Lattice specific heat of $YBa_2Cu_3O_7$

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We present a calculation of the lattice specific heat of the high-temperature superconductor $YBa_2Cu_3O_7$, based on a full lattice-dynamical description. The availability of a realistic lattice specific-heat function is of importance for separating the nonlattice (and possibly anomalous) contributions from the measured total specific heat. It provides a test for the appropriateness of the fitting functions and fitting ranges used in the literature, to separate the lattice contribution from the total. It is found that the Debye region [$\Theta(0)=465.5$ K] extends only up to 3 K [$\approx 0.006\Theta(0)$]. Strong deviations from Debye behavior in the range 3 to 20 K lead to a 30% drop in $\Theta(T)$; this roughly covers the range of Debye temperatures obtained from the experiments by various fitting procedures. One of the reasons for this spread in experimental Debye temperatures is that, if the lattice specific heat is assumed to be of the form βT^3 outside the Debye region, an improper fitting of the measured data can lead to the wrong Debye temperature and also to the appearance of spurious nonlattice contributions to c_v. Sound velocities are a natural by-product of this calculation; direct comparison with experimental values for ceramic samples is not possible.

Traditionally, specific-heat measurements have been an important tool in the study of superconductors since they reveal the value of the transition temperature T_c, and in general allow the investigation of the electronic, vibrational, and magnetic excitation spectra. Experimentally, the high-T_c superconductors (HTSC) pose special problems because of the unusually large lattice specific heat, and the occurrence of a variety of extrinsic effects, such as disorder, defects, structural instabilities, etc., all of which contribute to the measured specific heat. Many of the intrinsic and extrinsic effects are superimposed and the most interesting contributions are not necessarily the dominant ones. It is commonly accepted that the best manifestations of intrinsic properties are to be found for samples which have the smallest specific heats at low temperatures, and that the behavior of the specific heat at T_c provides one of the most stringent tests for the homogeneity of a superconducting sample. (For reviews of the specific-heat properties of HTSC we refer to Refs. 1–3.)

Of the various HTSC, the specific heat of $YBa_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O) has been the most extensively studied experimentally. Of particular interest is the presence, in the measurements, of a low-temperature contribution with an apparent linear temperature dependence, the origin and magnitude of which are still under active study.[4] In order to extract from the measured specific heat the various contributions (such as this linear contribution) and to identify and reliably establish their temperature dependence, it would be of great importance to have an accurate determination of the lattice specific heat, particularly because of its tendency to overwhelm the other specific-heat contributions.

In this paper we present a calculation of the lattice specific heat of Y-Ba-Cu-O based on a full lattice-dynamical treatment of the crystal. Of particular interest is the extent to which the results of our calculations can be used to analyze the experimental data. We find that qualitatively and quantitatively, the behavior of the lattice specific heat gives important clues for reduction of the measured specific-heat data. However, the numerical uncertainties in both the experimental and the calculated data are such that they preclude a detailed numerical comparison of the two sets of data at low temperatures. Thus, it is not possible to simply subtract the calculated specific heat from the measured data at low temperatures, and obtain the experimental nonlattice specific heat with sufficient accuracy to be amenable to a detailed and meaningful analysis.

Our calculations of the lattice dynamics of the HTSC are carried out in the framework of shell models which take into account short-range overlap and long-range Coulomb interactions, as well as ionic polarizabilities. The short-range interactions of the various ion pairs are represented by Born-Mayer potentials. Owing to the closed-shell-like electronic configurations of the ions, these potentials are to a large degree independent of the spatial arrangement and the crystal surrounding of the interacting ion pair. This has the advantage that the short-range potential parameters can be taken from shell models which have been developed for perovskites and metal oxides for which neutron measurements of phonon dispersion curves are available. Moreover, interaction potentials of ion pairs (such as Cu-O, Ba-O, etc.) common to the different HTSC can be transferred from one compound to another, which results in an internally consistent approach to the lattice dynamics of a broad class

