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ELECTRICAL AND MAGNETIC PROPERTIES

Investigation of the Magnetocaloric Effect in Correlated Metallic Systems with Van Hove Singularities in the Electron Spectrum

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Abstract—In this work, the magnetic contribution to the isothermal entropy change ΔS upon switching on a magnetic field has been investigated in correlated metallic ferromagnets within the Hubbard nondegenerate model. The analytical expression for ΔS obtained in the mean-field approximation depends substantially on the electronic structure (density of electron states), which presents new ways to increase the absolute value of ΔS relative to the known result obtained within the Heisenberg model. The temperature dependence of ΔS has been calculated at different values of the Coulomb interaction U and the number of electrons n for the Bethe infinite-dimensional lattice and square lattice with allowance for transfer integrals in the first (t) and the second (t') coordination shells. It has been found that the presence of Van Hove singularities in the electronic spectrum near the Fermi level makes it possible to considerably increase $|\Delta S|$ at a fixed magnetic field. The possibility of first-order magnetic phase transitions depending on the model parameters has been analyzed.

Keywords: magnetocaloric effect, Van Hove singularities, correlated metals
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1. INTRODUCTION

Warburg discovered the magnetocaloric effect (MCE) in 1881. However, to date, no loss of scientific interest in it has been observed. One of the most pronounced practical applications of MCE is the creation of refrigerating plants, which are more advantageous (to 30%) in terms of energy conservation compared to ordinary refrigerators based on the evaporation–condensation cycle of working substance. The prototype of this magnetocaloric refrigerator was constructed by Brown in 1976 with the use of metallic gadolinium as working magnet. For the last 40 years elapsed from the point a vast body of experimental data on the MCE in rare-earth elements and their compounds has been accumulated (see review [1]). The modern state of affairs in the area of materials used for magnetic cooling was described in reviews [2, 3]. A new enhanced interest in MCE arose in 1997 after discovery of the $Gd_5Si_2Ge_2$ system with a giant value of the isothermal entropy change, 20 J/(kg K), when a magnetic field of 5 T was switched on [4]. The giant value of the isothermal entropy change was obtained for FeRh alloys undergoing a first-order transition from the ferromagnetic into the antiferromagnetic state [5]. Since that time the quantity of papers on this subject has increased substantially in leading world journals (see reviews on MCE in perovskites [6] and, in particular, manganites [7] and other systems [8]). Nowadays, in addition, experimental investigations of MCE in nanomaterials, heterostructures, and thin films have been performed [9]. Approaches to studying MCE were described most comprehensively in review [10].

When theoretically investigating MCE the electronic contribution to the Hamiltonian is described by the Heisenberg model for systems with rare metals or by the Hubbard model for systems with transition metals. As a rule, in both cases the mean-field approximation for Hamiltonian terms describing interaction is used [10]. For metallic systems, however, the effect of Van Hove singularities of the electronic spectrum on the quantity ΔS was not investigated yet.

The purpose of this work is to investigate numerically and analytically the isothermal entropy change ΔS with switching-on of a magnetic field for metallic correlated ferromagnets in the presence of the Van Hove singularities in the electronic spectrum. To do this, we obtained the following analytical expression for the quantity ΔS with MCE for the single-band Hubbard model in the mean-field approximation. In addition, for the case where the system exhibits a sec-

ond-order phase transition, we obtained analytically the proportionality coefficient in explicit form for a dependence $\Delta S \propto H^{2/3}$ in low magnetic fields H at $T = T_C$, where T_C is the transition temperature (Curie temperature). For numerical calculations, the electron spectrum for the Bethe infinite-dimensional lattice taking into account transfer between first and second neighbors was chosen. This choice was due to the fact that, in this case, the density of electron states imitates the density of states for real three-dimensional lattices that reproduce Van Hove singularities. In addition, for the Bethe infinite-dimensional lattice, as distinguished from low-dimensional systems without anisotropy in which long-wave fluctuations destroy the magnetic order at finite temperatures [11], the Stoner theory can be considered to be a good approximation for studying MCE in metallic systems at rather low values of the local Coulomb interaction. The magnitude and position of the maximum of the absolute value of ΔS was analyzed at the transition point $T = T_C$ for a given magnetic field depending on the all model parameters, i.e., the Coulomb interaction U, the number of electrons n, and the ratio of transfer integrals t'/t. Appendix 1 contains analogous results of investigating ΔS for the square lattice that exhibits another type of Van Hove singularity. In Appendix 2, the possibility of the first-order magnetic transition is shown for the case where the Fermi level is near the Van Hove singularity and the temperature is fairly low, which opens the door to a fundamentally new MCE scenario in weakly correlated metallic systems.

2. METHOD

Entropy of metal depends on the magnetic field H and temperature T and consists of two contributions, i.e., the lattice S_{lat} and electron S_{el} (by creating a magnetic order, the conduction electrons contribute to the magnetic part of entropy)

$$S(T,H) = S_{lat}(T,H) + S_{el}(T,H). \quad (1)$$

As is shown in [12], the electronic contribution to the entropy change is dominant upon switching on the magnetic field and, as an approximation, we take

$$\begin{aligned}\Delta S(T,H) &\approx \Delta S_{el}(T,H)\\ &= S_{el}(T,H) - S_{el}(T,H=0).\end{aligned} \quad (2)$$

Let us consider the description of MCE for a ferromagnetic metallic correlated system within the single-band Hubbard model

$$H = \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U\sum_i n_{i\uparrow} n_{i\downarrow} - h\sum_{i\sigma} \sigma n_{i\sigma}. \quad (3)$$

Here, it is assumed that t_{ij} is nonzero for first and second neighbors i, j and is equal to t and t', respectively. In addition, it is assumed that $t, t' > 0$. $c_{i\sigma}^{\dagger}$ and $c_{i\sigma}$ are the operators of creation and annihilation of electron with the spin projection σ at site i; $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ is the operator of the number of electrons with the spin projection $\sigma = \pm 1$ at site i; U is the matrix element of the screened Coulomb interaction at the site; and $h = 2\mu_B H$ is the magnetic-field value in energy units. The first term in Eq. (3) describes the kinetic energy of electrons in the lattice field (electron transfer); the second term, the local Coulomb interaction; the third term, the Zeeman energy of electrons in magnetic field.

