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2005 J. Phys.: Condens. Matter 17 2397

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Determining the phonon density of states from specific heat measurements via maximum entropy methods

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Received 22 November 2004, in final form 19 January 2005

Published 1 April 2005

Online at stacks.iop.org/JPhysCM/17/2397

Abstract

The maximum entropy and reverse Monte Carlo methods are applied to the computation of the phonon density of states (DOS) from heat capacity data. The approach is introduced and the formalism is described. Simulated data are used to test the method, and its sensitivity to noise. Heat capacity measurements from diamond are used to demonstrate the use of the method with experimental data. Comparison between maximum entropy and reverse Monte Carlo results shows that the form of the entropy used here is correct, and that results are stable and reliable. Major features of the DOS are picked out, and acoustic and optical phonons can be treated with the same approach. The treatment set out in this paper provides a cost-effective and reliable method for studies of the phonon properties of materials.

1. Introduction

It is nearly a century since Einstein's paper 'The Planck theory of radiation and the theory of specific heat' was published [1]. This well cited paper detailed a simple approximation for the phonon contribution to the specific heat of solids. Along with Debye's theory of the specific heat due to acoustic phonons [2] it has become the stuff of textbook legends. Both methods are still used regularly (e.g. to separate the magnetic and phonon contributions to the specific heat [3]).

Interest in lattice vibrations is timely because of the discovery that phonons play a significant role in the physics of cuprates [4]. In this regard, it would be useful to have greater experimental access to information about phonons. Currently there are two major methods used to probe lattice excitations; Raman (and Raleigh) scattering, where only the zone-centre phonons are measured [2] and neutron scattering, which requires large scale facilities. Even with recent neutron scattering developments such as MAPS at ISIS, the observation of phonon modes across the entire Brillouin zone is extremely difficult, and an array of large single crystals is required. In a typical triple-axis instrument, only a few points along high symmetry directions are determined, with the phonon DOS inferred from a model of internuclear forces using the dynamical matrix formalism [2]. There have been some recent attempts to classify

the phonon DOS from specific heat measurements [5, 6]. The approach in [5] was relatively effective and could be applied to experimental data, but suffered from unphysical negative densities of states. Also, the basis set decomposition that was described is expected to be significantly less effective when applied to systems with both acoustic and optical phonons.

The method described in this paper may be used to classify the phonons in many different kinds of material, and has the advantage that the only equipment requirement is a heat-capacity rig and a modern personal computer. Both these pieces of equipment are very common in solid state laboratories and therefore I expect this method to be of great use to the condensed matter community. The paper is organized as follows. The formalism of the maximum entropy and reverse Monte Carlo methods is introduced in section 2. In section 3, I test the method using simulated heat capacity data. I also determine the phonon DOS of diamond. Finally, conclusions and recommendations are given in section 4.

2. Methodology and formalism

The maximum entropy method (MAXENT) is based on the principles of Bayesian inference and can be used to provide a general framework for the solution of inverse problems in physics. In this section, I describe how maximum entropy methods can be used to extract the density of phonon states from heat-capacity data.

The specific heat due to phonons is related to the phonon density of states according to the integral transform

$$c_v(T) = 3R \int_0^\infty d\omega D(\omega) \frac{\hbar^2 \omega^2 e^{\hbar\omega/kT}}{(kT)^2 (1 - e^{\hbar\omega/kT})^2} \quad (1)$$

where $D(\omega)$ is the phonon DOS and R is the gas constant. For non-magnetic insulators, this is the major form of the specific heat. The DOS may be discretized by writing $D(n\Delta\omega) \equiv s_n \Delta\omega$, so that the problem is reformulated as a matrix equation, $c_v(T_i) = \sum_j K_{ij} s_j$. The kernel matrix is written as $K_{ij} = 3Ry^2 e^y / (1 - e^y)^2$ and $y = \hbar\omega/kT$. The matrix may not simply be inverted, since there are typically more unknowns than data points, leading to a serious over-fitting of the data, while the integral transform can be inverted, but the problem is ill conditioned; it is very sensitive to errors in the data. In particular, experimental noise and discrete (incomplete) data will negate the results [7–9]. Some attempts have been made to ease the problems of ill conditioning by using alternative basis sets [5, 6]. However, these lead to negative densities of states, and in particular the results of [6] have a clearly unphysical form for low frequency phonons, which, being acoustic in nature, should tend to zero according to an ω^2 form rather than diverging. Similarly, one may not simply apply least squares fitting, since for useful results there are significantly more fitting parameters than data points. A common approach to avoiding over-fitting involves introducing a regularization process. Two schemes will be discussed in this paper: the maximum entropy scheme and the reverse (or Markov chain) Monte Carlo method.

