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THE INFLUENCE OF SHORT-RANGE ORDER ON THE SPECIFIC HEAT CLOSE TO A SECOND ORDER PHASE TRANSITION POINT

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An approximate expression has been obtained for the binary distribution function near a second-order phase transition point. This expression is used to find the specific heat above the Curie point.

LANDAU's[1] thermodynamic theory of second-order phase transitions explains many phenomena close to the transition point. Many properties of matter in more symmetric phases, however, are not explained by this theory. This is due to the fact that only long-range order is considered, because the thermodynamic potential is treated as a functional of the density function or of the unary distribution function $\rho(\mathbf{r})$.

The binary distribution function $\rho(\mathbf{r}_1, \mathbf{r}_2)$ plays an important role in describing the properties of matter. Allowance for the function $\rho(\mathbf{r})$ alone is equivalent to representing the binary function as the product of unary distribution functions. This causes the degree of the short-range order to be replaced by the square of the degree of the long-range order. Although such a description is sufficient in a less symmetric phase, a detailed knowledge of the binary distribution function is necessary in a phase with higher symmetry.

Let us consider the specific heat close to a second-order phase transition, using the binary distribution function. The greater the rate at which disordering proceeds as the temperature is increased, the higher the specific heat, so that inclusion of short-range order should lead to a slower increase of the specific heat below the Curie point and to anomalous behavior of the specific heat above the Curie point.

To find the binary distribution function, let us consider $n_\alpha(\mathbf{r})$, the density of particles of type α at the point $\mathbf{r}$. The mean value $\overline{n_\alpha(\mathbf{r})}$ of this function is the unary distribution function $\rho_\alpha(\mathbf{r})$, whereas $\overline{n_\alpha(\mathbf{r}_1)n_\beta(\mathbf{r}_2)}$ is the binary distribution function $\rho_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$. Let us first consider the binary distribution $\rho_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$ for a binary alloy with a superlattice. Ordinarily this function is approximated in the form of a product of unary distribution functions, assuming first that the probability of finding any atom on a lattice site is independent of the position of any other atom. Second, it is assumed that the probability of finding an atom of type α at a given site is independent of the types of atoms occupying the neighboring sites. The first assumption is of almost the same accuracy near and far from a phase transition point, and we may maintain it without introducing any significant error. The second assumption, on the other hand, becomes invalid close to the Curie point and must thus be dropped. Therefore in averaging $n_\alpha(\mathbf{r}_1)n_\beta(\mathbf{r}_2)$ we must take into account the correlation which thus arises.

Similar considerations, obviously, can also be applied to other second-order phase transitions related to symmetry changes in a body. In this connection, the time average of $n_\alpha(\mathbf{r}_1)n_\beta(\mathbf{r}_2)$ is performed in two stages. We first average each factor separately over a time interval large compared with the period of vibration of the atom, but smaller than the resorption time of fluctuations in the order. This leads to the expression

$$[\rho_\alpha(\mathbf{r}_1) + \Delta\eta(\mathbf{r}_1)\rho_{1\alpha}(\mathbf{r}_1)][\rho_\beta(\mathbf{r}_2) + \Delta\eta(\mathbf{r}_2)\rho_{1\beta}(\mathbf{r}_2)], \tag{1}$$

where $\rho_\alpha(\mathbf{r}) = \rho_{0\alpha}(\mathbf{r}) + \eta_0\rho_{1\alpha}(\mathbf{r})$ is the unary distribution function, η_0 is the equilibrium value of the degree of long-range order, and $\Delta\eta(\mathbf{r})$ is the fluctuation in the long-range order at the point $\mathbf{r}$. The function $\rho_{0\alpha}(\mathbf{r})$ has the symmetry of the more symmetric phase, whereas $\rho_{1\alpha}(\mathbf{r})$ has that of the less symmetric phase.

