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CORRELATION EFFECTS IN THE HEAT CAPACITY OF SEPARATING ^{3}He–^{4}He SOLID SOLUTIONS

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We propose to describe the impurity heat capacity of solid ^{3}He-^{4}He mixtures both below and above the phase separation temperature T_s by an extension of the Bethe–Guggenheim approximation for the lattice gas model. It is shown that at $T > T_s$, the temperature behavior of the heat capacity is completely defined by correlation effects in the impurity subsystem. The developed theory enables us to explain from the common standpoint the experimental data by Edwards, McWilliams, and Daunt for all concentrations of ^{4}He and make some conclusions about the structure of second phase nuclei.

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1. INTRODUCTION

Solid mixtures of helium isotopes are known [1–3] to decompose into two (^{3}He-rich and ^{4}He-rich) phases on cooling below the phase separation temperature T_s that depends on both the pressure and the mixture composition. The separation at $T = T_s$ is a first-order transition occuring with mass transport. It is clear that structure transformations of this type significantly affect thermodynamic properties of solid mixtures. In particular, a major contribution to the total heat capacity at $T < T_s$ is due to additional degrees of freedom of a heterophase system.

Heat capacity of separating solid ^{3}He–^{4}He mixtures has been experimentally investigated in close detail by several groups [1, 2, 4–7]. The most complete experimental results for a wide range of temperatures and concentrations n_0 of ^{4}He were reported by Edwards, McWilliams, and Daunt (EMD) [1, 2, 4]. Other concentrations were measured in Refs. [5–7].

In all the experiments, temperature dependences of the total heat capacity $C(T)$ are similar in character. At $T < T_s$, the experimental data for all impurity concentrations fall on a common curve. In this temperature region, $C(T)$ increases with the temperature. The total heat capacity drops sharply just above T_s and is completely determined by the lattice term $C_{lat} \propto T^3$ at $T > 0.3$ K. For $T_s < T < 0.3$ K, a deviation from the Debye T^3-law has been observed.

It is known that at $T < T_s$ (in the two-phase region), the thermodynamics of solid helium mixtures can be described very successfully within the regular solution model (the mean field approximation, MFA) [2, 8], but the behavior of $C(T)$ at $T > T_s$ cannot be explained by it. In Ref. [9], an effort was made to take fluctuations of the local concentration n into account; an expression for the heat capacity of ^{3}He–^{4}He mixtures above T_s was obtained there. The theory in Ref. [9] is in agreement with some experimental data in Refs. [1, 2], but the approach used in this work is not quite consistent. It has been critically discussed in great detail by Edwards and Pettersen (see Ref. [4]). Recently, the contribution of fluctuations to the heat capacity was calculated [10] in the framework of the random phase approximation (RPA) [11]. This allowed adequately interpreting the behavior of the concentrated mixtures in the entire temperature range. However, some additional considerations have been used to treat the limit of dilute solutions in a proper way [10]. Thus, it is clear that further improvements in the theoretical description of the thermodynamics of quantum solid ^{3}He–^{4}He mixtures remain urgent.

The purpose of the present work is to develop a rigorous theory that describes the temperature depen-

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dences of the heat capacity of separating helium solid solutions with arbitrary concentrations both below and above T_s. The proposed method is based on the quasi-chemical approximation [12, 13]. It enables us to properly take the contribution of fluctuations into account and make some conclusions about the structure of second phase nuclei. As we see in Sec. 4, our theory is in good agreement with the experimental data [1, 2]. It is significant that this agreement can be obtained without invoking any additional concepts about extraneous centers of a new phase nucleation such as dislocations, grain boundaries, and other lattice defects. We note that suggestions of this type were used in Ref. [14] to explain experimental results in Ref. [7].

2. GENERAL FORMALISM

The basis of the present theory is the lattice gas model [12]. Some simplifications can be made in applying this model to quantum solid mixtures of helium isotopes (which is in contrast to classical systems). First, we are interested in effects that occur at temperatures considerably below the Debye temperature Θ_D. This allows us to neglect heat vibrations of helium atoms and consider parameters of the interaction between impurities as temperature independent. Second, despite the low temperatures, the system approaches the thermodynamic equilibrium rather rapidly because of an intense quantum motion of helium atoms.