To obtain an analytical expression for ΔS, let us consider the mean-field approximation for Hamiltonian (3). This approximation corresponds to the following substitution of the term describing the interaction:

$$n_{i\uparrow} n_{i\downarrow} \to n_{i\uparrow} \langle n_{i\downarrow} \rangle + \langle n_{i\uparrow} \rangle n_{i\downarrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle. \quad (4)$$

It is assumed that the average number of electrons at site i $\langle n_{i\sigma} \rangle = n_\sigma$ is independent of the site number (ferromagnetic ordering). The total number of electrons $n = n_\uparrow + n_\downarrow$ and the magnetic moment (in units of $2\mu_B$) equal to $m = (1/2)(n_\uparrow - n_\downarrow)$ (these are per site) are determined by the equations

$$n = \frac{1}{N}\sum_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma}, \quad (5)$$

$$m = \frac{1}{2N}\sum_{\mathbf{k}\sigma} \sigma f_{\mathbf{k}\sigma}, \quad (6)$$

where $f_{\mathbf{k}\sigma} \equiv f_\mu(\varepsilon_{\mathbf{k}} - \sigma\Delta + Un/2)$ is the Fermi function taken at the given chemical potential μ, $\varepsilon_{\mathbf{k}}$ is the electronic spectrum, $\Delta = Um + h$ is the spin splitting of the electronic spectrum, and N is the total number of sites. Then, Hamiltonian (3) in the mean-field approximation has the form

$$\mathcal{H}_{MF} = \sum_{\mathbf{k}\sigma} \tilde{\varepsilon}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} - NU(n^2/4 - m^2), \quad (7)$$

where $c_{\mathbf{k}\sigma} = N^{-1/2}\sum_i c_{i\sigma} \exp(i\mathbf{k}\mathbf{R}_i)$, $\tilde{\varepsilon}_{\mathbf{k}\sigma} = \varepsilon_{\mathbf{k}} + Un/2 - \sigma\Delta$ is the effective electronic spectrum, and $\mathbf{R}_i$ is the radius vector of lattice site i.

As is known, the entropy of noninteracting electron gas with the spectrum $\tilde{\varepsilon}_{\mathbf{k}\sigma}$ per site takes on the form [10]

$$\begin{aligned}S_{el}(\mu,\Delta,T) = \frac{1}{N}\sum_{\mathbf{k}\sigma} [&\ln(1 + \exp(-(\tilde{\varepsilon}_{\mathbf{k}\sigma} - \mu)/T\\ &+ (\tilde{\varepsilon}_{\mathbf{k}\sigma} - \mu) f_{\mathbf{k}\sigma}/T].\end{aligned} \quad (8)$$

Here and below, the temperature is measured in energy units: $k_B T \to T$, where k_B is the Boltzmann constant.

It is convenient to represent sums over $\mathbf{k}$ in the right-hand side of Eqs. (5), (6), and (8) through the

density of non-interacting electron states per site by the following expression

$$\rho(\varepsilon) = \frac{1}{N}\sum_{\mathbf{k}} \delta(\varepsilon - \varepsilon_{\mathbf{k}}) \quad (9)$$

using the formula

$$\frac{1}{N}\sum_{\mathbf{k}} F(\varepsilon_{\mathbf{k}}) = \int \rho(\varepsilon) F(\varepsilon) d\varepsilon. \quad (10)$$

It should be noted that, for metallic systems, as distinguished from the results for ΔS, which were obtained for localized electron systems (see, e.g., [14]), the growth of ΔS in the general case can be reached not only by a decrease in the Curie temperature T_C or an increase in the spin value but also by fitting of the electronic spectrum.

Below, we calculate the quantity ΔS, which was determined by Eqs. (2) and (8) from the self-consistent solution of Eqs. (5) and (6) depending on the model parameters U and n.

3. ISOTHERMAL ENTROPY CHANGE OF A METALLIC SYSTEM IN LOW FIELDS

The magnetic-field strength attainable in experiments is rather small compared to the other energy parameters that characterize the system. Let us calculate the entropy change ΔS caused by switching on magnetic field h in the limit of low magnetic fields $h \to 0$. Here and below, we assume that the magnetic phase transition is a second-order transition. The determination of the domain of parameters for which this assumption holds is discussed in Appendix 2 (see also [15]). For all the results presented below, this assumption was satisfied.

In the paramagnetic phase, the parameter Δ (see Eq. (6)) becomes nonzero when a magnetic field is switched on, while in the ferromagnetic phase, this is the case at $h = 0$. When a magnetic field is switched on, the chemical potential changes as follows: $\mu \to \mu + \delta\mu$ to satisfy the requirement n = const. In the lowest order in h, from Eq. (5), we have

$$\delta\mu = \frac{\Delta^2}{2}(\chi_1/\chi_0), \quad (11)$$

where the notations for magnetic susceptibility of the non-interacting electron gas with the spectrum $\varepsilon_{\mathbf{k}}$ are introduced as follows:

$$\chi_0 = -\frac{1}{N}\sum_{\mathbf{k}} f_{\mathbf{k}}' \quad (12)$$

and

$$\chi_1 = -\frac{1}{N}\sum_{\mathbf{k}} f_{\mathbf{k}}'', \quad (13)$$

where, at $\Delta = 0$, $f_{\mathbf{k}\sigma}$ is independent of σ and we suppose that $f_{\mathbf{k}} \equiv f_{\mathbf{k}\sigma}$. In Eqs. (12) and (13), we used designations $f_{\mathbf{k}}' \equiv \partial f_{\mathbf{k}}/\partial\varepsilon_{\mathbf{k}}$ and $f_k'' \equiv \partial^2 f_{\mathbf{k}}/\partial\varepsilon_{\mathbf{k}}^2$. Expanding the right-hand side of Eq. (8) into a series in powers of Δ and $\delta\mu$ up to the lowest order, we obtain

$$\Delta S = \Delta^2(K_2 - (\chi_1/\chi_0)K_1), \quad (14)$$

where

$$K_1 = \frac{1}{TN}\sum_{\mathbf{k}} (\varepsilon_{\mathbf{k}} + Un/2 - \mu_0) f_{\mathbf{k}}', \quad (15)$$

$$K_2 = \frac{1}{TN}\sum_{\mathbf{k}} \left(f_{\mathbf{k}}' + (\varepsilon_{\mathbf{k}} + Un/2 - \mu) f_{\mathbf{k}}'' \right). \quad (16)$$

