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The Magnetic Properties of Manganese(II) Phthalocyanine

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The magnetic transition from the ferro- to the para-magnetic state of manganese(II) phthalocyanine ($C_{32}H_{16}N_8Mn$) has been observed by measurements of the magnetic susceptibility, the magnetization and the proton magnetic resonance in the low-temperature range. The positive Weiss constants were obtained from the static susceptibility measurements and the proton magnetic measurements. Moreover, the magnetic-field dependences of the experimental results were found in the low-temperature range. All of those findings confirm the ferromagnetic behavior of this substance in the lower-temperature region. From the measurements of the frequency shift in the resonant circuit of the proton magnetic resonance apparatus, the transition temperature was determined to be 8.6 K. A possible mechanism of long-range ordering was also discussed on the basis of the crystal structure of this substance.

The phthalocyanines are interesting organo-metallic compounds which have been extensively studied for their semiconductive and photoconductive properties. Moreover, most of the transition-metal phthalocyanines are known to be paramagnetic; some of them have been studied in terms of their electronic structures by the electron spin resonance[1–4] or magnetostatic methods.[5]

The magnetic behaviors[6] of transition-metal phthalocyanines have been investigated in the temperature range above 77 K; the results obey the Curie-Weiss law, with mostly negative Weiss constants, thus implying the existence of large zero-field splittings or of antiferromagnetic exchange interactions among molecules. So far we know, most reports of the magnetic properties have been concentrated upon an investigation of the electronic structures of the molecule. However, the investigations of the magnetic properties themselves, especially from a viewpoint of the magnetic-phase transition, are still not well-established.

The magnetic properties of manganese (II) phthalocyanine (hereafter abbreviated as PcMn) are of considerable interest. This substance obeys the Curie-Weiss law in the high-temperature range, and its Weiss constant has a positive sign, unlike those of the other metal-phthalocyanines. The magnetic susceptibilities of PcMn have been measured by Lever,[6] who found the positive Weiss constant to be 6 K. Recently, Mitra and his co-workers[7] measured the magnetic susceptibilities and anisotropies of PcMn over quite a wide temperature range (1.7—300 K) and reported the existence of the ferromagnetic interaction among molecules; they added some speculations about the spin state of the molecule that a divalent-manganese ion might have at $s=3/2$. However no detailed discussion of the occurrence of the magnetic ordering has been made so far.

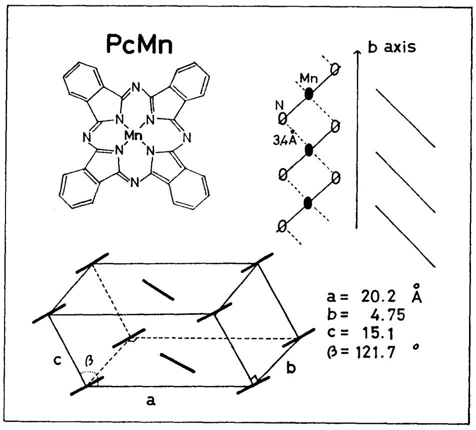

Fig. 1. Molecular and schematic crystal structures of manganese(II) phthalocyanine ($C_{32}H_{16}N_8Mn$). The molecular plane is approximately normal to the ab-plane.

We have studied the magnetic properties of PcMn in more detail and obtained affirmative evidence for the occurrence of the magnetic-phase transition of PcMn.

Experimental

PcMn was prepared by the method of Linstead *et al.*[8] The product was extracted with α-chloronaphthalene and then sublimed in an atmosphere of pure nitrogen at the temperature of 550 °C. The single crystals grown by sublimation were ground and powdered. Found: C, 67.54; H, 2.76; N, 19.19%. Calcd: C, 67.7; H, 2.8; N, 19.7%.

All the measurements were carried out in the microcrystalline state. The measurements of the static (dc) susceptibility and the temperature dependence of the magnetization were performed on powder samples of about 10—50 mg between 1.8 and 77 K in the magnetic fields of 0.82, 1.12, 1.88, 7.0, 8.3, and 10.2 KOe, by means of a magnetic torsion balance described elsewhere.[9] The temperatures of the samples were measured with a carbon resister

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[1] D. J. E. Ingram and J. E. Bennett, *Discuss. Faraday Soc.*, **19**, 140 (1955).