A. Hamiltonian

For definiteness, we hereafter treat the ^{4}He component as an impurity subsystem in the mixture. The Hamiltonian of the system has the form

$$H = \varepsilon_0 \sum_{\mathbf{f}} n_{\mathbf{f}} - \frac{1}{2} \sum_{\mathbf{f}\mathbf{f}'} V_{\mathbf{f}\mathbf{f}'} n_{\mathbf{f}} n_{\mathbf{f}'}, \qquad (1)$$

where $n_{\mathbf{f}}$ is the occupation number of ^{4}He impurity atoms at a lattice site $\mathbf{f}$, ε_0 is the energy of a ^{4}He atom in the ^{3}He matrix, and $V_{\mathbf{f}\mathbf{f}'} = V(|\mathbf{f} - \mathbf{f}'|)$ is the interaction energy of impurities placed at the sites $\mathbf{f}$ and $\mathbf{f}'$. Hamiltonian (1) can be represented in a somewhat different form for the following reason. In the $n_0 - T$ coordinates, where n_0 is the average ^{4}He concentration, the phase separation curve of solid ^{3}He–^{4}He mixtures is practically symmetrical about $n_0 = 0.5$ (see Ref. [4]) and has the maximum T_c at this point. The critical temperature T_c is the highest temperature at which phase separation occurs [3]. This means that the Hamiltonian must be explicitly invariant under the replacement $n_{\mathbf{f}} \to 1 - n_{\mathbf{f}}$, and we can therefore rewrite Eq. (1) as

$$H = \frac{1}{2} \sum_{\mathbf{f}\mathbf{f}'} V_{\mathbf{f}\mathbf{f}'} n_{\mathbf{f}} (1 - n_{\mathbf{f}'}), \quad \varepsilon_0 = \frac{1}{2} \sum_{\mathbf{f}} V_{\mathbf{f}\mathbf{f}'}. \qquad (2)$$

As can be seen from (2), it is irrelevant whether ^{3}He or ^{4}He is chosen as the impurity subsystem. We also note that Hamiltonian (2) can be reduced to the Ising model with the spin 1/2 [12].

B. Interaction between impurities

Because of the difference in atomic volumes of helium isotopes, a ^{4}He impurity is the dilatation center in the ^{3}He matrix [4]. It is known [15] that the interaction between two dilatation centers is long-range; at a large separation r, it decreases as $1/r^3$ for cubic and hexagonal lattices. Moreover, it is anisotropic with a complicated angular dependence [16–18]. If many impurities exist in the matrix, their elastic fields overlap and the effective interaction becomes essentially isotropic, but remains long-range. To describe the interaction $V_{\mathbf{f}\mathbf{f}'}$ in the mixtures with arbitrary concentrations of ^{4}He, we use a rather simple model well-known in the literature [11]. Namely, the interaction of an impurity atom placed at a lattice site $\mathbf{f}$ with another impurity atom is assumed to be constant (equal to V_0) if the distance between them is less than R_0 and equal to zero otherwise. Thus,

$$V_{\mathbf{f}\mathbf{f}'} = \begin{cases} V_0 & \text{if } |\mathbf{f} - \mathbf{f}'| \le R_0, \\ 0 & \text{otherwise.} \end{cases} \qquad (3)$$

We introduce the effective coordination number z that can be considered as the number of impurities interacting with the given impurity atom. The effective radius R_0 of the impurity–impurity interaction is related to z as $R_0 = (3\omega_0 z/4\pi)^{1/3}$ (where ω_0 is the volume per atom). In the present theory, z is considered as a fitting parameter.

C. Quasi-chemical approximation

Although the exact solution for the lattice gas model is not available in the three-dimensional case, there are several rather efficient approximate methods for its analysis. To analyze the model, we use the Bethe–Guggenheim method [12, 13] also known as the quasi-chemical approximation (QCA). It provides a sufficiently accurate description for the system under study. In this approximation, the lattice symmetry is of significance and the final results only depend on the effective coordination number z. This method is precise in the limit of dilute solutions. It also gives an accurate result for artificial models of the Bethe lattice type.