The essence of the MAXENT approach is that the most probable fit to an inverse problem in the absence of data is located where a large number of similar data configurations are present. A large number of similar configurations corresponds to a minimally contorted spectrum (or DOS in this case). Small changes in the DOS then lead to small changes in the value of χ^2 . In the current problem, over-fitting would lead to a $D(\epsilon)$ that rapidly oscillates from negative to positive values, which is clearly unphysical since the DOS must be positive. Formally, the regularization is introduced via a ‘free energy’, which is a sum of the familiar χ^2 goodness of fit parameter and an entropy term, S ,

$$\mathcal{F} = \chi^2\{s_i\} + \alpha S\{s_i\} \quad (2)$$

where

$$\chi^2 = \sum_{i=1}^{N_d} \frac{c_{\text{obs}}(T_i) - c_{\text{calc}}(T_i)}{\sigma_i^2} \quad (3)$$

$$S = \sum_{i=1}^{N_s} \left[m_i - s_i + s_i \ln \left(\frac{s_i}{m_i} \right) \right] \quad (4)$$

σ^2 is the standard deviation, N_d is the number of data, and N_s is the number of discrete points in the DOS.

The entropy is multiplied by a hyper-parameter (nuisance parameter), α , which has a similar role to temperature in the analogous statistical system. An additional spectrum, m_i , is introduced, which is known as the default model. The default model contains information that is already known about the system, and is the default result of minimizing the free energy (equation (2)) in the absence of data, i.e. without the χ^2 term. Since in this problem I examine the density of states, it is known that the spectrum, s_i , may only contain positive values. It is also known that the normalization of the spectrum is the number of atoms in the unit cell. Therefore, the default model chosen throughout this work is a flat positive distribution normalized to the number of modes. Nothing else is assumed.

The maximum entropy method comes in several different flavours. In this paper, I use Bryan's algorithm [10]. Bryan's algorithm differs somewhat from the historic approach since the hyper-parameter α is chosen from a continuous probability distribution. In historic MAXENT, α is typically chosen so that $\chi^2 = N_d$. This is intuitive, but will normally lead to under-fitting of the data, since neighbouring data points can have closely related values. Closely related data points result in an effective error of the combined points which is lower than that of individual points considered separately.

When implementing Bryan's algorithm, the spectrum is calculated from the weighted average of spectra calculated for all α values,

$$s_i = \int_0^\infty P[\alpha|s_\alpha] s_{i\alpha} d\alpha. \quad (5)$$

The probability distribution $P[\alpha|s]$ is calculated as in [10]. A singular value decomposition is also introduced to reduce the total number of search directions. The resulting algorithm is fast and with the integration over the nuisance parameter is fully consistent with Bayesian analysis. Furthermore, a positive density of states is guaranteed.

The reverse Monte Carlo (RMC) method is used to validate the MAXENT results and to demonstrate an alternative scheme. The RMC method treats all possible data configurations as an ensemble, and averages over all possible data sets, weighted by the likelihood function $e^{-\chi^2/2T}$. A new parameter, T , is introduced, which is a nuisance parameter similar to α .¹ In the spirit of statistical mechanics, the Metropolis algorithm with $E \equiv \chi^2$ is used here as an efficient approach to the averaging of the spectrum over the ensemble defined by the likelihood.

The algorithm proceeds as follows. A change to a variable is suggested. If the change leads to a reduction in χ^2 , then it is accepted. Otherwise, it may still be accepted according to the probability $P = \exp(-\Delta E/kT)$ (ΔE is the difference between χ^2 values before and after the change). Such a scheme is one of the simplest which is consistent with the principle of detailed balance. It is instructive to note the close relationship between reverse Monte Carlo and MAXENT algorithms. In the event of uncontorted data, there will be many available states for the RMC algorithm, and the overall sampling rate is greatly increased. Put another way, the local entropy of the configuration space is higher. In this way, states with higher entropy

¹ Note that T acts as a temperature, but is not the same as the temperature argument of the specific heat.

are favoured, and the conceptual similarity between the methods can be seen². The advantage of the RMC algorithm is that no form for the entropy is assumed, and it is conceptually very simple. However, it is computationally intensive, and as I demonstrate the spectra resulting from MAXENT and RMC are essentially identical.

