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The Magnetic Susceptibilities and ESR of Wurster's Ions in Crystals

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The magnetic susceptibilities and the electron spin resonances of Wurster's blue bromide, blue iodide, and red bromide have been measured over a wide temperature range. The results show that the paramagnetism of Wurster's blue bromide above 210°K and of iodide can be explained by the linear Ising model, consistent with the crystal structure. Wurster's blue bromide showed a deviation from the linear Ising model below 210°K; the dimer model is most appropriate for the explanation of the experimental data.

The intensities of the single ESR line are consistent with the results of the static susceptivility measurements. The hyperfine structures are not observed, perhaps because of the rapid movement of the triplet exciton. The magnetic results are explained in terms of the *J*-values, the origin of which are discussed on the basis of the interaction between the charge-transfer states and the singlet state. The values are resonably correlated with the interaction parameter, β, as estimated from the crystal structure and the electronic spectral measurements.

The magnetic susceptibilites of Wurster's radical salts are of particular interest, as they show the effects of intermolecular spin coupling between the radicals. The electronic interaction between the radicals may be observed in several physicochemical properties; the electronic spectra have been shown to be greatly influenced by the charge-transfer effect.1) The singlet-triplet energy gap of the radical crystal may be produced by two mechanisms; one is a convalent-like exchange interaction between the radicals, and the other is the stabilization of the singlet ground state by the charge-transfer state. The charge-transfer interaction is more important than the exchange effect, because the electron overlap is very small between the radicals, and because the exchange interaction is second-order compared to the electron overlap.

In the present paper the result of magnetic susceptibility measurements of several Wurster's salts will be presented, together with the results of ESR measurements over a wide temperature range. The magnetic data will be discussed in terms of the exchange parameter, *J*. The localized spin models are most adequate for the consideration of the electronic behavior of the organic radical crystals. The observed *J*-values will be correlated with the calculated stabilization energies of the

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1) J. Tanaka and M. Mizuno, This Bulletin **42**, 1841 (1969).

ground state by means of the charge-transfer effects.

Experimental

The materials used in this investigation were prepared by the method of Michaelis and Granick.[2] The magnetic susceptibilities of Würster's blue iodide and bromide and Würster's red bromide have been measured by the Gouy method at temperatures between 80—300°K.

The results are shown in Fig. 1. Since the radicals are not very stable, some fluctuations are observed in the magnetic data. The accuracy of the absolute values was estimated to be about ±5%. Corrections were made for diamagnetic contributions (in 10^{-6} emu/mol) from neutral tetramethyl-*p*-phenylenediamine (−118), the bromide ion (−36), and the iodide ion (−52).[3] The value for the neutral amine was based on the observed susceptibility of *p*-phenylenediamine.[4] The susceptibility of Würster's blue iodide increases with decrease in the temperature; the maximum is reached at 140°K. The susceptibility of Würster's blue bromide gradually decreases with a lowering of the temperature and it reaches its minimum at 120°K. The susceptibility of Würster's red bromide shows only the diamagnetism at 300°K.

The ESR spectra have been observed by means of a conventional spectrometer at 9310 MHz. The intensity of the absorption lines was measured in comparison with the intensity of a small crystal of $CuSO_4 \cdot 5H_2O$ mounted in the same resonant cavity.

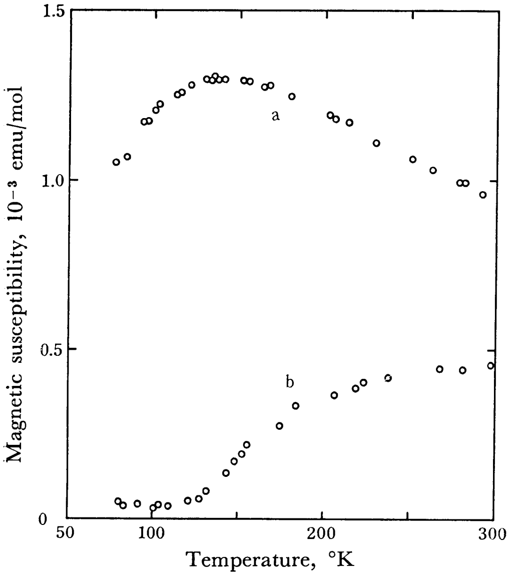

Fig. 1. Magnetic susceptibilities of Würster's Blue iodide (a) and bromide (b) at 70—300°K.

Discussion

The crystalline structure of Würster's blue iodide have been found to be a regular one-dimensional chain;[5] the structure of Würster's blue bromide has also been found to be a regular chain at room temperature.[6] The magnetic susceptibility of a regular antiferromagnetic chain will be given by the linear Ising model as

$$\chi = \frac{N_0 g^2 \mu_B^2 \exp(J/\mathbf{k}T)}{4\mathbf{k}T} \qquad (1)$$

where $g=2.00$ is the g-factor, μ_B is the Bohr magneton, $\mathbf{k}$ is the Boltzmann constant, N_0 is the Avogadro number, and J is the exchange parameter between the radical pairs.