In the QCA framework, a two-component solid mixture involving A-type and B-type atoms can be represented as a set of independent atomic pairs of the AA, BB, and AB types. The partition function has the form [12]

$$Z_0 = \sum_N y^N \sum_{N_{AB}} g(N, N_{AB}, \mathcal{B}) \times \\ \times \exp(-E(N_{AB})/T), \quad (4)$$

where $\mathcal{B}$ is the total number of lattice sites, N is the number of sites occupied by A-type atoms (^{4}He impurities), $y = \exp(\mu/T)$, and μ is the chemical potential of the impurity subsystem. We choose the units such that the Boltzmann constant $k_B = 1$. The function $g(N, N_{AB}, \mathcal{B})$ is the number of configurations containing N impurities and N_{AB} pairs. Each of these configurations has the energy

$$E(N_{AB}) = \frac{V_0}{2} N_{AB}.$$

Within the QCA, the function g is assumed to be

$$g = G \frac{(z\mathcal{B}/2)!}{N_{AA}! N_{BB}! [(N_{AB}/2)!]^2}, \quad (5)$$

where

$$N_{AA} = \frac{1}{2}(zN - N_{AB}), \quad N_{BB} = \frac{1}{2}[z(\mathcal{B} - N) - N_{AB}]$$

are the respective total numbers of the AA-type and BB-type pairs. The constant G is determined by the obvious relation

$$\sum_{N_{AB}} g(N, N_{AB}, \mathcal{B}) = \frac{\mathcal{B}!}{N!(\mathcal{B} - N)!}.$$

Setting the number of unlike pairs N_{AB} entering Eqs. (4) and (5) equal to its average value in the mixture, we obtain the well-known mean-field approximation [12]. In the limit as $\mathcal{B}, N, N_{AB} \to \infty$ with $N/\mathcal{B}$ and $N_{AB}/\mathcal{B}$ constant, the sum in Eq. (4) can be replaced by its maximum term. We let

$$\frac{N}{\mathcal{B}} \to n, \quad \frac{2N_{AB}}{z\mathcal{B}} \to a.$$

The quantities n and a are chosen such that they vary from zero to unity. We now introduce the long-range order parameter σ related to the local impurity concentration n by $\sigma = 1 - 2n$. We note that the quantity a is related to the short-order parameter x introduced in Ref. [19] by $a = (1 + x)/2$.

Using the Stirling formula, we obtain the thermodynamic potential Ω_0 (per site) as

$$\Omega_0 = -\frac{T}{\mathcal{B}} \ln Z_0 = E - TS - \frac{\mu}{2}(1 - \sigma), \quad (6)$$

where E is the internal energy per site and S is the entropy per site. In accordance with the above-mentioned approximations, we find

$$E = \frac{V_0}{4} za, \quad (7)$$

$$S = \frac{1}{\mathcal{B}} \ln g = \left(1 - \frac{z}{2}\right) \ln 2 + \frac{z-1}{2} \times \\ \times [(1-\sigma)\ln(1-\sigma) + (1+\sigma)\ln(1+\sigma)] - \\ - \frac{z}{4}[(1-\sigma-a)\ln(1-\sigma-a) + \\ + (1+\sigma-a)\ln(1+\sigma-a) + 2a\ln a]. \quad (8)$$

The parameters σ and a satisfy the set of equations

$$(z-1)\ln\frac{1-\sigma}{1+\sigma} + \frac{z}{2}\ln\frac{1+\sigma-a}{1-\sigma-a} + \frac{\mu}{T} = 0, \quad (9)$$

$$\ln\left[(1-a)^2 - \sigma^2\right] - 2\ln a - \frac{V_0}{T} = 0. \quad (10)$$

If we put $\mu = 0$, the system of Eqs. (9) and (10) is invariant under the inversion $\sigma \to -\sigma$, which means that the two-phase mixture occurs. One phase (^{4}He-weak) corresponds to $\sigma > 0$ $(0 < n < 1/2)$ and the other (^{4}He-rich) to $\sigma < 0$ $(1/2 < n < 1)$. It follows from Eq. (10) that

$$a = \frac{1-\sigma^2}{\gamma + 1}, \\ \gamma = \left\{1 + (1-\sigma^2)\left[\exp\left(\frac{V_0}{T}\right) - 1\right]\right\}^{1/2}. \quad (11)$$