To determine the behavior of Δ depending on the magnetic field h at $T \geq T_C$, let us expand the right-hand side of Eq. (6) in powers of Δ to the third order inclusive, assuming Δ to be small as follows:

$$m = \Delta\chi_0 - \frac{\Delta^3}{2}(\chi_1^2/\chi_0 - \chi_2/3), \quad (17)$$

where $\chi_2 = -(1/N)\sum_{\mathbf{k}} \partial^3 f_{\mathbf{k}}/\partial\varepsilon_{\mathbf{k}}^3$. It can be seen from Eq. (17) that, in the lowest order in h, when $T > T_C$ (and, hence, $U\chi_0 < 1$),

$$m = \frac{\chi_0}{1 - U\chi_0} h, \quad (18)$$

which results in a dependence $\Delta S \propto h^2$. At $T = T_C$,

$$U\chi_0 = 1 \quad (19)$$

and, in the lowest order in h, we have

$$m = (2\chi_0/g)^{1/3} U^{-1} h^{1/3}, \quad (20)$$

where $g = (\chi_1^2/\chi_0 - \chi_2/3)$. Substituting expression (20) into Eq. (14), we obtain

$$\Delta S = \alpha(U, n) h^{2/3} + o(h^{2/3}), \quad (21)$$

where the dependence of the coefficient

$$\alpha(U, n) = (2\chi_0/g)^{2/3}(K_2 - (\chi_1/\chi_0)K_1)) \quad (22)$$

on n is determined through the solution of Eq. (5) at $\Delta = 0$, which specifies the Fermi level $\mu_{\text{eff}} = \mu - Un/2$ in the paramagnetic phase as a function of n. Note that the dependence $\Delta S \propto h^{2/3}$ at $T = T_C$ follows from the Landau theory of second-order phase transitions [13], whereas the expression (22) for coefficient α obtained through parameters of the model of weakly correlated metal is the original result. Formula (21) means that in a fixed magnetic field the greatest value of $|\Delta S|$ is reached at those values of parameters U and n at the transition point $T = T_C$, for which α is maximum in absolute value. Within the mean-field approximation, the $|\Delta S|$ as a temperature function is always maximum

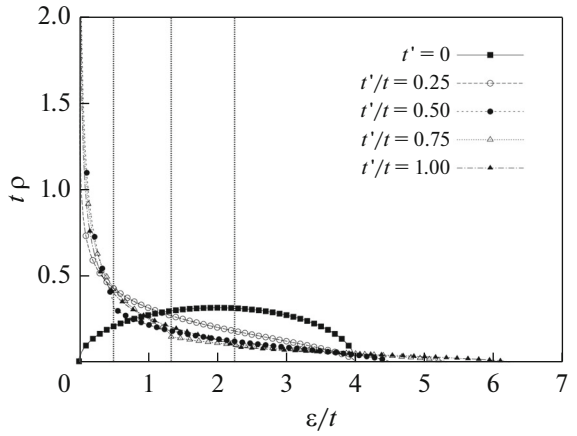

Fig. 1. Density of electron states ρ(ε) in units of t^{-1}, (see definition (9)) for the Bethe infinite-dimensional lattice at different values of t'/t. Vertical dash lines show the position of Van Hove singularities.

at $T = T_C$, whereas experimentally, the point of the maximum of ΔS is located near T_C and does not coincide exactly with it.

Note that expression (21) can be obtained directly via the differentiation of the known expansion of the free energy F in powers of the order parameter m in the Stoner theory (see [16], formula (2.22)). This formula actually yields explicit expressions through the electronic spectrum for the coefficients of the expansion of the free energy that are used within the phenomenological approach.

Note that the analogous dependence of ΔS on h was obtained for the Heisenberg model in the mean-field approximation (see, e.g., [14]) and for a given magnetic field H, the maximum value of ΔS is entirely determined by the spin value and the Curie temperature.

It is shown below that, when Van Hove singularities determine the physical features of the system, $|\Delta S|$ is great (see also Appendix 1) and T_C is small; therefore, it is reasonable to consider an estimate of expression (21) within the low-temperature expansion (Sommerfeld expansion). At low temperatures $T \ll \varepsilon_0$ (where $\varepsilon_0 \sim |\rho(\mu_{eff})/\rho'(\mu_{eff})|$ is the typical energy scale of changes in ρ(ε) near the Fermi level $\varepsilon = \mu_{eff}$), we have the following main contributions:

$$\chi_0 = \rho(\mu_{eff}) + o(T), \quad (23)$$

$$\chi_1 = -\rho'(\mu_{eff}) + o(T), \quad (24)$$

$$\chi_2 = \rho''(\mu_{eff}) + o(T), \quad (25)$$

$$K_1 = -T(\pi^2/3)\rho'(\mu_{eff}) + o(T^2), \quad (26)$$

$$K_2 = T(\pi^2/3)\rho''(\mu_{eff}) + o(T^2). \quad (27)$$

From Eqs. (21) and (22), we obtain the following estimate of ΔS at $T = T_C$:

$$\Delta S = -T_C\rho\frac{\pi^2}{3}(2/F_1)^{2/3}\,Rh^{2/3}, \quad (28)$$

where notations $F_1(\mu_{eff}, T = 0) = (\rho'/\rho)^2 - \rho''/(3\rho)$ and $R = (\rho'/\rho)^2 - \rho''/\rho$ are used [16], and the density of electron states ρ and all its derivatives are taken at $\varepsilon = \mu_{eff}$. It is seen that the quantity ΔS is determined by the density of states and its derivatives and the dependence of the parameter U enters implicitly through T_C, which in the used approximation has the form

$$T_C = \frac{1}{\pi R^{1/2}}\sqrt{6(1 - 1/(U\rho))}. \quad (29)$$

Let us generalize definition of $F_1(\mu_{eff}, T)$ for finite temperatures T:

$$F_1(\mu_{eff}, T) = g/\chi_0 = \left(\frac{\chi_1}{\chi_0}\right)^2 - \frac{\chi_2}{3\chi_0}. \quad (30)$$

The sign of this expression coincides with the sign of the fourth-order coefficient in the Landau expansion in powers of the order parameter (magnetization) and determines the phase-transition order. The condition $F_1(\mu_{eff}, T) < 0$ directly indicates the necessity of considering first-order magnetic transitions (see details in Appendix 2), which opens up the possibility of a new MCE scenario, since inhomogeneous states participate in the magnetic transition (phase separation exists). This is a difference between the MCE scenario for metallic systems exhibiting first-order transitions and the scenario for systems with local moments. For these latter, no abrupt change in the concentration of carriers takes place at the point of the first-order magnetic transition (review of thermodynamics for such systems in the MCE context is given in [17]). This fact can be used as the basis for fundamentally new technical applications of MCE.