The plot of log $(4\mathbf{k}\chi T/N_0\mu_B^2)$ against the inverse temperature is shown in Fig. 2. The experimental values of Würster's blue iodide coincide with the line calculated by the linear Ising model, although a slight deviation from the line is found at lower temperatures. The deviation from the calculated line is monotonous; therefore, it may be ascribed to the gradual increase in the J-value, which is accompanied by a decrease in the interplanar spacing as a result of a shrinkage of the lattice dimensions. The J-values are estimated from Eq. (1) to be $-59\ \text{cm}^{-1}$ at 300°K and $-83\ \text{cm}^{-1}$ at 80°K; the average value is $-71\ \text{cm}^{-1}$ for the 80—300°K range. Since the crystal structure of Würster's blue iodide is a regular chain, the use of the linear Ising model will be most

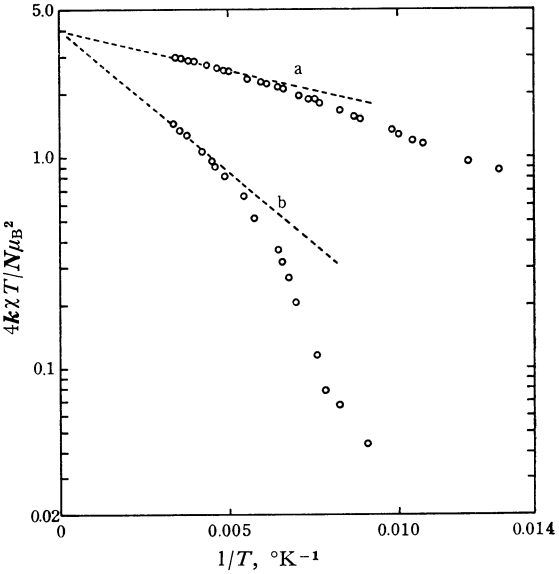

Fig. 2. The plot of magnetic data against inverse temperatures.

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[2] L. Michaelis and S. Granick, *J. Amer. Chem. Soc.*, **65**, 1747 (1943).

[3] P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, New York, N.Y. (1956).

[4] G. Foëx, "Constantes Sélectionèes, Diamagnétisme et Paramagnétisme," Mason, Paris (1957).

[5] J. L. DeBoer, A. Vos and K. Huml, *Acta Crystallgr.*, **B24**, 542 (1968).

[6] Unpublished results of this laboratory.

suitable. In addition, it is most probable that the equal spacing between the radicals is maintained down to low temperatures, for no sharp change in the susceptibility with the temperature is observed. The increase in the J-values at low temperatures is also reasonable, since the interaction will be enlarged by close contact between radicals.

The results on Würster's blue bromide are in contrast to those on the iodide; a sudden change in the slope is observed at 210°K. The abnormal decrease in the susceptibility below this temperatures implies that a phase transition may take place at this temperature. Several discussions have been presented with regard to the stability of the linear interacting system;[7-9] a phase transition has actually been reported on the crystal of Würster's blue perchlorate.[9-11] Although no X-ray results have yet been found for Würster's blue bromide, a similar transition is plausible at lower temperatures. Therefore, the linear Ising model will be used above 210°K and the dimer model will be employed below this temperature. From Eq. (1) the J-value is estimated to be $-210\ \mathrm{cm}^{-1}$ in the 210—310°K range. According to the dimer model, the susceptibility is given by:

$$\chi = \frac{N_0 g^2 \mu_\mathrm{B}^2}{3kT[(1 + (1/3)\exp(2|J|/kT))]} \tag{2}$$

By the use of Eq. (2), the J-value for 120—210°K is determined to be $-350\ \mathrm{cm}^{-1}$. This value is justified in view of the value above a phase transition, since the charge-transfer interaction will be much increased by the dimer formation at low temperatures.