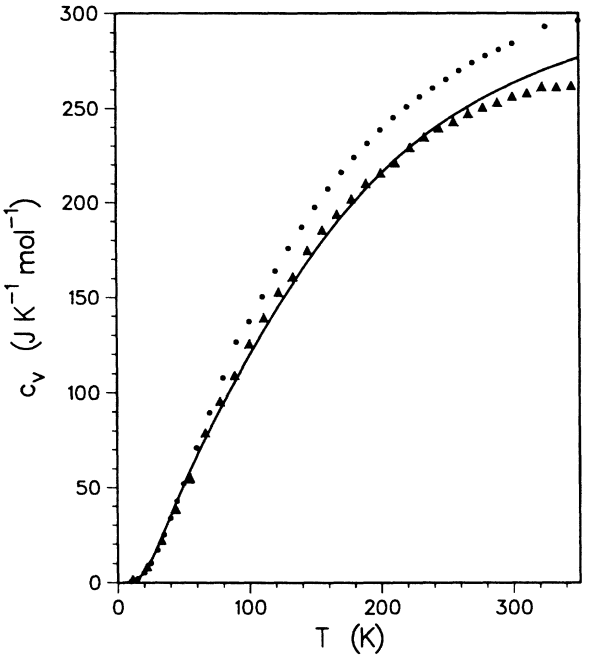

FIG. 1. Calculated lattice specific heat $c_v(T)$ vs T (solid line). Measurements of Lang *et al.* (Ref. 12) (▲) and of Shaviv *et al.* (Ref. 13, Table II) (●).

of HTSC.[5–10]

Solving the dynamical equations for a suitably chosen set of wave vectors in the Brillouin zone allows one to construct the (normalized) phonon density of states function $F(\omega)$. Using $F(\omega)$ one evaluates the lattice specific heat $c_v(T)$ using the customary expression

$$c_v(T)=\frac{k_B^2 T}{\hbar}\int_0^\infty \frac{x^2 e^x}{(e^x-1)^2}F\left[x\frac{k_B T}{\hbar}\right]dx\ , \tag{1}$$

where $x=\hbar\omega/k_B T$. Unfortunately, for very low temperatures the practical use of Eq. (1) can lead to inaccurate results, because of inaccuracies in the calculated $F(\omega)$ for very small ω. This has to do with the fact that in a root sampling method there inevitably occurs a smallest acoustical frequency $\omega_{\min}$; for temperatures below $\hbar\omega_{\min}/k_B$, c_v will become anomalously small. However, one can always choose sampling meshes in the Brillouin zone so that these difficulties appear in the linear dispersion region of the acoustic modes, where the Debye approximation is strictly valid. Under these conditions, the method of de Wette *et al.*[11] will give results for c_v to any desired degree of accuracy.

In Fig. 1 we display the calculated $c_v(T)$ in the range 0 to 350 K together with the measurements of Lang *et al.*[12] and Shaviv *et al.*[13] To the eye the calculated $c_v(T)$ agrees quite well with both sets of measurements at least up to 50 K. This makes it clear that the specific heat itself is not a very sensitive tool to judge the subtle differences which may be important at low temperatures, nor does it allow us to determine the extent of the Debye region where $c_v=\beta T^3$. For this purpose, c_v/T^3 or the Debye temperature $\Theta(T)$ provide much more sensitive measures. In Fig. 2 we have plotted $c_v(T)/T^3$ in the temperature ranges 0 to 100 K and 0 to 10 K, respectively. From Fig. 2(b) it is evident that the Debye region [$\Theta(T)\approx\Theta(0)$, the "initial" Debye temperature] does not extend beyond 3 K. Furthermore, it is interesting to note that in the range 5 to 12 K, c_v/T^3 is linear in T, i.e., $c_v(T)\approx\beta' T^3+\delta T^4$. Finally, for $T>12$ K, where c_v/T^3 is no longer linear in T, the power expansion of $c_v(T)$ becomes more complicated, with the highest power of T less than four. These facts provide clues for the fitting of the experimental low-temperature specific heat; in particular they call into question the appropriateness of the fitting functions as well as fitting ranges used in the literature (cf. Refs. 1–4).