4. RESULTS

Figure 1 displays plots of ρ(ε) for the Bethe infinite-dimensional lattice at different t'/t [18]; the bottom of the band is chosen as the origin of energy. It can be seen that, with growth in the ratio t'/t, the density of states becomes an appreciably asymmetric function of ε relative to the center of the band as follows: at $t' \geqslant 0.25t$ on the low-energy edge of the band, a Van Hove singularity arises in the form of divergence $\rho(\varepsilon) \propto \varepsilon^{-1/2}$ and, inside the band, Van Hove singularities, appear in the form of kinks. The band width remains constant or increases with growth

of t' and equals $W = 4t$ at $t' \geq 0.25t$ and $W = 4t + (t^2 + 4t'^2)/(4t')$ at $t' \leq 0.25t$.]

As was discussed in Section 3, $|\Delta S|$ for fixed parameters $U, n, t'/t$, and h is the greatest in temperature at $T = T_C$. When the h value is fixed, the quantity ΔS is completely determined by a function $\alpha(U, n)$ (see Eq. (22)). Let us maximize $|\alpha(U, n)|$ in parameters U and n on a rather fine-mesh grid when solving Eqs. (5) and (19) for each pair U, n in the paramagnetic phase. When numerically solving systems of equations at low temperatures the range $T \geqslant 2\times10^{-9}t$ limits the change in T because of problems with accuracy.

Figure 2 depicts constructed maps of $\Delta S(T_C, h) = \alpha(U, n)h^{2/3}$ in variables U/t and n (ΔS is shown by the degree of gray) for different values of t'/t from 0 to 1 (from top to bottom) and $h = 10^{-4}t$. Note that, in the presented diagrams, fairly small values of U were chosen compared to the band width W. The dynamic mean-field theory offers a reasonable estimate of the critical $U \sim 1.5W$ for the metal–dielectric transition in the Hubbard model [19]. Accordingly, we limit the change in parameter U by $U < 5t$.

Let us denote the values of U and n yielding the maximum of ΔS at a given t'/t as $U_{max}(t'/t)$ and $n_{max}(t'/t)$. With increasing $t' \geq 0.5t$, the value of $U_{max}(t'/t)$ and $n_{max}(t'/t)$ become small in this range of parameters and the proximity of the Fermi level μ_{eff} to the position of the Van Hove singularity located in the paramagnetic phase on the bottom of the band is of great importance. Let us denote the value of T_C, which corresponds to the parameters $U = U_{max}(t'/t)$ and $n = n_{max}(t'/t)$, as $T_C(t'/t)$. With growth of t'/t, the temperature $T_C(t'/t)$ decreases markedly at $t' \geq 0.25t$ and reaches near-zero values at $t' \geq 0.5t$.

To illustrate the temperature dependence of ΔS, Fig. 3 displays graphs of $\Delta S(T, h)$ as functions of T at $U = U_{max}(t'/t)$ and $n = n_{max}(t'/t)$ for different t'/t (see Fig. 2). It can be seen that $\Delta S(T, h)$ is negative and exhibits a sharp maximum related to the transition through the Curie temperature T_C. The calculation was performed for a magnetic field $h = 10^{-4}t$, which corresponds (if the characteristic value of t for metals is estimated as 1 eV) to a magnetic field of about 5 T, i.e., the strength that currently is experimentally attainable [10]. With growth in t'/t, the maximum of $|\Delta S(T_C, h)|$ shifts toward the low-temperature range because of a significant increase of $\rho(\varepsilon)$ near the bottom of the band (see Fig. 1). In our calculations, $|\Delta S(T_C, h)|$ reaches an absolute maximum at the least considered value of Coulomb interaction $U = 0.1t$ and occupancy $n = 0.04$ for $t' = 0.5t$. When choosing the transfer integral $t = 1$ eV, we can obtain an estimate of the maximum value of $|\Delta S(T, h)| = 0.076$ J/(mol K) at T_C of about 10 K. This value corresponds to not high