Expression (1) is then averaged over a time interval long compared with the resorption time of fluctuations in the order, as a result of which we obtain

$$\begin{gathered}\rho_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = \rho_\alpha(\mathbf{r}_1)\rho_\beta(\mathbf{r}_2) \\ + \overline{\Delta\eta(\mathbf{r}_1)\Delta\eta(\mathbf{r}_2)}\rho_{1\alpha}(\mathbf{r}_1)\rho_{1\beta}(\mathbf{r}_2).\end{gathered} \tag{2}$$

The mean value $\overline{\Delta\eta(\mathbf{r}_1)\Delta\eta(\mathbf{r}_2)}$ can be found by means of the thermodynamic theory of fluctuations. We expand $\Delta\eta(\mathbf{r})$ in a Fourier series

$$\Delta\eta(\mathbf{r}) = \sum_{\mathbf{f}} c_{\mathbf{f}} e^{i\mathbf{f}\mathbf{r}}. \tag{3}$$

Then

$$\overline{\Delta\eta(\mathbf{r}_1)\,\Delta\eta(\mathbf{r}_2)} = \sum_{\mathbf{f}}\sum_{\mathbf{f}'} \bar{c}_{\mathbf{f}}\,\bar{c}_{\mathbf{f}'}\, e^{i(\mathbf{f}\mathbf{r}_1+\mathbf{f}'\mathbf{r}_2)}.$$

Averaging this expression over the volume of the crystal, we obtain

$$\overline{\Delta\eta(\mathbf{r}_1)\,\Delta\eta(\mathbf{r}_2)} = \sum_{\mathbf{f}} \overline{c^*_{\mathbf{f}} c_{\mathbf{f}}}\, e^{i\mathbf{f}\mathbf{R}}, \tag{4}$$

where

$$\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2.$$

According to Landau,[2] if there are fluctuations in the order, the thermodynamic potential of the crystal can be written

$$\Phi = \Phi_0 + \int\left[\frac{A}{2}\eta^2 + \frac{C}{4}\eta^4 + \frac{\alpha}{2}(\nabla\eta)^2\right]dV, \tag{5}$$

where $\eta = \eta_0 + \Delta\eta(\mathbf{r})$. Inserting the value of $\Delta\eta(\mathbf{r})$ from (3) into (5) and keeping only those terms which are linear in $c^*_{\mathbf{f}}c_{\mathbf{f}}$, we obtain

$$\Phi = \Phi_{\text{equil}} + \Delta\Phi,$$

where Φ_{equil} is the equilibrium value of the thermodynamic potential when $\eta = \eta_0$, and

$$\Delta\Phi = \frac{V}{2}\sum_{\mathbf{f}}(A + \alpha f^2)\,\overline{c^*_{\mathbf{f}} c_{\mathbf{f}_0}} \quad T > \Theta, \tag{6}$$

$$\Delta\Phi = \frac{V}{2}\sum_{\mathbf{f}}(2|A| + \alpha f^2)\,\overline{c^*_{\mathbf{f}} c_{\mathbf{f}}}, \quad T < \Theta, \tag{7}$$

where Θ is the temperature of the Curie point.

From this we obtain

$$\overline{c^*_{\mathbf{f}} c_{\mathbf{f}}} = kT/(A + \alpha f^2)V, \quad T > \Theta, \tag{8}$$

$$\overline{c^*_{\mathbf{f}} c_{\mathbf{f}}} = kT/(2|A| + \alpha f^2)V, \quad T < \Theta. \tag{9}$$

It should be noted that in the immediate neighborhood of a second-order phase transition point at which A vanishes, Eqs. (8) and (9) become invalid for small $\mathbf{f}$, for in this case one cannot retain only the linear terms in $\overline{c^*_{\mathbf{f}} c_{\mathbf{f}}}$ in the expression for $\Delta\Phi$.

Using the inverse Fourier transform and inserting (8) into (4), we find that for $T > \Theta$

$$\overline{\Delta\eta(\mathbf{r}_1)\,\Delta\eta(\mathbf{r}_2)} = (kT/4\pi\alpha R)\exp\{-(A/\alpha)^{1/2}R\}. \tag{10}$$

Similarly, for $T < \Theta$

$$\overline{\Delta\eta(\mathbf{r}_1)\,\Delta\eta(\mathbf{r}_2)} = (kT/4\pi\alpha R)\exp\{-(2|A|/\alpha)^{1/2}R\}. \tag{11}$$

