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Phase Transition and Spin-exchange Interaction in Ion Radical Salts. Some Information Derived from ESR Measurements

Yôichi Iida

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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The prominent magnetic properties of solid ion radical salts have been the subject of many theoretical and experimental investigations over the past several years.[1-7] In certain ion radical salts, the extra electrons on the ion radical molecules appear to be paired by means of an exchange interaction.[1-7] In this case, the paramagnetic contribution to the susceptibility of these materials at any temperature, T, can be fitted approximately to the expression:

$$\chi_p = (2Ng^2\mu_B{}^2/3kT)\left(1+\frac{1}{3}e^{J/kT}\right)^{-1}, \tag{1}$$

which corresponds to an assembly of N quasimolecules with a singlet ground state and a triplet state lying an energy, J, above the ground state.

The intensity of the electron-spin-resonance (ESR) absorption, I, is known to be proportional to the value of χ_p. Therefore, since a plot of ln (IT) *versus* T^{-1} yields an approximately straight line, the singlet-triplet energy separation, J, can be estimated from the slope value of this straight line.[1,2,4]

If these ion radical salts undergo first-order phase transitions, an abrupt change in the singlet-triplet energy separation should be associated with the phase transition.[4-7] The J values in the low- and high-temperature phases have both been estimated by using this slope method. However, the slope method is not applicable when the intensity measurements cannot be made over a wide temperature range. In this case, the relative intensity ratio of the ESR absorptions at the transition temperature is useful for the determination of the J values below or above the transition temperature.

At the transition temperature, T_c, in the lower and higher temperature ranges, the singlet-triplet energy separations are represented by J and J', while the ESR absorption intensities are represented by I and I'. It is assumed, in Eq. (1), that only a change in the singlet-triplet energy separation is involved; that is, the value of N, g, or μ_B in the lower temperature range is assumed to be equal to the corresponding one in the higher temperature range. On this assumption, we obtain:

$$\frac{I'}{I} = \frac{3+\exp(J/kT_c)}{3+\exp(J'/kT_c)}. \tag{2}$$

Therefore, if the values of (I'/I), J, and T_c are known experimentally, the value of J' can be estimated by means of:

$$J' = kT_c \ln\left\{3\left(\frac{I'}{I}-1\right)+\frac{I'}{I}\exp(J/kT_c)\right\}. \tag{3}$$

We shall apply this method, for example, to the phase transition of $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\overline{\cdot}}$, one of the anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ).

Several years ago, we examined the ESR spectra of $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\overline{\cdot}}$ and its variation with the temperature.[6] For this anion radical salt, the paramagnetism due to the excited triplet state has been established from the anisotropic zero-field splitting in the ESR absorption at low temperatures.[1] The phase transition takes place at T_c=315.7K,[8] where the intensity of the ESR absorption increases abruptly in the higher temperature range by a factor of (I'/I)= 1.9.[6] Although the singlet-triplet energy separation in the low-temperature phase, J, is known to be 0.065 eV by Kepler's susceptibility measurements,[5,9] there have been no experimental data on the value in the high-temperature phase. If J=0.065 eV in the low-temperature phase holds at the transition temperature, the singlet-triplet energy separation in the high-temperature phase, J', can be determined to be 0.039 eV by putting those values into Eq. (3). The appreciable reduction of the singlet-triplet energy separation in the high-temperature phase is found to be caused by the phase transition. On the other hand, the J' value estimated from the slope method is 0.03 eV or less, which is somewhat smaller than that estimated from the relative intensity-ratio method. However, since the observation of the ESR absorption intensities in the high-temperature phase was done over a limited temperature range,[6] the slope value for the singlet-triplet splitting in the high-temperature phase should be taken as only an indication.

The present intensity-ratio method in ESR absorption can be applied, in general, to the phase transitions of ion radical salts which possess a magnetic system composed of a singlet ground state and a triplet excited state. In some cases, this method gives more accurate information on the singlet-triplet energy separation than does the slope method.

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9) Rigorously speaking, the J value was found to depend slightly on the temperature. However, the variation in J with the temperature is not observed in the ESR measurements, because one measures only the relative intensity. The ESR intensity, I, is proportional to $\exp(-J/kT)$, and if J varies as $J_0+\alpha T$, the linear term in T will appear only as a constant and, therefore, not show up in relative intensity measurements. By using the slope method of the ESR intensity, Chesnut and Phillips reported the J value to be 0.062 eV,[1] while Iida *et al.* reported it to be 0.08 eV.[6]