[2] J. F. Gibson, D. J. E. Ingram, and D. Schonland, *ibid.*, **26**, 72 (1958).

[3] S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, **40**, 365 (1964).

[4] J. M. Assour and S. E. Harrison, *Phys. Rev.*, **136**, A1368 (1964).

[5] R. L. Martin and S. Mitra, *Chem. Phys. Lett.*, **3**, 183 (1969); *Inorg. Chem.*, **9**, 182 (1970).

[6] A. B. P. Lever, *J. Chem. Soc.*, **1965**, 1821.

[7] C. G. Barraclough, R. L. Martin, and S. Mitra, *J. Chem. Phys.*, **53**, 1638 (1970).

[8] P. A. Barret, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, **1936**, 1719.

[9] M. Mekata, *J. Phys. Soc. Jap.*, **17**, 796 (1962).

and an AuCo–Cu thermocouple calibrated by measuring not only the magnetic susceptibility of Mn-Tutton salt, but also the vapor pressures of liquid helium, liquid hydrogen, and liquid nitrogen. Moreover, the susceptibility measurements were made by means of a Hartshorn bridge between 13.8 and 20.2 K in the temperature region attainable by the pumping out of liquid hydrogen. The temperature was determined from the known susceptibility of the standard sample, $Cr(NH_3)_6Cl_3$, and from the vapor pressures of liquid hydrogen.

The proton NMR absorption spectra were observed between 10.8 and 20 K using the usual Pound-Watkins-type oscillator with a 80 Hz field modulation and a field sweep. The oscillator coil with a sample tube was directly immersed in liquid hydrogen. The temperatures were measured with a calibrated carbon resister and by means of the vapor pressure of liquid hydrogen. The proton NMR absorption of liquid hydrogen was used as a standard for the estimation of the absorption line-shift. The magnetic field was calibrated by means of the proton absorption of H_2O.

Results

Magnetic Suscetibility. The diamagnetic correction was within the range of experimental error at low temperatures.[10] The results of the dc susceptibility measurements in the field of 10.2 KOe obey the Curie-Weiss law between 30 and 77 K; thus, a positive Weiss constant, 18.4 K, was obtained, one which agrees almost entirely with those reported by Mitra *et al.* From the slope of the $1/\chi_M$ *vs.* T plots, we obtained a g-value of 2.25, assuming that $s=3/2$ (the effective moment, $\mu_{eff}=4.36\ \mu_B$). At temperatures below about 20 K, the molar susceptibility deviates from the Curie-Weiss law and reaches a constant maximum value below 7 K; this behavior is dependent on the magnetic-field strength.

Avoiding the effect of an extensive magnetic field, as will be discussed later, the ac susceptibilities were also measured in the temperature range between 13.7 and 20.2 K.

The results precisely obey the Curie-Weiss law for $s=3/2$ and $g=2.93$ in this temperature range, in contrast with the results of the dc susceptibilities, and they show a positive Weiss constant of 9.0 K.

Magnetization. The field dependence of the magnetization was measured at the temperatures of 4.2, 11.1, and 20.3 K, as is shown in Fig. 2. At 20.3 K, the magnetizations are linearly dependent on the magnetic field as the usual paramagnetic substance, but at 11.1 K they deviate from a linear dependence and at 4.2 K they become larger. We have rewritten the data in relation with σ^2 to H/σ in Fig. 3. It is also worth-while to notice that, in Fig. 2, the value of the saturation magnetization extrapolated from the value at 4.2 K is much smaller than the value calculated using $s=3/2$ and $g=2$. The temperature dependence of the magnetization at several constant fields between 0.84 KOe and 10.2 KOe is shown in Fig. 4. The dependence of the magnetization on the magnetic-field strength is then found, as in the usual ferro-magnetic substances.