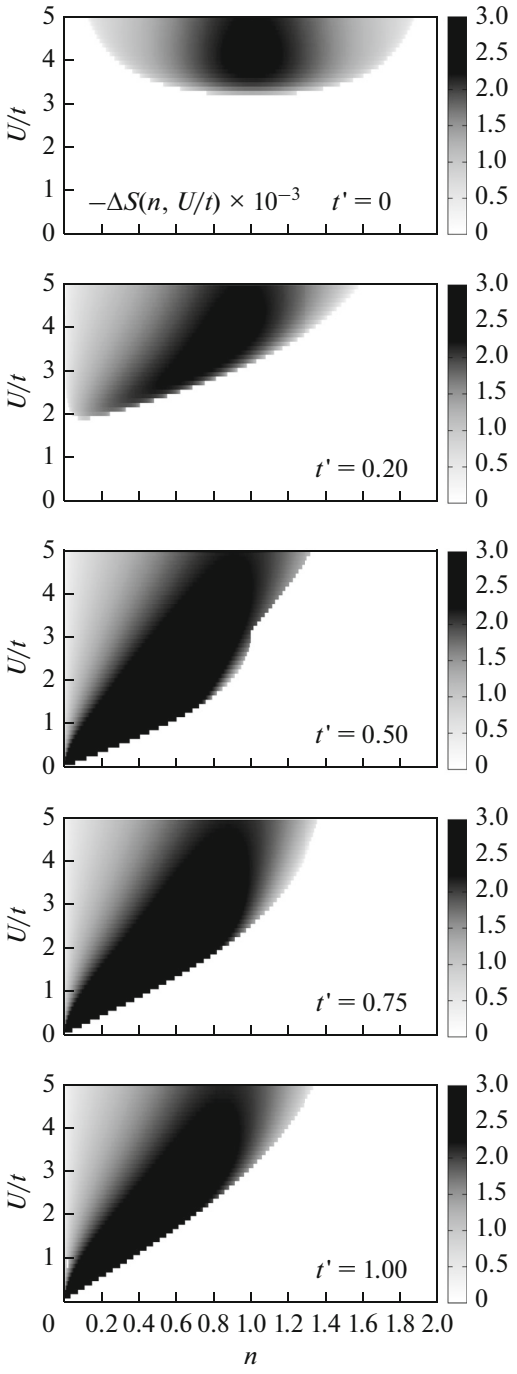

Fig. 2. Maps of $\Delta S(T_C, h)$ in the single-band Hubbard model in the mean-field approximation in coordinates U/t and n for the Bethe infinite-dimensional lattice with t'/t from 0 to 1 (from top to bottom). Magnetic field is $h = 10^{-4}t$.

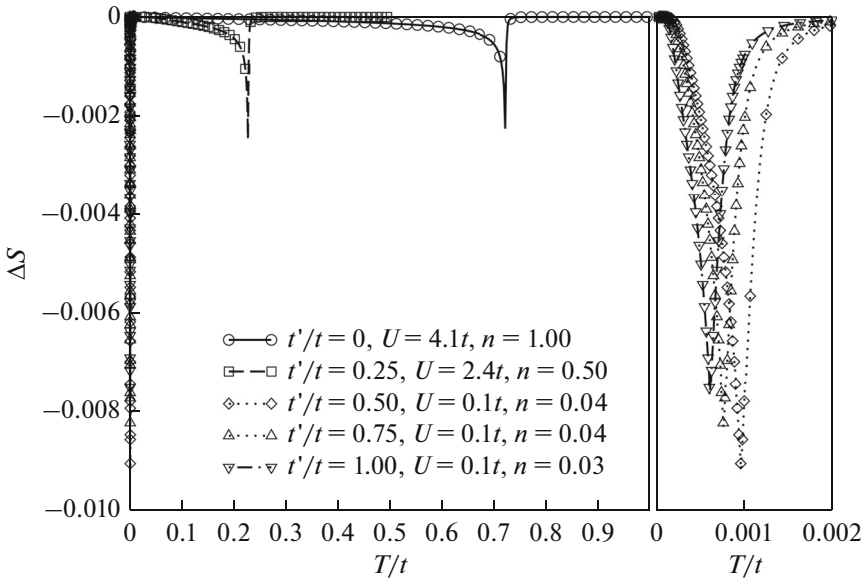

Fig. 3. Dependence $\Delta S(T,h)$ on the temperature T in the single-band Hubbard model in the mean-field approximation for the Bethe infinite-dimensional lattice. At the chosen values of $U = U_{\max}(t'/t)$ and $n = n_{\max}(t'/t)$ (shown in the figure), $\Delta S(T,h)$ reaches the maximum in parameters U and n at the point $T = T_C$ for different t'/t (see Fig. 1). Magnetic field is $h = 10^{-4}t$. Left: general view of lines of $\Delta S(T,h)$. Right: $\Delta S(T,h)$ lines for large values of t'/t are shown in detail in the low-temperature range.

values of ΔS compared to results, e.g., for gadolinium. When t'/t increases further, $|\Delta S(T_C,h)|$ begins to decrease insignificantly. Note that, at the considered values of $t' < 0.5t$, the maxima of $\Delta S(T_C,h)$ are much the same in magnitude, four times smaller than at $t' \geq 0.5t$, and are obtained at appreciably higher values $U = U_{\max}(t'/t)$ and $n = n_{\max}(t'/t)$.

For comparison, Appendix 1 contains the results of calculating ΔS for square lattice. It is shown that the magnitude of t'/t markedly affects the maximum value of $|\Delta S(T_C,h)|$ in parameters U and n. For a square lattice, the temperature $T_C(t'/t)$ reaches a minimum in the low-temperature range at $t'/t = 0.5$. For the Bethe lattice, the tendency of the maximum of $|\Delta S|$ to shift toward smaller values of U and n with growing t'/t from 0 to 1 is clearly seen. For a square lattice, as distinguished from the Bethe lattice, this dependence is nearly symmetric about $t' = 0.5t$. It can be seen that the presence of the Van Hove root singularity $\rho(\varepsilon) \propto \varepsilon^{-1/2}$ in the vicinity of the Fermi level substantially enhances the maximum value of $|\Delta S(T_C,h)|$ in parameters U and n.

These results for a square lattice should be used with greater caution than the results for the Bethe infinite-dimensional lattice, which corresponds to higher dimensionality, since the mean-field approximation disregards magnetic fluctuations. At any finite temperature, these long-wave fluctuations in low-dimensional systems are so strong that they destroy the long-range magnetic order [11]. In real experiments, the layered compounds in which the presence of weak interplanar transfer results in some smearing of singularities of the density of states, which leads to its boundedness, as a function of energy, correspond to a square lattice. For these compounds, the critical temperature of the transition is low and, above it, the transition occurs into the state without long-range order and with strong fluctuations of short-range order with exponentially high correlation length in the reciprocal temperature, in which the strong and finite response to a magnetic field can be retained [20]. If the magnetic field strength in experiments with layered compounds is rather high, the obtained results should be consistent with experimental data on the isothermal change in ΔS. However, for low magnetic fields, it is impossible to rely even on a qualitative agreement relative to ΔS between the experimental data and the theoretical results obtained.

Note that, in [10], for the model that, in addition to the interactions we accounted for also contains the lattice contribution to the entropy and magnitoelastic interaction, ΔS was calculated in the same approximation. In doing so, the electron density of states was modeled with the simplest dependences (rectangular, triangular), whereas no parametric dependences of ΔS were studied in detail. The results presented complement the results of [10] with the comprehensive investigation of the role of Van Hove singularities and theoretical study of the maximality conditions of $|\Delta S|$ depending on the system parameters.