Debye temperature $\Theta(T)$. The "initial" Debye temperature $\Theta(0)$ is usually obtained from the coefficient of the Debye term βT^3 of the fitting function, namely,

$$\Theta(0)=(1.943\,73\times 10^3 N/\beta)^{1/3}\ , \tag{2}$$

where N is the number of particles in the unit cell. At finite temperatures $\Theta(T)$ is obtained by equating, at each

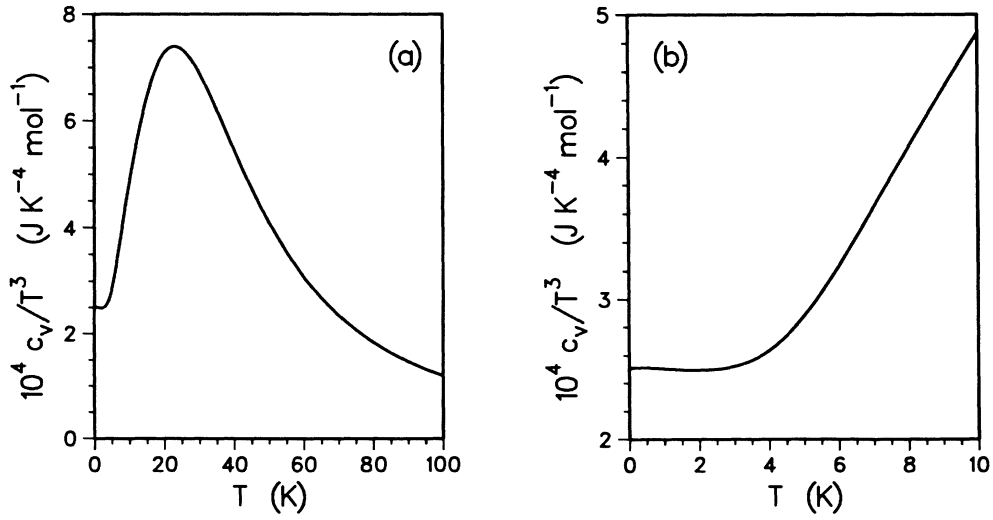

FIG. 2. Plot of calculated $c_v(T)/T^3$ vs T.

temperature, the Debye specific-heat expression

$$c_v^D(T)=9k_B\frac{N}{V}\left[\frac{T}{\Theta}\right]^3\int_0^{\Theta/T}\frac{x^4e^x}{(e^x-1)^2}dx \tag{3}$$

to the calculated value of $c_v(T)$, and inverting Eq. (3) to obtain $\Theta(T)$. (Here V is the volume of the unit cell.) In Fig. 3(a) we show $\Theta(T)$ in the range 0 to 350 K and in Fig. 3(b) the low-temperature region (0 to 40 K) is enlarged (solid lines). As we have already seen from c_v/T^3, the true Debye region where $\Theta(T)\approx\Theta(0)=465$ K exists only for $T\leq 3$ K, i.e., for $T\leq 0.006\Theta(0)$. In the range 3 to 20 K $\Theta(T)$ drops from 465 K down to 325 K, i.e., spanning the entire range of experimental $\Theta(0)$ values quoted for Y-Ba-Cu-O in the literature (cf. Ref. 3). This is a direct result of the fact that these experimental $\Theta(0)$ determinations are based on βT^3 terms of fitting functions, which either do not contain the appropriate powers of T or have been fitted over a temperature range where c_v is no longer Debye-like.

Having established the general low-temperature behavior of $\Theta(T)$ [Fig. 3(b)], one can obtain a quick indication of the presence of nonlattice contributions in the measured specific heat, by expressing the experimental data directly in a $\Theta(T)$ plot. As an example we have used the data of Shaviv *et al.*,[13] which were available to us in numerical form. The "experimental" function $\Theta_{\text{expt}}(T)$ so obtained is also plotted in Fig. 3 as dots. It is seen that $\Theta_{\text{expt}}(T)$ drops precipitously for decreasing T below 15 K. Since decreasing Θ means increasing c_v, this drop in Θ_{expt} indicates the presence of a significant nonlattice contribution to the measured specific heat at these temperatures.