ESR Spectra. The intensities of the ESR spectra were measured with Würster's blue bromide and iodide for the temperature range of 80—300°K. The results are nearly in agreement with the static measurements, as is shown in Fig. 3, where the results for Würster's blue bromide is presented. The ESR spectra of these radical salts do not show any hyperfine structures; a single line is observed in both salts. The lack of the hyperfine structures may suggest that the movement of the triplet exciton is so rapid that the triplet dipolar structure is washed out.[12,13]

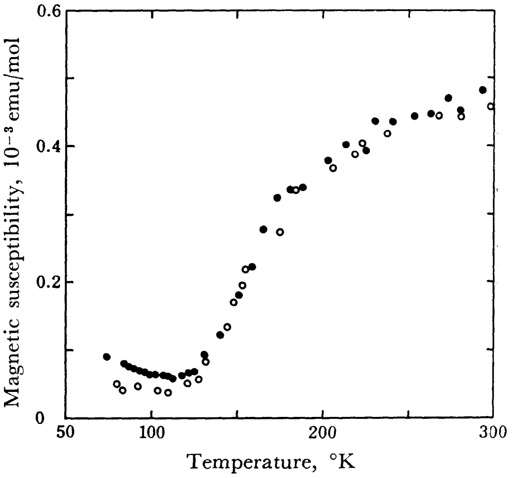

Fig. 3. The Comparison of Susceptibility Measurements by Static (○) and the ESR (●) methods.

The g-factors are those of the free spin values; the values are $g=2.0028\pm0.0005$. The measurement of the single crystal of the iodide shows no anisotropy on the g-values and the line-width. The line widths are 11 Oer (31 Mc) for iodide and 4 Oer (14 Mc) for bromide. The line-width is not changed markedly with the temperature for Würster's blue iodide. The width of Würster's blue bromide is decreased in the 120—170°K range, where the dimer is presumably formed, and it increases below 120°K because some impurities may contribute dominantly in this temperature range.

Singlet-Triplet Energy Gap. The observed J-values can theoretically be correlated with the intermolecular electronic interactions between the radicals; the values can be calculated if the molecular wave functions and the energies of the intermolecular interactions are known precisely. In a previous paper[1] we have presented the calculations for the triplet state of the dimer system.

The wave functions for the singlet ground state and the triplet state are given by;

$$\left.\begin{aligned}
\Psi_\mathrm{S} &= \frac{1}{\sqrt{2(1+S^2{}_{mm})}}[\phi_a{}^m(1)\phi_b{}^m(2) + \phi_a{}^m(2)\phi_b{}^m(1)] \\
&\qquad \times[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\
\Psi_\mathrm{T} &= \frac{1}{\sqrt{2(1-S^2{}_{mm})}}[\phi_a{}^m(1)\phi_b{}^m(2) - \phi_a{}^m(2)\phi_b{}^m(1)] \\
&\qquad \times\begin{cases}\alpha(1)\alpha(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \\ \beta(1)\beta(2)\end{cases}
\end{aligned}\right\} \tag{3}$$

where $\phi_a{}^m$ and $\phi_b{}^m$ denote the highest molecular orbitals which are half-occupied, where α and β are spin functions, and where S_{mm} is the overlap integral between the $\phi_a{}^m$ and $\phi_b{}^m$ orbitals.

The Hamiltonian and notations for the molec-

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[7] Y. Ooshika, *J. Phys. Soc. Jap.*, **12**, 1238, 1246 (1957); **14**, 747 (1959).

[8] H. C. Longuet-Hitggins and L. Salem, *Proc. Roy. Soc. Ser. A*, **251**, 172 (1959).

[9] D. D. Thomas, H. Keller and H. M. McConnell, *J. Chem. Phys.*, **39**, 2321 (1963).

[10] K. Okumura, *J. Phys. Soc. Jap.*, **18**, 69 (1963).

[11] H. Chihara, M. Nakamura and S. Seki, This Bulletin, **38**, 1776 (1965).

[12] D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961).

[13] Z. G. Soos and H. M. McConnell, *ibid.*, **43**, 3780 (1965).

ular integrals are the same as in the previous paper.[1)] The diagonal energy for the triplet state and the separation of the singlet and the triplet state are:

$$\left.\begin{aligned}E_\mathrm{T} = {} & 2\varepsilon_a - 2\langle\phi_a{}^m|1/R_b|\phi_a{}^m\rangle \\ & + (\phi_a{}^m\phi_a{}^m|\phi_b{}^m\phi_b{}^m)(1+S^2{}_{mm}) \\ & + \sum\frac{\delta_i\delta_j}{R_{a_i,b_j}} + 2S_{mm}\langle\phi_a{}^m|1/R_b|\phi_b{}^m\rangle \\ & - 2S^2{}_{mm}\langle\phi_a{}^m|1/R_b|\phi_a{}^m\rangle \\ & - (\phi_a{}^m\phi_b{}^m|\phi_a{}^m\phi_b{}^m) \\ \Delta(T-S) = {} & 4S_{mm}\langle\phi_a{}^m|1/R_b|\phi_b{}^m\rangle \\ & - 4S^2{}_{mm}\langle\phi_a{}^m|1/R_b|\phi_a{}^m\rangle \\ & + 2S^2{}_{mm}(\phi_a{}^m\phi_a{}^m|\phi_b{}^m\phi_b{}^m) \\ & - 2(\phi_a{}^m\phi_b{}^m|\phi_a{}^m\phi_b{}^m)\end{aligned}\right\} \quad (4)$$