5. CONCLUSIONS

In this work, for ferromagnetic metallic correlated systems in the presence of Van Hove singularities in the electronic spectrum, the magnetic-field contribution to the isothermal entropy change ΔS was investigated when switching on a magnetic field. The maximality conditions for this quantity in parameters T, U, and n were determined. The analytical expressions for ΔS at the transition point $T = T_C$, which yield an explicit relation to the electronic structure of the system, were obtained. It is shown that the absolute value of $\Delta S(T,h)$ exhibits the maximum at the Curie temperature T_C, when the Fermi level in the paramagnetic phase is located in the proximity of the position of the Van Hove singularity near the bottom of the band. We obtained estimates of the maximum of $|\Delta S|$ for the considered lattices, and their values were compared with typical experimental data for gadolinium. The presence of the Van Hove root singularity ($t' \geq 0.5t$ for the Bethe infinite-dimensional lattice and $t' = 0.5t$ for a square lattice) in the vicinity of the Fermi level enhances appreciably the maximum value of $|\Delta S|$ for a given magnetic field.

In this work, the possibility of first-order magnetic transitions was analyzed. It has been shown that, for a square lattice, the logarithmic Van Hove singularity ($t' \neq 0.5t$) enables the first-order transition, when the Fermi level lies in the vicinity of width on the order of t near the given Van Hove singularity. At the same time, for the Bethe infinite-dimensional lattice, the first-order transition is only possible at t' close to $0.25t$, when the position of the Fermi level is near the bottom of the band. It has also been demonstrated that, for both lattices, the first-order transition is only possible at fairly low temperatures $T \leq 0.1t$. A detailed investigation of MCE in metallic systems undergoing first-order transitions will be presented in subsequent works.

APPENDIX 1: ΔS FOR SQUARE LATTICE

In this appendix, we consider the quantity ΔS for the case of square lattice. This case is treated separately, since the mean-field approximation is not well justified for low-dimensional systems at finite temperatures because of disregarding long-wave collective magnetic excitations that destroy the long-range magnetic order. Let us consider the density of electron states for square lattice with the electronic spectrum in the nearest- and next-nearest-neighbor approximation as follows:

$$\varepsilon_{\mathbf{k}} = -2(\cos k_x + \cos k_y) + 4t'(\cos k_x \cos k_y + 1), \quad (31)$$

where the lattice parameter is taken to be equal to unity and the constant $4t'$ displaces the origin of energy and brings the position of a Van Hove singularity into coincidence with the zero of energy when $t' \leqslant t/2$. Note that, in this case, the Van Hove singularity arises from points $\mathbf{k} = (0,\pi)$ and $\mathbf{k} = (\pi,0)$. At $t' \leqslant t/2$, the density of states per spin projection has the form

$$\rho(\varepsilon) = \frac{2}{\pi^2\sqrt{\kappa_2(\varepsilon)}}\mathcal{K}\left(-\frac{\kappa_1(\varepsilon)}{\kappa_2(\varepsilon)}\right), \quad (32)$$

where $\mathcal{K}(x) \equiv \int_0^1 \frac{dt}{\sqrt{(1-t^2)(1-xt^2)}}$ is the complete elliptic integral of the first kind, $\kappa_1(\varepsilon) = (4t + 8t' - \varepsilon)(-4t + 8t' - \varepsilon)$, and $\kappa_2(\varepsilon) = 16(t^2 + t'\varepsilon - 4t'^2)$. At $t' < t/2$ $\rho(\varepsilon) = A\ln(t/|\varepsilon|) + \mathbb{O}(1)$, and at $t' = 0.5t$ $\rho(\varepsilon) = A'\varepsilon^{-1/2} + \mathbb{O}(1)$, where A, A' are the constants.

When $t' > t/2$, we have

$$\rho(\varepsilon) = \frac{4}{\pi^2}\begin{cases} \frac{1}{\sqrt{\kappa_1(\varepsilon)}}\mathcal{K}\left(\frac{\varepsilon^2}{\kappa_1(\varepsilon)}\right), & 0 < \varepsilon < 4t' - t^2/t', \\ \frac{1}{\sqrt{\kappa_2(\varepsilon)}}\mathcal{K}\left(-\frac{\kappa_1(\varepsilon)}{\kappa_2(\varepsilon)}\right), & 4t' - t^2/t' < \varepsilon < -4t + 8t', \\ \frac{1}{2\sqrt{\kappa_2(\varepsilon)}}\mathcal{K}\left(-\frac{\kappa_1(\varepsilon)}{\kappa_2(\varepsilon)}\right), & -4t + 8t' < \varepsilon < +4t + 8t'. \end{cases} \quad (33)$$

In this case, the Van Hove singularity is available at $\varepsilon = 4t' - t^2/t'$ and corresponds to four hot points $\mathbf{k} = (k_0, \pm k_0)$, which are determined by the condition $\cos(k_0) = t/(2t')$. The abrupt change in the density of states at $\varepsilon = -4t + 8t'$ is connected with the presence of a local maximum $\varepsilon_{\mathbf{k}}$ at $\mathbf{k} = (0,0)$. The plots of the density of states for different t'/t are shown in Fig. 4.

In Fig. 5, for a square lattice, analogously to the results for the Bethe infinite-dimensional lattice presented in the main text in Fig. 2, maps of $\Delta S(T_C,h) = \alpha(U,n)h^{2/3}$ in variables U/t and n (the ΔS value is shown by the degree of gray) were constructed for different values of t'/t from 0 to 1 (from top to bottom) and $h = 10^{-4}t$.

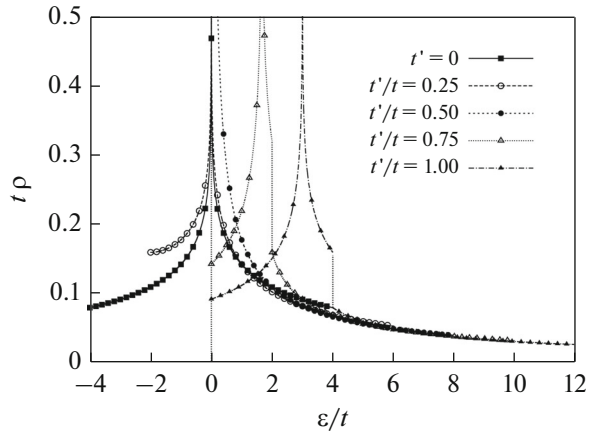

Fig. 4. Density of electron states ρ(ε) in units of t^{-1} (see definition (9)) for square lattice at different values of t'/t.

