Thermodynamics of a Narrow-Band Bose Gas on a Lattice

A. S. Alexandrov
Moscow Engineering Physics Institute, Moscow, Union of Soviet Socialist Republics

J. Ranninger
Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique, 38042 Grenoble Cédex, France

and

S. Robaszkiewicz[a]
Laboratoire d'Etude de Propriétés Electroniques des Solides, Centre National de la Recherche Scientifique, 38042 Grenoble Cédex, France

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In strong-coupling electron-lattice systems local pairs of electrons form—the so-called bipolarons. They behave like a Bose liquid on a lattice and have very small bandwidth t. We show that the specific heat for those bosons in the normal phase is extremely similar to that obtained for electrons in equivalently narrow bands: a behavior linear in T for low temperature ($T \ll t$) and a T^{-2} law for high temperature ($T \geq t$). In contrast, the magnetic susceptibility for triplet bosons differs qualitatively from that of electrons in the low-temperature regime. We discuss those results in view of a possible application to compounds exhibiting heavy-mass carriers.

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In 1975 Anderson[1] pointed out that in amorphous semiconductors, for sufficiently strong electron-lattice interaction, local on-site electron pairs can occur. Similarly, in crystal lattices, locally bound states of two small polarons (so-called bipolarons) occur in quite a natural way resulting in the covalent bonding of adjacent metal ions. Probably the first such systems ever reported in the literature[2] were Ti_4O_7 and β-$Na_xV_2O_5$. In the meantime numerous other compounds have joined their rank: WO_{3-x}, PbTe(Tl), $LiTi_2O_4$, polypyrrole, etc.

What type of bipolarons will form depends to a great extent on the detailed lattice structure. In general it can be expected to be rather difficult to form on-site bipolarons since the on-site Coulomb repulsion which has to be overcompensated by the effective lattice-induced attractive interaction is rather big. The formation of intersite bipolarons, in contrast, is much easier to achieve. This is because the lattice-induced attractive intrabipolaron interaction decreases only very weakly as the intrabipolaron distance increases. In contrast, the Coulomb repulsion for on-site bipolarons is considerably bigger than that for intersite bipolarons.

Whether bipolarons form singlet or triplet pairs will depend essentially on the orbital degeneracy of the atomic wave functions, where the Hund exchange interaction would favor triplet versus singlet bipolarons. This applies for intersite bipolarons and in particular for such systems which are composed out of electronically well-defined clusters, such as Chevrel phases. There a bipolaron spreads over six metal atoms and the likelihood of orbital degeneracy is big. As a consequence a system like $EuMo_6S_8$ could possibly exhibit triplet bipolarons. Other substances where triplet bipolarons might play a role are materials which show coexisting superconductivity and ferromagnetism.

The picture of mobile, spatially separated electron pairs on a lattice permitted us[3] to make the link with liquid ^{4}He. As it turns out, the bipolaronic system is an even better candidate than ^{4}He for a Bose liquid on a lattice.

As previously shown,[3] in narrow-band crystals the strong electron-phonon interaction leads to the well-defined narrow bipolaronic band. Its band half-width t is significantly reduced with respect to the initial electron bandwidth D by an exponential factor:

$$t \lesssim (D^2/z\Delta)\exp(-2g^2), \tag{1}$$

where Δ is the bipolaronic binding energy.

In the simplest case of on-site electron pairing Δ is given by the difference between twice the polaronic binding energy ϵ_b (or in other words the polaronic atomic level shift) and the on-site Coulomb repulsion. $g^2 = \epsilon_b/\omega$, where ω denotes the characteristic phonon frequency, and z is the number of nearest neighbors.

In such a way d- or f-band electrons in narrow-band crystals with strong electron-lattice interaction (such that $\lambda = 2zg^2\omega/D > 1$, where λ denotes the usual dimensionless coupling parameter in BCS theories) form small bipolarons which behave as hard-core bosons on effective sites (single atoms, dimers, clusters of metal atoms) on a lattice. They tunnel through the crystal, having a large but finite mass. Quite different from Cooper pairs, small bipolarons exist above the critical temperature T_c of their superfluid phase, and we shall show that they can be determinant in the thermodynamical properties in the normal state in a number of d- and f-band compounds.

In this Letter, we report on the unusual temperature dependence of the specific heat of such a Bose gas in a narrow band. It turns out that it is practically the same as in the case of electrons in equivalently narrow bands. This is true over the entire temperature regime. These results on the specific heat, together with the temperature dependence of the magnetic susceptibility of triplet bosons, some estimation of such parameters as the effective mass of the carriers (based on a microscopic theory[3]), and a power-law behavior for C_s—the specific heat in the superconducting phase—lead us to the speculation that some of the d- and f-band compounds with strong electron-lattice interaction may indeed represent a heavy Bose liquid of small bipolarons.