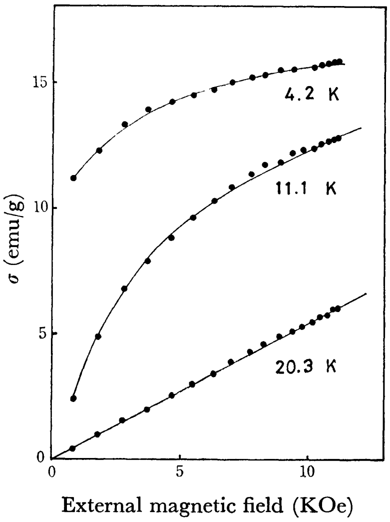

Fig. 2. Magnetization curves at 20.3, 11.1, and 4.2K.

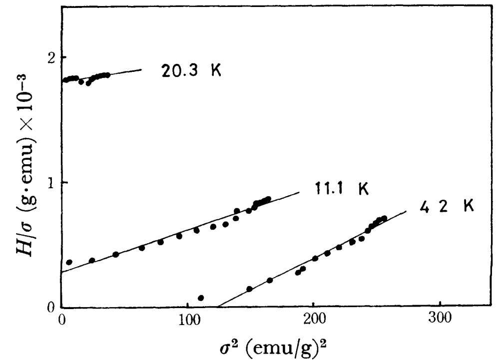

Fig. 3. H/σ *vs.* σ^2 plots of the magnetization curve at 20.3, 11.1, and 4.2 K.

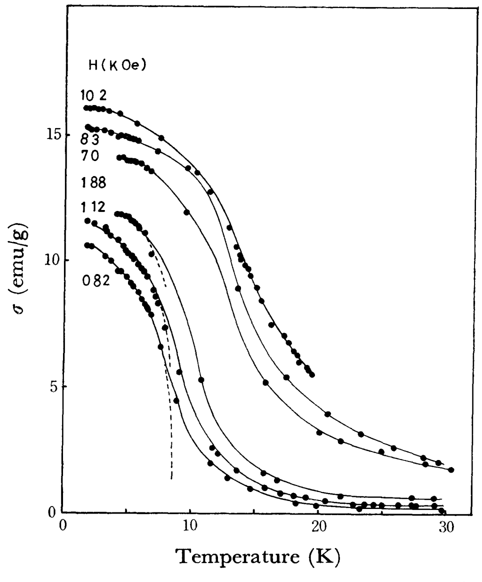

Fig. 4. Temperature dependences of the magnetization at the field of 0.82, 1.12, 1.88, 7.0, 8.3, and 10.2 KOe.

Proton Magnetic Resonance. The proton magnetic resonance (PMR) measurements were carried out at the frequencies of 18 and 12 MHz. In the first, when measured at the frequency of 18 MHz and the tem-

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[10] C. G. Barraclough, R. L. Martin, and S. Mitra, *J. Chem. Phys.*, **55**, 1426 (1971).

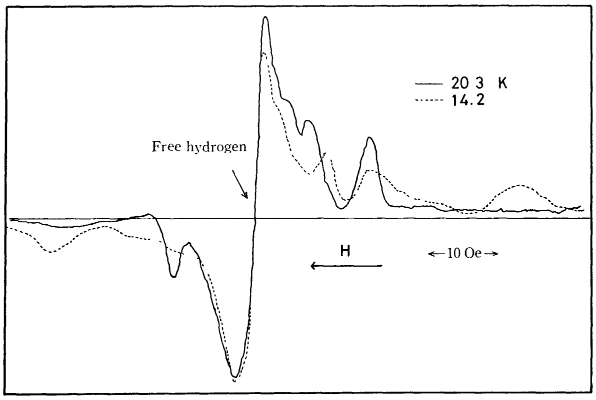

Fig. 5. PMR spectra of the polycrystalline sample at 20.3 and 14.2 K at 12 MHz. In the figure, *free hydrogen* means a free proton absorption of the coolant.