Inserting (11) in (9), we obtain

$$y \equiv \exp(\mu/T) = \frac{1-\sigma}{1+\sigma}\left[\frac{(1+\sigma)(\gamma-\sigma)}{(1-\sigma)(\gamma+\sigma)}\right]^{z/2}, \quad (12)$$

where y is equal to unity for all temperatures below T_s. As the temperature is increased, the long-range order parameter decreases and becomes equal to $\sigma_0 = 1 - 2n_0$ at $T = T_s$, where n_0 is the equilibrium concentration given by the coexistence curve. It follows from (12) that the phase separation temperature T_s is given by

$$T_s^{-1} = \frac{2}{V_0}\ln\left[\frac{1-u^z}{u(1-u^{z-2})}\right], \quad u = \left(\frac{1-\sigma_0}{1+\sigma_0}\right)^{1/z}. \quad (13)$$

As $z \to \infty$, $V_0 \to 0$, and $V_0 z \to$ const, Eq. (13) goes into the well-known expression for T_s resulting from the regular solution model [11]. At $T > T_s$, the mixture becomes homogeneous with the constant long-range order parameter σ_0. Equations (9) and (10) then determine the temperature dependences of the chemical potential μ and the parameter a.

3. FLUCTUATION EFFECTS

To make the results of the quasi-chemical approximation more precise, spatially inhomogeneous fluctuations in parameters σ and a must be taken into account. Assuming that the spatial scale of fluctuations is much larger than the lattice parameter, we consider these fluctuations in the continuum approximation. We let

$$\sigma \to \sigma + \eta(\mathbf{r}), \quad a \to a + \alpha(\mathbf{r}), \tag{14}$$

where the variations $\eta(\mathbf{r})$ and $\alpha(\mathbf{r})$ are functions of the coordinate $\mathbf{r}$ satisfying the conditions

$$\int d\mathbf{r}\, \eta(\mathbf{r}) = 0, \quad \int d\mathbf{r}\, \alpha(\mathbf{r}) = 0. \tag{15}$$

Assuming that the variations of the long-range order parameter and the parameter a from their equilibrium values are sufficiently small, we expand (6) in $\eta(\mathbf{r})$ and $\alpha(\mathbf{r})$. The partition function of the system can then be written as

$$Z = Z_0 Z_{fl},$$

where Z_0 is the partition function in the QCA given by Eq. (4). The contribution from fluctuations Z_{fl} is given by the functional integral

$$Z_{fl} = A \int\int \mathcal{D}[\eta(\mathbf{r})]\mathcal{D}[\alpha(\mathbf{r})] \exp\left(-\frac{\delta\Omega}{T}\right), \tag{16}$$

where the normalization factor A is determined below. The quantity $\delta\Omega$ consists of two terms,

$$\delta\Omega = \delta\Omega_1 + \delta\Omega_2. \tag{17}$$

The first one is the series expansion of (6) to the second order in $\eta(\mathbf{r})$ and $\alpha(\mathbf{r})$. It is given by

$$\delta\Omega_1 = \frac{Tz}{4\omega_0 ab} \int d\mathbf{r} \left\{ f_{11}(\sigma, a)\eta^2(\mathbf{r}) + \right. \\ \left. + 2f_{12}(\sigma, a)\eta(\mathbf{r})\alpha(\mathbf{r}) + f_{22}(\sigma, a)\alpha^2(\mathbf{r}) \right\}, \tag{18}$$

where

$$f_{11} = \frac{ab}{1-\sigma^2}\left(2 - z + 2a^2 f_{22}\right), \\ f_{22} = 1 - a - \sigma^2, \quad f_{12} = a\sigma, \tag{19}$$