A few modifications to the algorithm are made for the current application. To reduce the parameter space, the spectrum is constrained to be normalized to N_{ph} . In practical terms, this means that for every change $s_i \rightarrow s_i + r_i$ there is an equivalent $s_j \rightarrow s_j - r_j$ with $i \neq j$. I will term this spectral RMC. The spectrum is also constrained to positivity, so any updates that violate that condition for either of s_i or s_j are discarded. The calculation of the difference in χ^2 which scales as $\mathcal{O}(N_d N_s)$ can be rewritten as an $\mathcal{O}(N_d)$ process when only one variable in the spectrum is changed, leading to a massive increase in speed. The energy landscape of χ^2 is complicated and has many troughs, some of which may be deep. To ensure that all troughs are sampled, r_i is chosen from a random variate obeying the Cauchy distribution,

$$P(r_i) = \frac{\sigma_i}{\sigma_i^2 + r_i^2}. \quad (6)$$

The Cauchy distribution has been widely applied to fast simulated annealing, and is designed to cover the parameter space quickly. It is also ideal for Monte Carlo simulations with continuous variables where the temperature is held fixed while expectation values of variables are taken. The width of the distribution, σ_i , is changed every few iterations to keep the acceptance rate close to 70%. This is essential for a fast computation (otherwise spectral points with a larger magnitude are favoured in the update).

To initialize the algorithm, the update scheme is run for a few hundred thousand iterations until thermal equilibrium is reached. Data are measured using a blocking scheme, where the blocking size is much greater than the correlation time. In this way a reliable estimate of the error on each point can be obtained. Finally, the algorithm is stopped when the data error is approximately 1%. Since the data error scales as $1/\sqrt{N}$, this is the best accuracy achievable on a modern workstation in a few hours of calculation.

3. Results

In this section, I present results showing the determination of the phonon DOS from a simulated specific heat measurement. The densities of states that are used here are simpler in form than those expected in a real solid. However, they contain the sort of features that might be expected in real systems, such as narrow high-energy optical phonon modes, discontinuities associated with Brillouin-zone boundaries and the typical low-energy ω^2 behaviour associated with acoustic phonons, and therefore constitute a fair test of the method.

An example of simulated data for a Debye spectrum with $\omega_D = 50$ meV is shown in figure 1. Also shown is the fit to the data from the MAXENT method. Gaussian noise is added to the data, and several ‘data sets’ are calculated. The average and RMS values are then computed to determine the mean and variance, from which the error can be calculated. A similar approach to calculating the error should be used when carrying out an experiment. For a better estimate of the χ^2 value, the covariance matrix may be determined, and will lead to improvements in the results. This is unnecessary for simulated data where the noise added to neighbouring data points is statistically independent, and off-diagonal terms in the covariance vanish. Simulated data points were calculated to cover the full temperature range from low temperatures ($T \ll 50$ meV) to high temperatures approaching the saturation associated

² If the local entropy could be measured in the RMC method, then it would be possible to show that RMC and MAXENT are fundamentally equivalent.

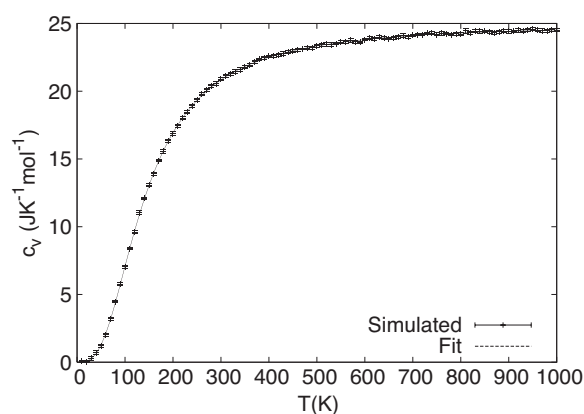


Figure 1. Simulated data corresponding to a Debye spectrum with $\omega_D = 50$ meV. An error of 0.3% has been added. Also shown is the fit to the data using Bryan's algorithm. The Debye spectrum has the correct low frequency behaviour and also has a sharp cut-off typical of the phonon DOS at the Brillouin zone boundary.