The $|\Delta S(T,h)|$ reaches the absolute maximum at Coulomb interaction $U = 1.5t$, occupancy $n = 0.3$, and $t'/t = 0.5$. At these model parameters, T_C is low because of a stronger Van Hove singularity in the density of electron states as follows: at $t' = 0.5t$, the root singularity (which singles out this case) and, at $t' \neq 0.5t$, the logarithmic singularity that is suppressed much more strongly by temperature fluctuations. At all other values of $t' \neq 0.5t$, the maximum values of $|\Delta S(T,h)|$ are much the same in magnitude and are observed at large parameters U and n. The maximum value of $|\Delta S(T,h)|$ (at $t \sim 1$ eV) is estimated as 0.015 J/(mol K), which corresponds to not high values of ΔS and remains nearly unaltered with changing t'/t.

APPENDIX 2: ON THE POSSIBILITY OF FIRST-ORDER MAGNETIC PHASE TRANSITIONS FOR THE BETHE AND SQUARE LATTICES

In this appendix, the sign of the parameter $F_1(\varepsilon,T)$ (see Eq. (30)) is considered for the Bethe infinity-dimensional lattice and square lattice depending on the temperature T and Fermi level ε. (In the main text, instead of ε, we use μ_{eff}.) When $F_1(\varepsilon,T) < 0$, the theory of second-order phase transitions ceases to be applicable. Figure 7 displays the dependence $F_1(\varepsilon,T=0)$ on ε at different t'/t for the Bethe infinity-dimensional lattice; Fig. 8 displays the dependence for a square lattice. In the first case, $F_1(\varepsilon,T=0)$ is positive definite, except for the value $t'/t = 0.25$, when $F_1(\varepsilon,T=0) \to -\infty$ at $\varepsilon \to 0$, i.e., near the point of divergence ρ(ε) on the bottom of the band. In the second case, $F_1(\varepsilon,T=0) < 0$ in the interval of width on the order of t in the proximity of the position of a Van Hove singularity and likewise tends to $-\infty$ at $\varepsilon \to 0$ for all values of t'/t, exclusive of 0.5.

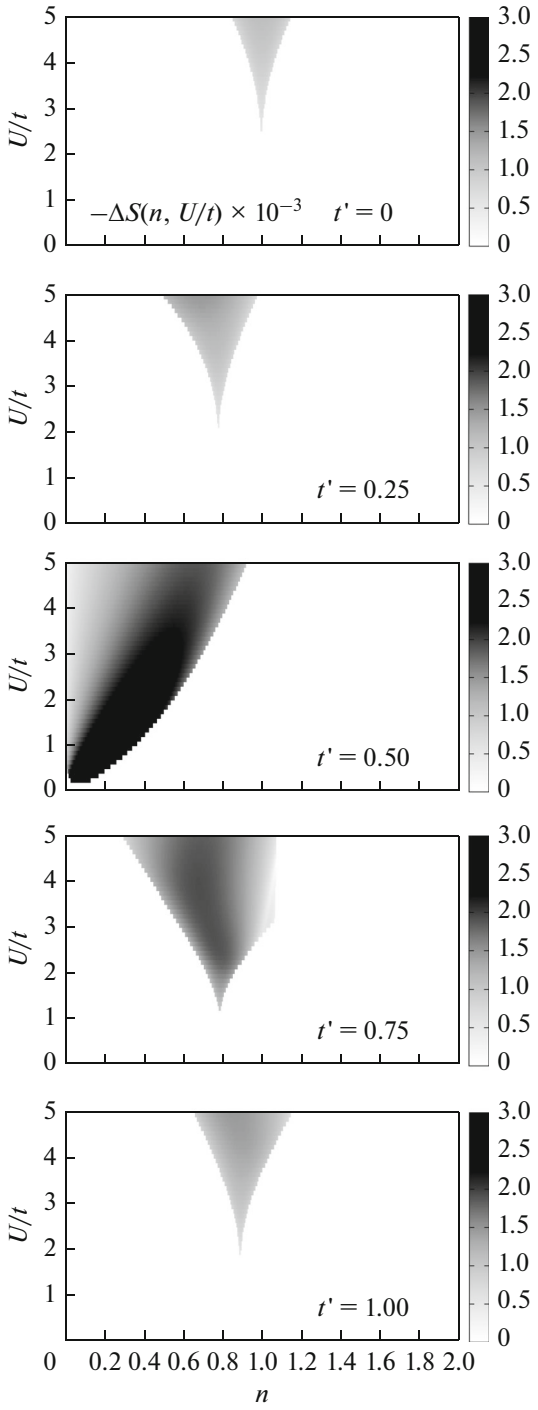

Fig. 5. Same as in Fig. 2, only for square lattice.

Let us consider how stable this result is relative to a rise in temperature. As an example, Figs. 7 and 8 show a dependence $F_1(\varepsilon,T)$ on ε at different temperatures with $t' = 0.25t$ for the Bethe infinity-dimensional lattice and square lattice, respectively. It can be seen that,

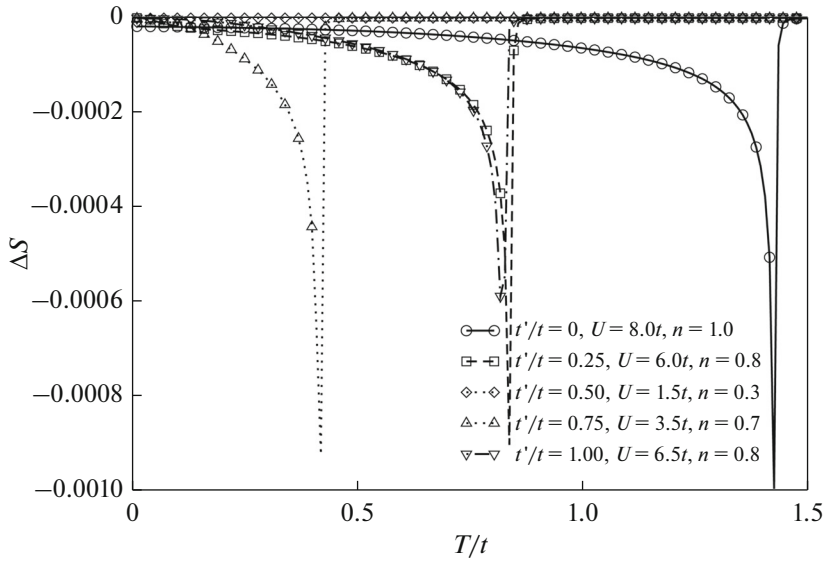

Fig. 6. Same as in Fig. 3, only for square lattice. Chosen values of the parameters are $U = U_{\max}(t'/t)$ and $n = n_{\max}(t'/t)$ (shown in the figure); see Fig. 5. $h = 10^{-4}t$.