and $b = (1-a)^2 - \sigma^2$. The second term in (17), $\delta\Omega_2$, was introduced by the following reason. Because of spatial inhomogeneity, an expansion of the thermodynamic potential must contain not only powers of $\eta(\mathbf{r})$ and $\alpha(\mathbf{r})$ but also their spatial derivatives. These latter are introduced by $\delta\Omega_2$ to suppress short-wave spatial fluctuations that have no physical meaning. To understand the structure of $\delta\Omega_2$, we confine ourselves to the simplest case. Namely, assuming that the form of $\delta\Omega_2$ is identical to the MFA one, we obtain

$$\delta\Omega_2 = -\frac{1}{8\omega_0^2} \int d\mathbf{r} \int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}')\eta(\mathbf{r})\eta(\mathbf{r}'). \tag{20}$$

However, nonlocal term (20) written in this form gives a nonzero contribution to $\delta\Omega$ in the spatially homogeneous case, i.e., for $\eta(\mathbf{r}) =$ const. Thus, expression (16) includes fluctuations of the homogeneous system that have already been taken into account in deriving formulas of Sec. 2. In Eq. (20), we must therefore separate the part that vanishes at $\eta(\mathbf{r}) =$ const and, consequently, contains the contribution from spatially inhomogeneous fluctuations only. Thus, finally, $\delta\Omega_2$ can be written as

$$\delta\Omega_2 = \frac{1}{16\omega_0^2} \int d\mathbf{r} \int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') \left[\eta(\mathbf{r}) - \eta(\mathbf{r}')\right]^2. \tag{21}$$

We note that fluctuations of the long-order and short-order parameters are related to each other. Therefore, although Eq. (21) only describes nonlocality in the long-range order parameter, the spatial fluctuations of the short-order parameter are also smoothed out. Because of conditions (15), $\delta\Omega$ does not contain linear terms in $\eta(\mathbf{r})$ and $\alpha(\mathbf{r})$.

In view of (18) and (21), the right-hand side of Eq. (16) represents a Gaussian functional integral, which can be easily evaluated [20]. The integration yields

$$Z_{fl} = A \left(\frac{8bQ}{\gamma z}\right)^{\mathcal{B}z/2} \prod_{\mathbf{q}} \left[1 - Q\frac{v(\mathbf{q})}{T}\right]^{-1/2}, \tag{22}$$

where $v(\mathbf{q})$ is the Fourier transform of $V(\mathbf{r})$ and we have introduced the notation

$$Q = \frac{T}{V_0 z \lambda}, \\ \lambda = 1 + \frac{2T}{V_0 \gamma (1-\sigma^2)}\left(1 - \gamma\frac{z-2}{z}\right). \tag{23}$$

For $z \gg 1$, Eq. (22) goes into the well-known expression for Z_{fl} corresponding to the random-phase approximation [11]. This allows us to determine the factor A in (22) as

$$A = \left(\frac{\gamma z}{8bQ}\right)^{\mathcal{B}z/2}.$$

We thus obtain the contribution to the thermodynamic potential $\Delta\Omega$ related to fluctuations,

$$\Delta\Omega = -\frac{T}{\mathcal{B}} \ln Z_{fl} = \frac{T}{2\mathcal{B}} \sum_{\mathbf{q}} \ln \left[1 - Q \frac{v(\mathbf{q})}{T} \right].$$

The contribution of fluctuations to the internal energy is given by

$$\Delta E = -T^2 \frac{\partial}{\partial T} \left(\frac{\Delta\Omega}{T} \right) = = -\frac{1}{2T\mathcal{B}} \sum_{\mathbf{q}} \frac{Q^2 v^2(\mathbf{q})}{1 - Qv(\mathbf{q})/T}. \quad (24)$$

In writing Eq. (24), we used the condition $\sum_{\mathbf{q}} v(\mathbf{q}) = 0$ to eliminate the terms that are responsible for the self-action of impurities.