perature of liquid helium (4.2 K), no signals could be observed by sweeping the magnetic field between 500 Oe and 12 KOe. In the second, when measured between 10.8 and 20 K, a temperature range attainable by the pumping out of liquid hydrogen, several absorption lines were observed, as is shown in Fig. 5, where the absorption of the hydrogen molecule used as a coolant is superimposed upon them. We could confirm at least four lines, three in the lower field and one in the higher field. These signals can not be interpreted by the model of the two different proton sites in the molecule, but they may be attributed to the different local fields caused by the magnetic short-range ordering effect at the individual proton sites. We are now engaged in clarifying this point further. The shifts of the higher- and lower-field absorptions were measured from the position of that of the hydrogen molecule; the reciprocals of the shifts are plotted as a function of the temperature in Fig. 6. At 12 MHz, the results are linearly proportional to the temperature between 14 and 20.2 K. The straight line intersects the abscissa displaying the temperature of 9.6 K. Similarly, at 18 MHz, the reciprocal shifts are linear to the temperature between 15 and 20.2 K and intersect the abscissa at the same point, 9.6 K. However, the deviation from the linearity appears at a higher temperature, 15 K, and is much larger than that at 12 MHz.

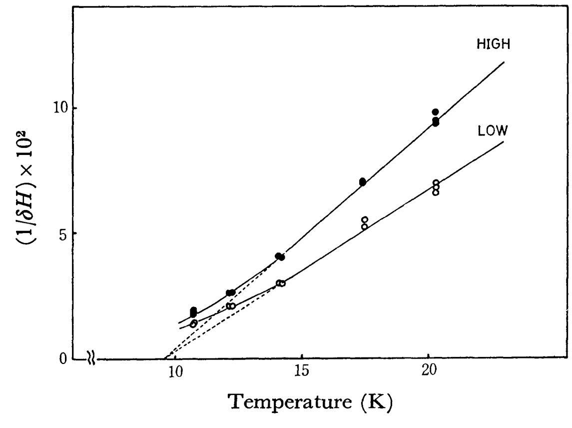

Fig. 6. Reciprocals of the PMR line shifts $(1/\delta H)$ as a function of temperature at 12 MHz. HIGH and LOW mean higher and lower portions of the spectrum, as shown in Fig. 5, respectively.

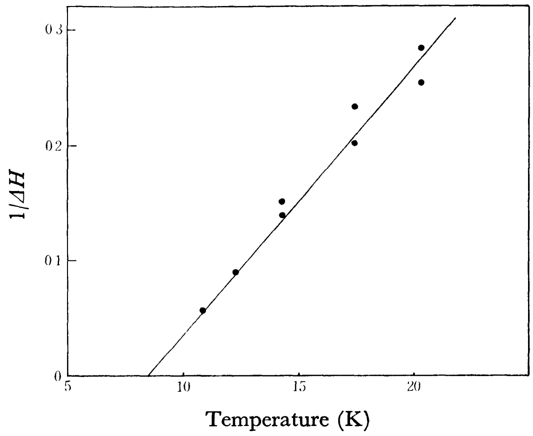

Fig. 7. Reciprocal PMR line-width $(1/\Delta H)$ of the lower portion in Fig. 5 as a function of temperature.

The reciprocal line-width of the lower portion at 12 MHz is also shown as a function of the temperature in Fig. 7. The reciprocal PMR line-widths are linearly proportional to the temperature between 10.8 and 20.2 K.

To determine the transition temperature more accurately,[11] a powdered sample was placed in the coil of an oscillator used for PMR, and the relative ac susceptibilities (detected as a frequency shift in the resonant circuit) in a zero field and at 8 KOe were measured as a function of the temperature from 4.2 to 30 K. A typical measurement is shown in Fig. 8. The frequency shift in the zero field reaches a maximum around 9.2 K, but the point of intersection of the two gradients on the upper and the lower sides of the maximum is 8.6 K; this is regarded as the magnetic transition temperature. The shift at about 8 KOe also shows a broad maximum, but the transition point is obscured by the influence of the magnetic field.

Ferromagnetic Resonance. In order to investigate the magnetic-ordered state of PcMn, ferromagnetic resonance measurements using an X-band ESR spectrometer were carried out in both powder and needle-like

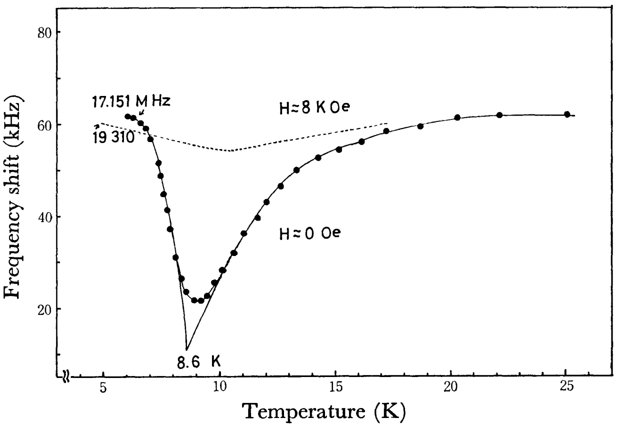

Fig. 8. Frequency shift (relative ac susceptibility) as a function of temperature.