This gives the expression

$$\begin{aligned}\rho_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) &= \rho_\alpha(\mathbf{r}_1)\,\rho_\beta(\mathbf{r}_2)\\ &+ (kT/4\pi\alpha R)\exp\{-(A/\alpha)^{1/2}R\}\,\rho_{1\alpha}(\mathbf{r}_1)\,\rho_{1\beta}(\mathbf{r}_2)\end{aligned} \tag{12}$$

for the binary distribution function for $T > \Theta$, and

$$\begin{aligned}\rho_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) &= \rho_\alpha(\mathbf{r}_1)\rho_\beta(\mathbf{r}_2)\\ &+ (kT/4\pi\alpha R)\exp\{-(2|A|/\alpha)^{1/2}R\}\,\rho_{1\alpha}(\mathbf{r}_1)\,\rho_{1\beta}(\mathbf{r}_2)\end{aligned} \tag{13}$$

for $T < \Theta$.

The binary distribution function can be used to find the energy and specific heat of a crystal. As an example, let us consider the specific heat of a binary alloy of the type of β-brass close to the second-order phase transition point. The interaction energy of the atoms of the alloy will be

$$\begin{aligned}E_{\text{int}} = {}& \frac{N_a(N_a - 1)}{2V^2}\iint u_{aa}(\mathbf{r}_1 - \mathbf{r}_2)\,\rho_{aa}(\mathbf{r}_1, \mathbf{r}_2)\,dV_1\,dV_2\\ &+ \frac{N_aN_b}{V^2}\iint u_{ab}(\mathbf{r}_1 - \mathbf{r}_2)\,\rho_{ab}(\mathbf{r}_1, \mathbf{r}_2)\,dV_1\,dV_2\\ &+ \frac{N_b(N_b - 1)}{2V^2}\iint u_{bb}(\mathbf{r}_1 - \mathbf{r}_2)\,\rho_{bb}(\mathbf{r}_1, \mathbf{r}_2)\,dV_1\,dV_2,\ .\end{aligned}$$

where N_α is the number of atoms of type α, and $u_{\alpha\beta}$ is the interaction energy between atoms of type α and type β. We shall use the binary distribution function as given by Eqs. (12) and (13), where the unary distribution function can be written in the form $\rho_\alpha(\mathbf{r}) = \rho_{0\alpha}(\mathbf{r}) + \eta_0\rho_{1\alpha}(\mathbf{r})$. If we now recall that for an alloy of the type of β-brass $\rho_{1a}(\mathbf{r}) = -\rho_{1b}(\mathbf{r})$ and neglect unity compared with N_a and N_b, we obtain

$$\begin{aligned}E_{\text{int}} = {}& E_0 + \frac{N^2}{8V^2}\iint u(\mathbf{r}_1 - \mathbf{r}_2)\\ &\times\left[\eta_0^2 + \frac{kT}{4\pi\alpha|\mathbf{r}_1 - \mathbf{r}_2|}\exp\{-(2|A|/\alpha)^{1/2}|\mathbf{r}_1 - \mathbf{r}_2|\}\right]\\ &\times \rho_1(\mathbf{r}_1)\,\rho_1(\mathbf{r}_2)\,dV_1\,dV_2, \quad T < \Theta,\end{aligned}$$

$$\begin{aligned}E_{\text{int}} = {}& E_0 + \frac{N^2}{8V^2}\iint u(\mathbf{r}_1 - \mathbf{r}_2)\\ &\times \frac{kT}{4\pi\alpha|\mathbf{r}_1 - \mathbf{r}_2|}\exp\{-(A/\alpha)^{1/2}|\mathbf{r}_1 - \mathbf{r}_2|\}\\ &\times \rho_1(\mathbf{r}_1)\,\rho_1(\mathbf{r}_2)\,dV_1\,dV_2, \quad T > \Theta,\end{aligned}$$

where $u = u_{aa} + u_{bb} - 2u_{ab}$, N is the total number of atoms in the alloy, and E_0 is the interaction energy of the atom in the completely disordered alloy.