In our model of the impurity–impurity interaction, the Fourier transform $v(\mathbf{q})$ is given by

$$v(\mathbf{q}) = V_0 z f(qR_0), \quad f(x) = \frac{3}{x^3}(\sin x - x \cos x).$$

On the interval from 0 to the fist zero of $f(x)$, this function can be approximated to a sufficient accuracy as

$$f(x) \approx 1 - \left(\frac{x}{4} \right)^2,$$

and $f(x) = 0$ otherwise. This gives

$$v(\mathbf{q}) = \begin{cases} V_0 z \left[1 - (q/q_0)^2 \right], & q \le q_0, \\ 0, & q > q_0. \end{cases} \quad (25)$$

The quantity q_0 is related to the effective coordination number z by

$$q_0 = \frac{4}{R_0} = 4 \left(\frac{4\pi}{3z\omega_0} \right)^{1/3}. \quad (26)$$

Replacing summation by integration in Eq. (24) and using (25) and (26), we obtain

$$\Delta E = \frac{64T}{9\pi z} \times \left\{ 1 - 3\lambda \left(1 - \sqrt{\lambda - 1} \operatorname{arctg} \frac{1}{\sqrt{\lambda - 1}} \right) + \frac{2}{5\lambda} \right\}, \quad (27)$$

where λ is defined by Eq. (23).

4. RESULTS AND DISCUSSION

The total heat capacity of the mixture is equal to

$$C = C_{imp} + C_{lat} + C_{ex}, \quad C_{imp} = C_0 + \Delta C,$$

where

$$C_0 = \frac{V_0 z}{4T\gamma} \left(\frac{V_0 b}{2T} - T\sigma \frac{d\sigma}{dT} \right) \quad (28)$$

is the heat capacity in the quasi-chemical approximation. The contribution of fluctuations ΔC is given by

$$\Delta C = \frac{\Delta E}{T} + \left[\left(\frac{3}{2} - \frac{1}{\lambda} \right) \frac{\Delta E}{T} + \frac{256}{45\pi z \lambda^2} \right] \times \left\{ 1 + \frac{1}{\gamma(\lambda - 1)(1 - \sigma^2)} \left[1 - \frac{\sigma^2}{\gamma^2} + \frac{4\sigma T^2}{V_0(1 - \sigma^2)} \left(\frac{3}{2} - \gamma \frac{z - 2}{z} - \frac{1}{2\gamma^2} \right) \frac{d\sigma}{dT} \right] \right\}. \quad (29)$$

Using (12), we find

$$T \frac{d\sigma}{dT} = \begin{cases} -\sigma / \left[\gamma(\lambda - 1) \right], & T < T_s, \\ 0, & T > T_s. \end{cases}$$

To obtain $C(T)$, we have added two terms to the impurity contribution C_{imp}. The first term is the lattice heat capacity $C_{lat} = (12\pi^4/5)(T/\Theta_D)^3$ and the second term is associated with the exchange interaction between ^{3}He atoms. It can be represented as [21]

$$C_{ex} = \frac{3}{4}(1 + \sigma)^2 \left(\frac{I}{T} \right)^2 \left[1 - \frac{I}{T} + \frac{7}{4} \left(\frac{I}{T} \right)^2 \right], \quad (30)$$

where I is the exchange integral. Term (30) is only essential at very low temperatures. In comparing our results with the experimental data, we always take C_{lat} and C_{ex} into account. We note that because term (30) is small, we neglect the pressure dependence of I and set I equal to its maximum value ≈ 1 mK at the molar volume 24.2 cm^3/mol (see Ref. [21]). In addition, we neglect the temperature dependence of Θ_D because the corresponding correction is inessential for the temperature range where the relevant effects take place. We put $\Theta_D = 17.3$ K in accordance with Ref. [21]. This value of Θ_D provides the best agreement with the experimental data [1, 2] above $T \approx 0.3$ K, where the contribution C_{lat} prevails.