The specific heat of bosons in the normal phase as well as of electrons is given by the usual expression

$$C_{b,e} = -(2s+1)T\int_{-t-\mu}^{t-\mu} d\xi\, N(\xi)\frac{\partial f_{b,e}}{\partial \xi}\left[\left(\frac{\xi}{T}\right)^2+\left(\frac{\xi}{T}\right)\frac{\partial \mu}{\partial T}\right], \tag{2}$$

where s denotes the spin of the carriers ($s=0$ for singlet bosons, $s=1$ for triplet bosons, and $s=\frac{1}{2}$ for electrons). $N(\xi)$ denotes the density of states per atom and per spin; $f_{b,e}$ is the Bose (b) or Fermi (e) distribution function. The chemical potential μ is defined by the atomic concentration of the carriers n, which is supposed to be temperature independent:

$$n = (2s+1)\int_{-t-\mu}^{t-\mu} d\xi\, N(\xi) f(\xi). \tag{3}$$

We are interested in the temperature dependence of the thermodynamic quantities on a temperature scale which is of the order of the bandwidth (a few millielectronvolts in the systems of interest). Moreover, we restrict ourselves to a discussion of the normal-state properties, well above T_c—the transition temperature to the superfluid phase. Under these conditions the fine structure of the density of states of the low-energy states is of no importance. Hence we choose a square density of states,

$$N(\xi) = (2t)^{-1}, \tag{4}$$

for which $T_c = 0$ and which permits us to treat the normal phase in a consistent fashion. In such a way we can compare self-consistently the thermodynamical behavior of electrons and bosons in the normal phase down to zero temperature.

Introducing the dimensionless parameters $\beta = t/T$ and $\mu^* = \mu/T$, we obtain for bosons, using Eqs. (2)–(4),

$$C_b = \frac{2s+1}{8\beta}\int_{-\beta-\mu^*}^{\beta-\mu^*} dx\left[x^2+x\left(\mu^*-\beta\frac{\partial \mu^*}{\partial \beta}\right)\right]\sinh^{-2}\left(\frac{x}{2}\right), \tag{5}$$

$$\mu^* = \ln\left[\frac{1-\exp(-2n^*\beta)}{\exp\beta-\exp[(-2n^*+1)\beta]}\right], \quad n^* = \frac{n}{2s+1}. \tag{6}$$

In the high-temperature limit ($\beta \lesssim 1$), we find from Eq. (6) that

$$\mu^* \simeq \ln[n^*/(n^*+1)] - \beta^2 \times \tfrac{1}{6}(1+2n^*). \tag{7}$$

Substituting Eq. (7) into Eq. (5) we obtain

$$C_b \simeq n[1+n/(2s+1)]\beta^2/3, \quad \beta \lesssim 1. \tag{8}$$

The coefficient of the T^{-2} term in expression (8) is physically quite understandable. Specific heat is connected with the probability of the absorption of thermal energy, which is proportional to the number of occupied initial states, n^*, times n^*+1 coming from the final states, reflecting the two contributions characteristic for Bose systems, i.e., processes connected with spontaneous as well as induced emission.

Let us next consider the low-temperature behavior of the specific heat. In this temperature regime ($\beta n, \beta >> 1$) we obtain from Eq. (7)

$$\mu^* \simeq -\beta - \exp(-2n^*\beta), \tag{9}$$

which shows that the chemical potential at low temperature is locked near the bottom of the band ($\mu \simeq -t$) and is practically temperature independent. Substituting Eq. (9) into Eq. (5) we thus obtain

$$C_b = (2s+1)\pi^2/6\beta, \quad \beta, \beta n >> 1. \tag{10}$$

This result shows that bosons in narrow bands at low temperature have a temperature-independent specific-heat coefficient, $\gamma = C/T$, just as for electrons. The linear temperature dependence in fermion as well as in boson systems is linked to the existence of a quasi-locked chemical potential. For comparison we quote here the results for electrons in the two extreme temperature regimes. On the basis of the same square density of states as before [Eq. (4)], we obtain[4]

$$\begin{aligned} C_e &\simeq n(1-n/2)\beta^2/3, \quad \beta \lesssim 1, \\ C_e &\simeq \pi^2/3\beta, \quad \beta, \beta n > 1. \end{aligned} \tag{11}$$