We now make use of the fact that close to the phase transition point $\eta_0^2 = -A/C$ and $A = a(T - \Theta)$ and keep only the largest terms. This leads to the following expressions for the specific heat at constant volume:

$$\begin{aligned}C_v = C_{v0} + \left(-\frac{a}{C} + \frac{k\Theta a^{1/2}}{4\pi\alpha^{3/2}\sqrt{2(\Theta - T)}}\right)\\ \iint u(\mathbf{r}_1 - \mathbf{r}_2)\,\rho_1(\mathbf{r}_1)\,\rho_1(\mathbf{r}_2)\,dV_1\,dV_2, \quad T < \Theta,\end{aligned} \tag{14}$$

$$C_v = C_{v0} - \frac{k\Theta a^{1/2}}{8\pi\alpha^{3/2}\sqrt{T-\Theta}}\iint u(\mathbf{r}_1 - \mathbf{r}_2)\,\rho_1(\mathbf{r}_1)\,\rho_1(\mathbf{r}_2)\,dV_1\,dV_2,$$

$$T > \Theta. \tag{15}$$

As has already been noted, Eqs. (8) and (9) are invalid for small **f** in the immediate neighborhood of the phase-transition point. This is true also for Eqs. (14) and (15). A necessary condition for their validity is $A\eta^2/2 \gg C\eta^4/4$, if $\eta^2 = (kT/4\pi\alpha d)\,e^{-nd}$. Here d is the distance between neighboring atoms, and $n = (a|T - \Theta|/\alpha)^{1/2}$

Noting that $a^2/2C$ is equal to the discontinuity in the specific heat per unit volume ΔC_p, and[2] that $\alpha \approx \Theta a d^2$, we obtain the following condition for the validity of Eqs. (14) and (15):

$$|T - \Theta|/\Theta \gg (k/16\pi d^3 \Delta C_p)\exp\{-(|T-\Theta|/\Theta)^{1/2}\}.$$

Using the value of Sykes and Wilkinson[3] for ΔC_p of β-brass, we obtain $|T - \Theta|/\Theta \gg 0.007$.

Within the limits of applicability of the expressions obtained, the inclusion of short-range order in the ordered phase leads to an insignificant decrease in the specific heat. In the disordered phase, the inclusion of short-range order adds the following correction term to the specific heat:

$$C_v = C_{v0} + \text{const}/\sqrt{T-\Theta}.$$

For β-brass, with $(T - \Theta)/\Theta = 3 \times 10^{-2}$, this additional correction term supplies about 5% of the discontinuity in the specific heat at the Curie point. This conclusion is in satisfactory agreement with the measurements performed by Sykes and Wilkinson.[3]

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[1] L. D. Landau and E. M. Lifshits, Статистическая физика (Statistical Physics), Gostekhizdat, 1951.

[2] L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **7**, 1232 (1937).

[3] C. Sykes and H. Wilkinson, J. Inst. Metals **61**, 223 (1937).

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CERTAIN SOURCES OF THE LOW-ENERGY ELECTRON-PHOTON COMPONENT OF COSMIC RAYS IN THE STRATOSPHERE

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It is shown that part (20 to 30%) of the low-energy flux (range $R < 1.7$ g-cm^{-2} Al) registered in the cosmic radiation of the stratosphere, is genetically related to nuclear-disintegration products.

FROM the number of particles N (cm^{-2}sec^{-1}) and the produced ionization I (pairs of ions per cm^3/sec), measured in the global intensity of cosmic rays,[1,2] it follows that the average ionizing ability of charged particles in the atmosphere, $K = I/N$, increases considerably with altitude, and that at an altitude of 10 to 17 km it exceeds the average ionizing ability of relativistic particles by a factor of 1.5 to 1.7 (Ref 3). This is evidence that there exists at these altitudes a considerable flux of secondary strongly-ionizing particles. The ionization due to these particles can be estimated from the value of the "excess" ionization, defined as the difference $I_{exc} = I - k_r N$ where k_r is the average ionizing ability of relativistic particles. The value of I_{exc} reaches one-third of the total ionization current.[4] Experiment has shown[4,5] that the variation of I_{exc} with altitude and its latitudinal effect are identical with the corresponding relations observed for stars in photoemulsions, and for ionization impacts observed in chambers. This suggests a possible genetic relationship between this variation and nuclear disintegrations.

Quantitative measurements of the ionization impacts, which experiments[5] have shown to be essentially due to strongly-ionizing protons and to heavi-