The present calculations are compared with the EMD experimental data in Figs. 1 and 2. As can be seen from the figures, the agreement between the theory and experiment is very good. To make the theory fit the data in [1, 2], the parameters of potential (3) must be specified. The potential is determined by the intensity V_0 and the effective interaction radius R_0 (or by z directly related to R_0). Both quantities must be treated as adjustable parameters. We note, however, that it is appropriate to choose the first fitting parameter as the product $V_0 z = v(0)$ rather than V_0. This

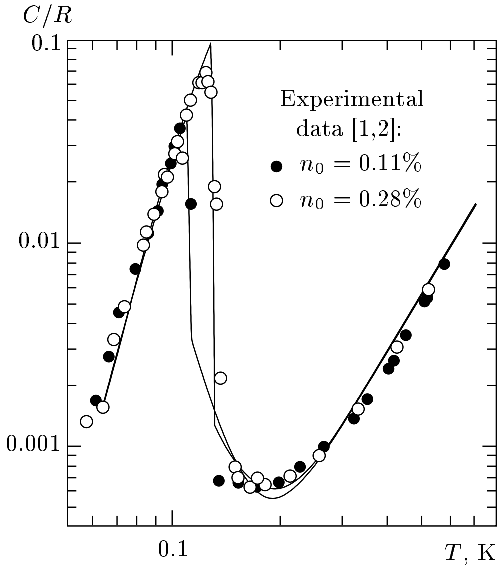

Fig. 1. Heat capacity of dilute ^{3}He–^{4}He solid mixtures as a function of temperature. The solid curves correspond to the present theory

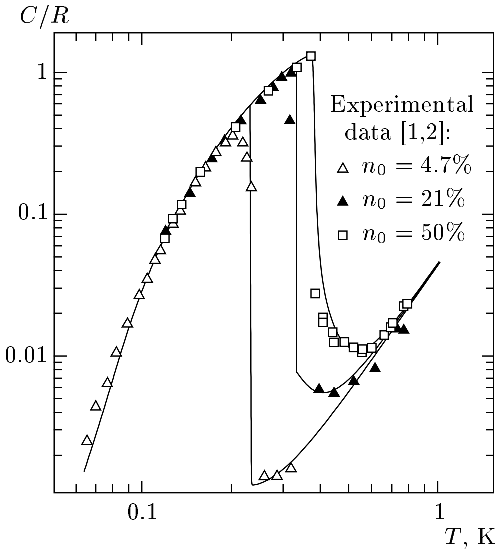

Fig. 2. Heat capacity of concentrated ^{3}He–^{4}He solid mixtures as a function of temperature. The solid curves correspond to the present theory

choice is dictated by the following reasons. At low temperatures, the impurity heat capacity can be obtained as a low-temperature series expansion [12, 22] without using any theoretical approximations. The leading term of this expansion is given by

$$C_{imp} \approx \left(\frac{V_0 z}{2T}\right)^2 \exp\left(-\frac{V_0 z}{2T}\right). \qquad (31)$$

Expression (31) is valid for all the mixtures irrespective of their concentration. It follows from Eq. (31) that the quantity C_{imp} depends only on the product $V_0 z$. Furthermore, as shown in Refs. [1, 2], the thermodynamics of the system at $T < T_s$ can be satisfactorily described within the MFA, which corresponds to the limit as $z \to \infty$ and $V_0 \to 0$ with $V_0 z \to$ const (see, e.g., Refs. [11, 12]). In this approximation, the quantity $V_0 z$ is also the only parameter determining the behavior of the system at $T < T_s$. Thus, it is evident that the product $V_0 z$ plays the role of a universal parameter of the theory[1]. For all the mixtures, the value $V_0 z$ is assumed to be equal to 1.51 K, which is determined by the condition that the impurity heat capacity (31) fit the experimental data. The magnitude of $V_0 z$ is in complete agreement with the Edwards–Balibar constant $A = V_0 z/2$ that was found empirically to be 0.76 K [2–4]. The theoretical value of A and its pressure dependence were calculated by Mullin [8].

As the second independent adjustable parameter, we choose the value z. Precisely this parameter characterizes the spatial correlation scale between impurities. Numerical analysis shows that the heat capacity $C_{imp}(T)$ is highly sensitive to the magnitude of z in the fluctuation region (at $T > T_s$). This makes it possible to unambiguously determine the value of the effective coordination number for both dilute and concentrated mixtures.