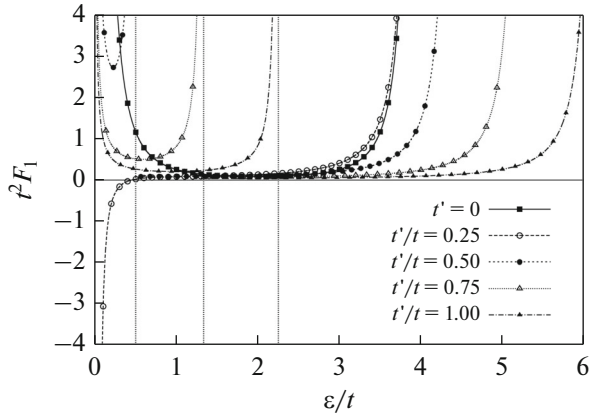

Fig. 7. $F_1(\varepsilon, T = 0) = (\rho'(\varepsilon)/\rho(\varepsilon))^2 - \rho''(\varepsilon)/(3\rho(\varepsilon))$ in units of t^{-2} for the Bethe infinity-dimensional lattice at different values of t'/t at the temperature $T = 0$.

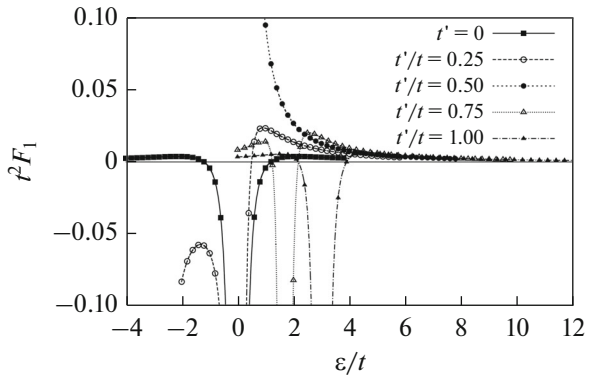

Fig. 8. $F_1(\varepsilon, T = 0) = (\rho'(\varepsilon)/\rho(\varepsilon))^2 - \rho''(\varepsilon)/(3\rho(\varepsilon))$ in units of t^{-2} for square lattice at different values of t'/t at the temperature $T = 0$.

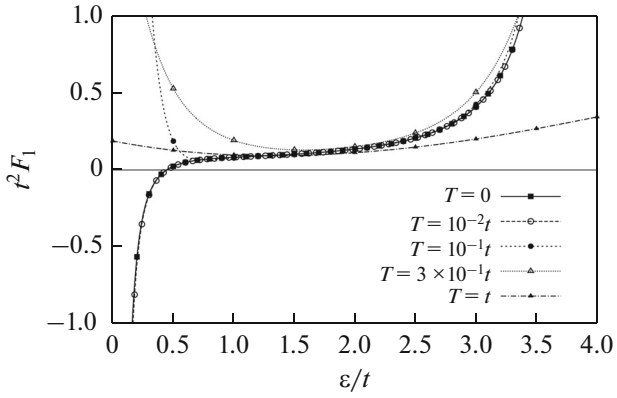

Fig. 9. Dependence of the coefficient $F_1(\varepsilon, T)$ (in units of t^{-2}) on ε at $t' = 0.25$ for Bethe infinite-dimensional lattice at different temperatures.

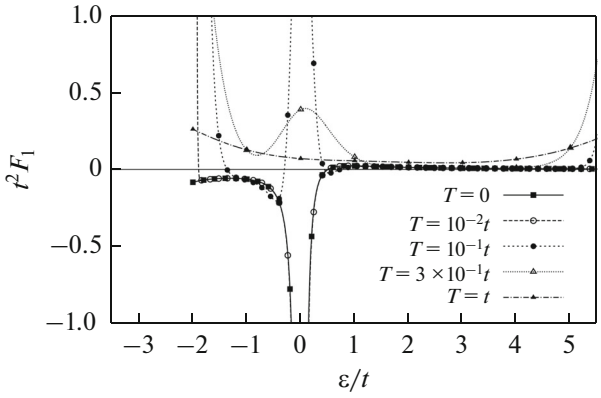

Fig. 10. Dependence of the coefficient $F_1(\varepsilon, T)$ (in units of t^{-2}) on ε at $t' = 0.25$ for square lattice at different temperatures.

in both cases, with growth in the temperature, the coefficient $F_1(\varepsilon, T)$ becomes positive because the singular contributions to $F_1(\varepsilon, T)$, which are caused by Van Hove features, are smeared by the temperature.

When the position of ε is near the Van Hove singularity at low temperatures, $F_1(\varepsilon, T) < 0$, which leads to the inapplicability of the theory of second-order phase transitions. The temperature rise $T \gtrsim 0.1t$ results in the positive definiteness of $F_1(\varepsilon, T)$.

Thus, $F_1(\varepsilon, T)$ can change the sign depending on both the ratio t'/t and the temperature for the Bethe and square lattices. The role of Van Hove singularities manifests itself not only in the fact that the density of states $\rho(\varepsilon)$ is not bounded as a function of ε (this is rapidly destroyed by temperature fluctuations), but also in that the coefficient $F_1(\varepsilon, T)$ can change the sign. The behavior of the coefficient $F_1(\varepsilon, T)$ substantially distinguishes the Bethe infinity-dimensional lattice and square lattice.

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