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[11] H. H. Wickman, A. M. Trozzolo, H. J. Williams, G. W. Hull, and F. R. Merritt, *Phys. Rev.*, **155**, 563 (1967).

single crystal samples at 4.2 and 77 K with fields up to 25 KOe. Assuming the obtained needle-like crystal to be an infinitely elongated cylinder in order to calculate its demagnetization factor, and estimating the saturation magnetization (M_0) as 1.7β/ion (*cf.* Fig. 2), we calculated the resonance frequency (ω) of PcMn based upon Kittel's resonance conditions[12] and concluded that the deviation from the usual resonant field should be much smaller than 10^3 Oe ($\omega/\gamma=H+2\pi M_0$, $2\pi M_0 \ll 10^3$ Oe). However, we observed only one weak absorption with $g\approx 2.0$, the line-width$\approx$6 Oe; they seemed to be a free-radical resonance characteristic of most of the phthalocyanine compounds reported by Assour and Harrison.[13]

Discussion

The Weiss constant derived from ac susceptibility measurements in the temperature range between 13.7 and 20.4 K has a positive value, 10 K; this suggests the existence of ferromagnetic interaction between molecules. As is well known,[14] when there is an applied magnetic field the ferromagnetic substance retains its magnetization in the vicinity of the Curie temperature. Thus, near the Curie temperature, the various magnetic properties of the ferromagnetic substance will be influenced by the applied magnetic field and, hence, the Curie temperature will be obscured. As is shown in Fig. 4, the dc susceptibility and the magnetization in the low-temperature range are dependent on the magnetic-field strength; the higher the magnetic field, the more gradually the magnetzation decreases when the temperature is raised, as is characteristic of the usual ferromagnetic substances (that is, as has been stated above, the influence of the magnetic field obscures the transition temperature from the para-magnetic state to the ferro-magnetic state). From the microscopic point of view, the results of PMR measurements between 10.8 and 20.2 K support the existence of a positive Weiss constant as well as the influence of the magnetic field, as will be shown below. The paramagnetic shift is proportional to the mean value, $\langle S_z \rangle$, of the electron-spin component and, consequently, to the bulk magnetic susceptibility of the sample. The Weiss constants obtained from the temperature variations of the paramagnetic shifts at 12 MHz and at 18 MHz are both 9.6 K; this is consistent with the results of the bulk ac susceptibility. The deviation from the Curie-Weiss law is larger at 18 MHz than at 12 MHz, indicating the influence of the magnetic field on the shifts. The positive Weiss constants obtained from the microscopic PMR measurements as well as from the bulk dc and ac susceptibility measurements, and the magnetic-field dependences of experimental results, all confirm the ferromagnetic behavior of this substance in the lower-temperature region.

Now, let us turn to the determination of the Curie temperature (T_c) of PcMn, in which spontaneous magnetization occurs. In Fig. 3, H/σ is plotted against σ^2. From the thermodynamic description[14] of the magnetization of a ferro-magnetic material, $H/\sigma = A + B\sigma^2$, where the coefficients, A and B, are the functions of the temperature. The Curie temperature (T_c) can be determined from the temperature at which the coefficient $A=0$. Taking this relation into account, it is evident that T_c exists between 4.2 and 11.1 K. As is shown in Fig. 2, the saturation magnetization (σ_s) extrapolated from the data at 4.2 K is 17.0 G cm^3/g, much smaller than the theoretically-estimated value, (29.5 G cm^3/g calculated from $s=3/2$ and $g=2.0$). Using the relation that $\sigma_s M = Ng\langle\mu\rangle$ on the assumption of $g=2.0$, the obtained average moment, $\langle\mu\rangle$, is 1.7 Bohr magneton. This value is about half the total spin value (3 Bohr magneton) expected from $s=3/2$. The temperature dependence of the magnetization in the magnetic field of 0.82 KOe suggests that the Curie temperature exists between 8 and 10 K, as is shown in Fig. 4.