Our analysis shows that the entire concentration interval ($n_0 \leq 50\%$) considered in Refs. [1, 2] can be conveniently divided into two parts: large concentrations $n_0 \geq 4.7\%$ and small concentrations $n_0 = 0.11\%$, 0.28%. The fitting parameter z is equal to 250 for all mixtures of the first group. This implies that the nearest-neighbor approximation is inadequate for interpreting the thermodynamics of mixtures with large concentrations. In this case, the long-range interaction is therefore very significant. The value $z = 250$ implies that the radius of interaction between impurities spreads over four or five coordination spheres. Within the QCA, the critical temperature T_c is equal to [12]

$$T_c = -\frac{V_0}{2\ln(1-2/z)} \approx \frac{V_0 z}{4} \approx 0.38 \text{ K},$$

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[1] It is remarkable that in considering various approximations for the theory of solid mixtures, Fowler and Guggenheim introduce the parameter $w = V_0 z/2$ (called *the energy of unmixing*) from the outset. They denote the pair interaction energy by $2w/z$ (see Ref. [13, p. 570]).

which is in excellent agreement with the experimental value.

For mixtures with small concentrations, the agreement between the theory and the experimental data can be reached for a unique choice of z, namely $z = 3$ for $n = 0.11\%$ and $z = 5$ for $n = 0.28\%$. We note that these values of z do not correspond to any regular three-dimensional crystal structure. This suggests that solid ^{3}He–^{4}He mixtures with small n_0 separate to yield the second (^{4}He-rich) phase in the form of a fractal (dendritic) structure.

There are several arguments supporting this assumption. The analysis shows that for low-concentration mixtures, the contribution ΔC of fluctuations is negligible. Thus, the heat capacity $C_0(T)$ obtained in the QCA can be considered as a rather accurate result for these mixtures. On the other hand, QCA is a precision method for structures of the Bethe lattice (or Cayley tree) type [11, 12]. It is therefore reasonable to assume that at low concentrations, the separation of the mixture occurs with formation of a new phase in the form of a fractal structure. For concentrated mixtures, the second phase nuclei are formed as three-dimensional precipitates.

In our opinion, this is not surprising because the difference between the effective coordination numbers z corresponding to the mixtures with small and large concentrations is related to the specific character of the impurity–impurity interaction. As mentioned above, the potential $V(\mathbf{r})$ decreases as $1/r^3$ at large distances r and has a complicated angular dependence [16–18]. In particular, it is attractive along some directions and repulsive along others. For small n_0, with the average distance between impurities by far exceeding the lattice parameter, the new phase can therefore grow as a fractal structure of the Cayley tree type such that the order of a node is determined by both the concentration and the number of crystallographic directions along which attraction occurs. In the opposite case of concentrated mixtures, elastic fields of impurities overlap and the effective interaction becomes essentially isotropic. As the result, the nuclei of the new phase grow in a compact form.

5. CONCLUSIONS

The results of the present work clearly demonstrate that thermodynamic properties of quantum solid ^{3}He–^{4}He mixtures can be successfully interpreted within the quasi-chemical approximation. The QCA has an essential advantage over the MFA because it accounts for the details of short-range correlations along with the long-range order. The QCA is therefore of primary importance for the description of the temperature region above T_s, where the main contribution to the heat capacity is due to fluctuations in the impurity subsystem. Another important point of the theory is that it takes the long-range nature of the impurity–impurity interaction into account, which is crucial for understanding the behavior of the system. It is significant, however, that we must not know this interaction in every detail. Rather simple model (3) is quite sufficient to properly describe the thermodynamics of solid ^{3}He–^{4}He mixtures.

The theory is in good agreement with the experimental data in [1, 2] for both dilute and concentrated solutions. Unfortunately, we do not know works where the heat capacity of mixtures with intermediate concentrations ($0.3\% < n_0 < 5\%$) has been measured. The availability of these results would provide more distinctive conclusions about the change of nucleation mechanisms as a function of the solid mixture composition.

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