If $n << 1$, an intermediate temperature region exists for $1/n >> \beta \gtrsim 1$ in which the boson and fermion

specific heats show logarithmic behavior:

$$C_{b,e} \simeq -2n \ln(n\beta). \tag{12}$$

In such a way bosons and electrons in narrow-band systems have extremely similar temperature dependences of their specific heats in the normal phase [see Figs. 1(a) and 1(b)] with the following ratio of γ's at low temperature: $\gamma_b/\gamma_e = s + \frac{1}{2}$. It is necessary to point out that the temperature region in which we expect the linear behavior of the specific heat can be very small if $n << 1$. In this case, we find for γ a fairly sharp rise as one approaches $T = 0$ which will abruptly turn over into a constant for extremely small temperature ($T \lesssim nt$). For real systems which show a transition to a superconducting phase, the region for the linear temperature behavior of C can practically disappear if the critical temperature is high enough. In particular, for ideal bosons we have[3] $T_c \sim n^{2/3}t$ with $n << 1$. In this case, the low-temperature behavior will be given by Eq. (12) down to T_c.

The T^{-2} law for the specific heat at high temperature, common to both fermions and bosons, originates from the finite value of the band for these particles, which is a direct consequence of the discreteness of the lattice. The classical value for the specific heat is only obtained for continuous media which have infinite bandwidth.

It might be of interest to compare the results for the specific heat for triplet bosons with the magnetic susceptibility χ_t for them (for singlet bosons the magnetic susceptibility is evidently zero). A simple calculation following the lines described above yields

$$\chi_t = \frac{4\mu_B^2}{t} \frac{(e^{2n\beta/3} - 1)(e^{2\beta} - e^{-2n\beta/3})}{e^{2\beta} - 1}, \tag{13}$$

where μ_B denotes the Bohr magneton.

At high temperatures ($n\beta, \beta \lesssim 1$) we obtain from Eq. (13) a Curie behavior (just as for narrow-band electrons[4] given below for comparison):

$$\chi_t \simeq (8\mu_B^2/3T)n(1 + n/3),$$
$$\chi_e \simeq (\mu_B^2/T)n(1 - n/2). \tag{14}$$

At low temperatures ($\beta n, \beta >> 1$) the behavior of the susceptibility of triplet bosons differs significantly from that of electrons (see Fig. 2):

$$\chi_t = (4\mu_B^2/t)\exp(\tfrac{2}{3}n\beta) \sim \exp(2nt/3T),$$
$$\chi_e = \mu_B^2/t \sim \text{const}. \tag{15}$$

In such a way we have shown that, while the specific heat for narrow-band systems is extremely similar for bosons and fermions, this is not true as far as the susceptibility is concerned. See for comparison Figs. 1(b) and 2.

In conclusion, we briefly discuss the possible application of the heavy-boson picture to a class of systems not mentioned above. The microscopic theory[3] which takes into account the main part of the strong electron-lattice and electron-electron correlations led Alexandrov and Elesin[4] to propose a small-polaron

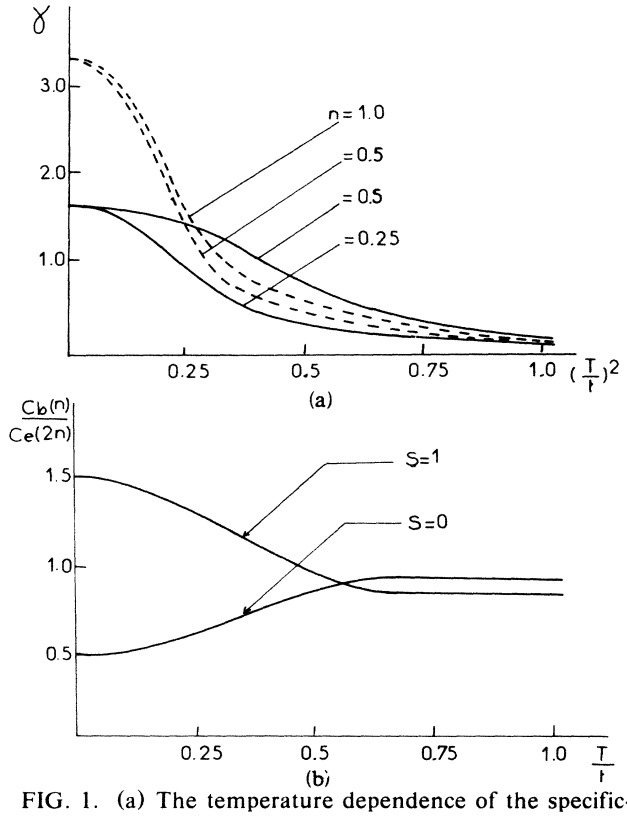

FIG. 1. (a) The temperature dependence of the specific-heat coefficient $\gamma = C\beta$ for electrons (dashed line) and for singlet bosons (solid line). (b): The ratios of the triplet ($s = 1$) and singlet ($s = 0$) boson specific heats to the electron one as functions of temperature ($n = 0.25$).

