solid WBP increased remarkably below transition temperature. Oohashi *et al.*[3] reported the extremely strong charge transfer band in solid Würster's red perchlorate (WRP), compared with those of WBP and of Würster's red bromide (WRB). No crystal sturcture of WRP was reported, while the cation in the solid WRB was reported by Tanaka and Mizuno[4] to be stacked at equal distances from each other.

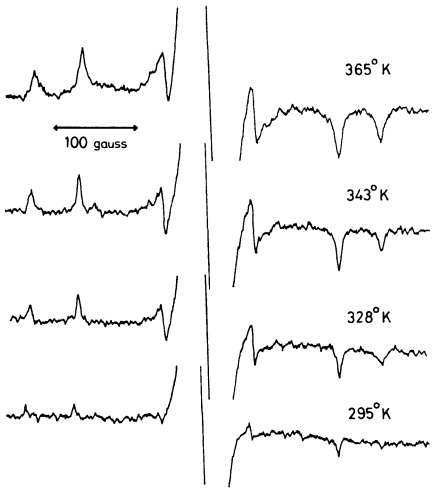

Fig. 1. The ESR spectra of the solid Würster's red perchlorate with random orientation at various temperatures.

We observed the ESR spectrum of triplet species in the powdered WRP[5] for the first time at various temperatures ranging from 290°K to 370°K. The results suggest the dimer structure of the cation in the solid WRP. Figure 1 shows a strong signal at $g=\sim 2.002$, and weak signals characteristic to the triplet species with random orientation at various temperatures. The ESR signals due to the triplet species showed reversible increment with increasing temperature up to the melting point of the crystal, while the central signal increased irreversibly with temperature. This might be due to the paramagnetic impurity decomposed in the crystal with increasing temperature. From three pairs of lines in ESR spectrum the zero-field splitting parameters were obtained to be $D=0.0189\ \mathrm{cm^{-1}}$ and $E=0.0098\ \mathrm{cm^{-1}}$ with $2D=406$ gauss.[6] The D value is consistent with a spin-spin dipolar interaction for an average distance of 5.1 Å.[7]

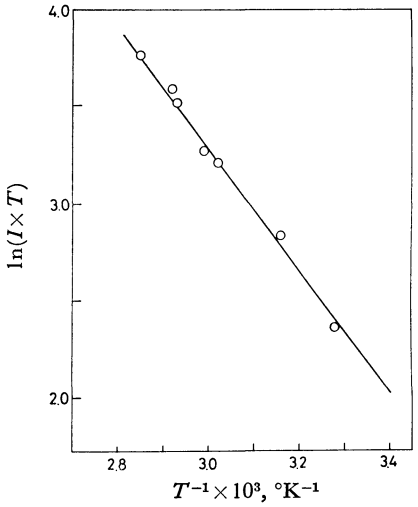

Fig. 2. Temperature dependence of the ESR spectrum due to the triplet species. Intensity of the signal obtained actually from the Y component[6] is in arbitary unit.

Figure 2 shows a linear relationship of $\ln(IT)$ against $1/T$, where I is the intensity of the ESR signal due to the triplet at various temperatures. From a slope of the straight line in Fig. 2, a singlet-triplet separation J was obtained to be $2100\pm 200\ \mathrm{cm^{-1}}$, where $I\propto \exp(-J/kT)$ was assumed because of $J\gg kT$. The value of J so obtained was compared with that in WBP (235—$246\ \mathrm{cm^{-1}}$).[1,2] The present results suggest that the WRP crystal consists of the dimer structure of the cation *at room temperature*. The large singlet-triplet separation is consistent with the extremely strong charge transfer band in WRP, and with the first observation of the ESR spectrum due to the triplet in the ion radical salts *at room temperature*.

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3) Y. Oohashi, T. Sakata, and S. Nagakura, The work was presented at the Symposium of Molecular Structure and Spectra, Tokyo (October, 1970).
4) J. Tanaka and M. Mizuno, This Bulletin, **42**, 1841 (1969).
5) The author is indebted to Drs. T. Sakata and Y. Oohashi for supplying a pure sample of WRP.
6) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).
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