The transition temperature was determined more accurately by relative ac susceptibility measurements using a PMR oscillator. In Fig. 8, the transition temperature is identified as 8.6 K on the basis of these data; this is consistent with the Weiss constants obtained by different methods of measurements. Similarly, as has already been mentioned, a remarkable magnetic-field dependence can be noticed, so that the transition temperature is obscured in the high magnetic field of 8 KOe. This is another piece of evidences for the ferromagnetic behavior of PcMn.

The reciprocal PMR line-width tends to broaden rapidly as the temperature is decreased, and it seems to diverge at T'_c (8.5 K), as may be extrapolated from Fig. 7. This temperature (T'_c) is surprisingly in agreement with the Curie temperature obtained above. So far we do not have a sufficient theoretical elucidation of the linewidth variation of PMR. However, provided that the divergence of the linewidth may be attributed to the onset of the long-range ordering of electron spins, we can recognize the coincidence of T'_c with T_c, because the rapid broadening of the line-width is the result of the critical fluctuation of spins in the neighborhood of the transition temperature.

From the experimental facts presented above, one may conclude that PcMn is the first example of a ferromagnet among the organo-metallic compounds and that its Curie temperature is 8.6 K.

A Possible Mechanism of Long-range Ordering. The above discussion has concentrated upon the magnetic properties. Now, let us briefly discuss the possible mechanism of long-range ordering. The crystal structure of PcMn is isomorphous with nickel(II) phthalocyanine,[15] whose structure is well known. As is shown in Fig. 1, the molecules are square planar ones stacked along the short monoclinic b axis of the crystal and the distance between these nearest molecules is 3.4 Å, which provides a possible pathway for magnetic ex-

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[12] C. Kittel, "Introduction to Solid State Physics," 3rd edition, J. Wiley & Sons., New York (1966), p. 525.

[13] J. M. Assour and S. E. Harrison, *J. Phys. Chem.*, **68**, 872 (1964).

[14] K. P. Belov; "Magnetic Transition," translated by W. H. Furry, Chaps. II and III, Consulants Bereau, New York (1961).

[15] J. M. Robertson, *J. Chem. Soc.*, **1935**, 615; **1937**, 219.

change interaction between electron spins. The unit cell contains two nonequivalent molecules with parameters of (0, 0, 0) and (1/2, 1/2, 0). The axes of symmetry of a couple of molecules in the unit cell are almost at right angles, and both of them are equally inclined to the ac plane by an approximate angle of 45°.

Therefore, PcMn may form a magnetic chain different from the three-dimensionally-interacting spin system, and the exchange coupling between the next-nearest-neighbor spins in different chains (that is, between the different sites) is much weaker than that between nearest-neighbor spins in the same chain (between the equivalent ions along the b-axis). Possible pathways for superexchange between nearest-neighbor spins in the same chain were considered by S. Mitra *et al.*7) It is well known theoretically16) that the isolated magnetic linear chains do not have any magnetic-phase transition, but, in the presence of a small interaction between chains, there occurs a magnetic transition to the long-range ordered state in the lower-temperature region. Considering the discussion of PcCu based on ESR measurements,4) there is a possibility for PcMn to go into a long-range ordered state, since the interaction between chains cannot be neglected. On the other hand, a reported speculation7) on the electronic structure has suggested the existence of the zero-field splitting of the ground state, which may dominate the spin structure of the ordered state. Perhaps, the small value of saturation magnetization in Fig. 2 and the absence of any absorption signals of ESR and PMR measurements at 4.2 K suggests the canted ferromagnetism of PcMn. At any rate, for the discussion of the finer mechanism of the ferromagnetic interaction and the spin structure of the ordered state, it would be necessary to know which interaction is more dominant and what type of exchange is involved. Study along this line is now under way.

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16) L. Onsager, *Phys. Rev.*, **65**, 117 (1944); H. E. Stanley and T. A. Kaplan, *Phys, Rev. Lett.*, **17**, 913 (1966).