The evaluation of those integrals would require extensive calculations; however, the order of magnitudes can be estimated by an empirical relation between the overlap integrals and the assumed β values, the charge-transfer matrix elements of the previous paper. The spectral data showed that the β value between the charge-transfer and the singlet-ground configuration of Würster's blue crystals are in the vicinity of 0.1—0.2 eV, and the formula for the matrix elements showed that β should be proportional to the overlap integrals times the integrals of the $\langle\phi_a{}^m|1/R_b|\phi_a{}^m\rangle$ type. Each term in $\Delta(T-S)$ of Eq. (4) is related to the square of the overlap integrals times $\langle\phi_a{}^m|1/R_b|\phi_a{}^m\rangle$. Therefore, if we use a rough relation that:

$$\beta \simeq kS^2{}_{mm} \quad (5)$$

then Δ may be approximated by:

$$\Delta \simeq kS^2{}_{mm} \quad (6)$$

If we put $k=40$ eV (which is estimated from spectral results) then Δ can be evaluated as being smaller than a few cm^{-1} by using the overlap integrals tabulated in Table 1. This obviously shows that the exchange interaction of this type is not the true origin of the separation of the triplet and singlet energy levels.

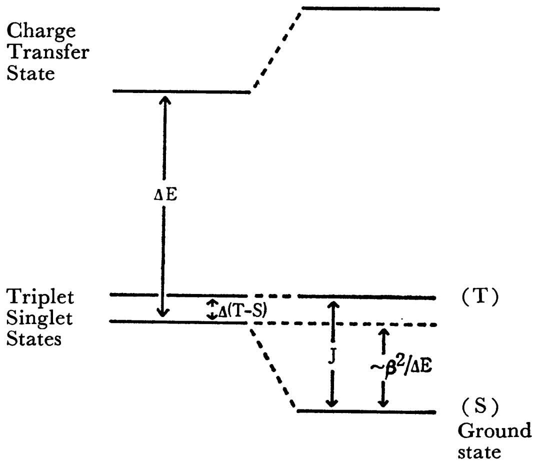

Fig. 4. Energy Levels of Singlet, Triplet and Charge Transfer States.

On the other hand, the singlet-ground state is stabilized by the charge-transfer effect, which is far more significant in the present system.[1)] This resonance effect is important only for the singlet-ground state (Fig. 4); the triplet state is not stabilized at all because of the lack of the intermolecular charge-transfer effect.

The stabilization energies have been evaluated by solving Eq. (10) of the previous paper[1)]; they are reproduced in Table 1. The β parameters in Table 1 were estimated by considering the spectral data, such as the energy and the intensity of the charge-transfer band.

Würster's red bromide shows only diamagnetism; this is consistent with the large stabilization energy calculated. By this mechanism it can be seen that Würster's red bromide is a diamagnetic crystal at room temperature. With other crystals,

TABLE 1.

		S_{mm}*	$-\beta$ (eV)	Stabilization	Energy	Observed J-value
Würster's red bromide	(II)†	0.025	0.9	−0.415 (eV)	−3352 (cm^{-1})	—
	(III)		0.6	−0.187	−1500	
Würster's blue bromide	(IV)	0.0034	0.25	−0.038	−300	−210 (cm^{-1})**
	(V)		0.23	−0.0298	−238	
Würster's blue iodide	(III)	0.0025	0.11	−0.0075	−60	−70
Würster's blue perchlorate	(IX)	0.0012	0.08	−0.004	−32	−16***

* S_{mm} is the overlap integrals between the half-filled molecular orbitals.

** The value is for the 210—300°K range.

*** The value is estimated from the data of Okumura.[10)]

† The numbers in parenthesis are referred to the Table 1 of Ref. 1.

the calculated energies are reasonably correlated with the observed *J*-values. These results show convincingly that the singlet-triplet energy gap is produced by the charge-transfer mechanism.

The magnetic interaction in such radical crystals is thus shown to be dominated by the charge-transfer mechanism. The stabilization of the ground state is approximately given by $-\beta^2/\Delta E$, where ΔE is the energy difference between the charge-transfer and the ground state and where β is the interaction energy. Since ΔE is almost constant at about 1.6—1.8 eV for all Würster's salts, the β value is very important in both spectral and magnetic studies. The motion of the triplet exciton in the crystal is governed by the transfer-matrix element between radicals and pairs; it is also connected with β-values and, hence, with the overlap integrals.

A more detailed approach to the evaluation of these intermolecular interactions would be desirable in future studies.