Fitting of $c_v(T)$: In an attempt to extract anomalous contributions to the low-temperature specific heat of Y-Ba-Cu-O, many investigators have fitted the measured data with polynomial expressions, containing some or all of the following powers of T: T^{-2}, T, T^3, T^5 (cf. Refs. 3 and 4). We caution against attaching too much significance to the physical meaning of the various terms in such an expansion. To get a feeling for how successful such fit can separate specific-heat contributions of different origin, we have carried out fits of our *calculated* lattice specific heat, which obviously does not contain any other contributions. This exercise showed that the relative importance of the various fitting terms depends on which terms are included in the fitting functions, and over which temperature range the fitting is carried out. In particular, if different fits (to the same data) lead to different values for the coefficient β of the cubic term, these fits will predict different values for $\Theta(0)$, according to Eq. (2). [This may be a partial explanation for the large range of $\Theta(0)$'s found for Y-Ba-Cu-O (cf. Ref. 3)]. Another source of error may be the absence in the fitting function of the leading power of T, for a certain temperature range. For instance, from Fig. 2(b) one sees that in the range 5 to 10 K, c_v/T^3 should be well approximated by $\beta'+\delta T$, so that for those temperatures the optimum fitting function for c_v would be $\beta' T^3+\delta T^4$ (β' is different from β in βT^3, which gives the best fit for 0 to 3 K). But of course, if a T^4 term is not included in the fitting function (as it has not been in any of the fits in the literature) then terms of different powers of T have to take up the slack, and one may be led to suspect the presence of anomalous (nonlattice) contribution in the specific heat.

The most desirable procedure to isolate the nonlattice contributions and establish their temperature dependence would be to subtract an accurate (calculated) lattice specific heat from the measured data and perform an appropriate fit to the remainder. Unfortunately, such a procedure is not a viable option at this time, for a variety of reasons: (1) The lattice dynamical calculations were performed with structural parameters determined at room temperature.[14] Correction for thermal expansion requires knowledge of the linear thermal expansion coefficient and the bulk modulus of the ideal crystal, but these are experimentally not accurately known. (2) Because of the uncertainties in the model parameters, errors of up to 10% can exist in the calculated frequencies, and therefore up to 30% in the calculated lattice specific heat. (3) Finally, the measured data reflect variability in the

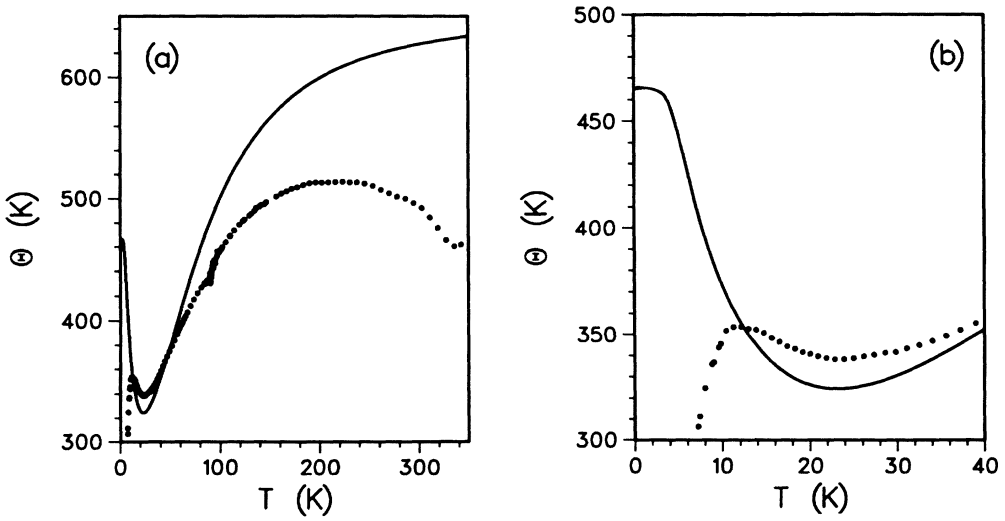

FIG. 3. Plot of temperature-dependent Debye temperature $\Theta(T)$. Solid line is from calculated lattice specific heat; dots (●) are from specific-heat measurements of Shaviv *et al.* (Ref. 13, Table I).