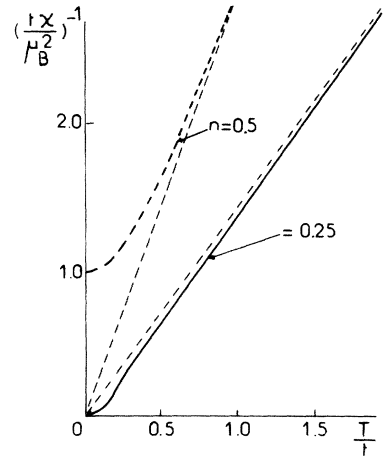

FIG. 2. The temperature dependence of the inverse magnetic susceptibility for electrons (dashed line) and for triplet bosons (solid line).

model for A-15 compounds which successfully explains their "anomalous" properties for a value of the electron-phonon coupling constant $g^2 \sim 2$. Some of these compounds as well as the Chevrel phases and other high-temperature narrow-band superconductors show normal-state γ and χ which are very similar to the ones presented in the present work.

Moreover, there remains a controversial issue of how the Fermi-liquid nature arises from original f electrons in the so-called "heavy fermion" systems such as $CeAl_3$, $CeCu_6$, $CeCu_2Si_2$, UBe_{13}, and others.[5] The main unresolved problem is the origin of a very narrow band ($t \sim 0.001$ eV) and the role of electron-phonon correlations. Possibly the answer can be obtained within the theory of bipolarons[3]: The strong electron-phonon interaction leads to the formation of the heavy Bose-type bipolarons which tunnel in a very narrow band. If we estimate the initial bandwidth of f states in a rigid lattice as $D \lesssim 0.1$ eV, and Δ is of the same order of magnitude,[2] we obtain the required value of $t \lesssim 0.001$ eV for a reasonable value of $g^2 \simeq 2$ [see Eq. (1)]. In this picture of heavy-boson liquid, we obtain quite naturally the main singularities of normal C and χ as well as the power-law behavior of C_s in the heavy-"fermion" superconductors.[5] It is well known that the specific heat of Bose gas in the superfluid region ($T < T_c$) has a power-law behavior $C_s \sim T^n$, where $n = \frac{3}{2}$ for the ideal gas, and $n = 3$ for the interacting one as well as the hard-core Bose gas on a lattice, provided that the interbipolaron Coulomb potential is screened. Most real materials for which we expect such a bipolaronic picture to hold are made up of generally two types of electrons: a very large band (10 eV) of itinerant electrons and a very narrow band (1 eV) of fairly localized electrons ($3d, 4f, 5f$). Only the latter electrons couple strongly to the lattice and give rise to bipolaron formation. In such a situation the highly itinerant electrons of the large band will screen the long-range Coulomb interaction between the bipolarons.

Suppose, however, that the number of itinerant electrons is too small to provide an effective screening mechanism on the bipolaron-bipolaron Coulomb interaction. In that case the low-lying excitation spectrum of the phase fluctuations of the order parameter will be determined by the plasmonlike density fluctuations of the bipolarons. This introduces a gap in the elementary excitation spectrum in the long-wavelength regime. At zero temperature this gap is given by the bipolaronic plasma frequency $\omega_p = [32\pi^2 e^2 n(n-1)/m^{**}]^{1/2}$, where m^{**} denotes the mass of a bipolaron which is typically 2 or 3 orders of magnitude bigger than the free-electron mass of the narrow-band electrons (without any coupling to the lattice). As the temperature approaches T_c, the gap in the elementary excitation spectrum tends to zero. As a consequence, for unscreened Coulomb interaction between bipolarons we might expect some sort of exponential behavior for the specific heat, $C \sim \exp(-\omega_p/T)$, for T well below T_c.

The applicability of the proposed model to concrete compounds evidently needs more detailed quantitative comparison with the experimental results as well as more refined calculations taking into account correlation effects between the bosons. We believe nevertheless that the simple picture presented here could have some intrinsic value in the understanding of the qualitative features of systems with heavy carriers.

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[a]Permanent address: Institute of Physics, A. Mickiewicz University, Poznan, Poland.

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