TABLE I. Calculated sound velocities of $YBa_2Cu_3O_7$ in 10^3 m/s. The propagation directions [q00], [0q0], and [00q] are along the a, b, and c axes, respectively. The polarization directions are given in parentheses. The averages are taken over *all* directions in the Brillouin zone.

Propagation direction	v_L	v_T^{high}	v_T^{low}
[q00]	8.14(a)	5.03(b)	1.81(c)
[0q0]	8.51(b)	4.96(a)	3.82(c)
[00q]	7.59(c)	4.09(b)	2.76(a)
Average	8.35	4.00	3.04

quality and preparation of the experimental samples (cf. Fig. 1).

Sound velocities. For comparison with measurements we give in Table I the longitudinal and transverse sound velocities averaged over directions, as well as for propagation in the *ab* plane and in the *c* direction. These values are substantially larger than the measured ones for ceramic samples,[2,15,16] which contain effects of porosity, microstructure, and grain size.

We have presented a calculation of the lattice specific heat and the Debye temperature of $YBa_2Cu_3O_7$ based on full-scale lattice dynamical treatment. Although for a number of reasons our results cannot be used for a direct numerical reduction of the measurements, the low-temperature behavior of the calculated lattice specific heat provides important clues for the separation of the lattice contributions from the measurements, thus allowing for a better determination of the other (partly anomalous) contributions and their temperature dependence.

Both $c_v(T)/T^3$ (Fig. 2) and the Debye temperature $\Theta(T)$ (Fig. 3) give a direct measure of the extent of the Debye region [i.e., $\Theta(T)\approx\Theta(0)$]. The cause for the onset of non-Debye behavior above 3 K is a noticeable curvature of the transverse acoustic dispersion curves already below 0.4 THz. This results from the repelling effect of the hybridization of the transverse acoustic and optical branches close to Γ. The full 30% drop in $\Theta(T)$ in the range 3–25 K arises from c_v contributions due to optical frequencies below 2 THz in the outer parts of the Brillouin zone.

The small extent (0 to 3 K) of the Debye region calls into question the low-temperature polynomial fitting procedures carried out in a number of experimental studies, which in some cases may lead to spurious nonlattice contributions. Aside from polynomial fits to the measured specific heat, it seems to be a useful procedure to display measured data directly in terms of the $\Theta_{expt}(T)$ function (dots in Fig. 3), because deviations of such a function from the general shape of $\Theta_{lattice}(T)$ (solid lines in Fig. 3) is a very graphical indication of the presence of nonlattice contributions in the measured specific heat.

In conclusion, we point out that our lattice-dynamical model was developed to give an overall coherent dynamical description for an entire series of high-temperature superconductors, and to obtain reasonable agreement with the measured optical phonons of these compounds. It is therefore not surprising that the model does not lead to optimum agreement with the measured acoustical dispersion curves[17] and the sound velocities of a single crystal of $YBa_2Cu_3O_7$. If one would be only interested in the sound velocities and the specific heat of this particular compound, one could modify the lattice-dynamical model to minimize the deviations between measured and calculated acoustical dispersion curves, and probably obtain results which could be used for the *numerical* separation of the lattice contribution from the measured total specific heat. However, the primary aim of this work was to explore the consequences of our *general* lattice-dynamical model for the specific heat of $YBa_2Cu_3O_7$.

Note added in proof. We thank Dr. J. C. van Miltenburg (University of Utrecht, the Netherlands) for making available to us unpublished heat capacity data for $YBa_2Cu_3O_{7-\delta}$ in the range 9.4–340 K. The c_v and $\Theta(T)$ plots of these data are essentially identical to those of Shaviv *et al.*[13] obtained by similar techniques.

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