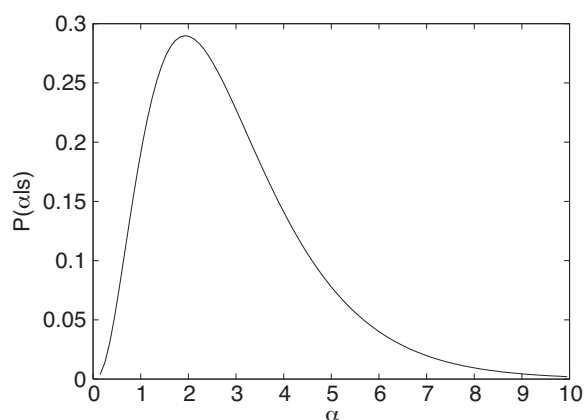


Figure 2. Alpha probability for Bryan's algorithm (left axis). Note that the distribution is not sharp as is assumed in the case of classic and historic MAXENT. Calculations are carried out for a series of α values, and then a weighted sum of resulting spectra is computed to arrive at the most probable DOS. The input data was a Debye specific heat with 0.3% data error as shown in 1.

with the Dulong–Petit law. The data error in this case is 0.3% of the saturation value, or $\sim 0.075 \text{ J K}^{-1} \text{ mol}^{-1}$. Such an error is easily achievable with standard laboratory equipment.

It is instructive to note that the integration over the nuisance parameter inherent in Bryan's algorithm is important. The distribution of $P[\alpha|s]$ is shown in figure 2. Note that the distribution is not a sharply peaked δ -function as is assumed in the case of classic and historic MAXENT. Clearly, the distribution is significant for $0 < \alpha < 12.5$. A weighted sum of the resulting spectra is therefore needed to arrive at the most probable DOS, and historic and classic methods which treat only one α value should be approached with care.

A very simple model is shown in figure 3. As before, the simulated spectrum was forward transformed to determine $c_v(T)$, and then Gaussian noise was applied before inverting the transform. The simulation technique ensures that there is an exact answer to compare with. The underlying DOS is a broadened 'optical' phonon represented as a Gaussian, and spectra

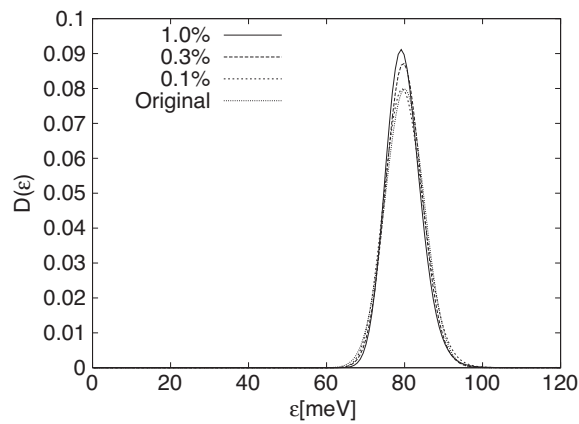


Figure 3. Simulated phonon DOS representing a broadened ‘optical’ phonon, and the spectra extracted using Bryan’s algorithm. The simulated density of states is a Gaussian centred about 80 meV with a full width at half maximum (FWHM) of 5 meV normalized to unity. The method performs well, and is accurate for an achievable data error. 100 simulated data points cover a complete temperature range from low temperatures ($T \ll 80$ meV) to high temperatures approaching the Dulong–Petit law. The simulated spectrum was forward transformed, and then Gaussian noise was applied before inverting the transform.

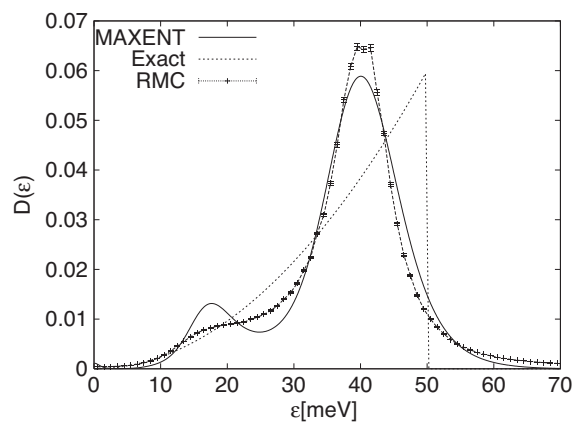


Figure 4. Simulated phonon DOS representing an acoustic phonon. The same approach as in figure 3 was used to simulate the data. Bryan’s algorithm was less successful in this case because the discontinuity in the phonon DOS leads to ringing. This suggests that decomposition into a non-Gaussian basis might be more appropriate. Also shown is the result from a reverse Monte Carlo calculation. RMC is quite general; however, calculations take a few hours, in contrast to a few seconds for the MAXENT algorithm. The RMC algorithm suffered from less ringing; however, anomalous high-frequency states were present. In both cases, the general features of the spectrum are recovered. It can be seen that as few as 100 data points are necessary to determine the spectrum. The accuracy used here was 0.3%.

computed using Bryan’s algorithm are shown for various data errors. The data error is a percentage of the Dulong–Petit saturation value. The method performs well with all spectra having a reasonable agreement. As expected, the method performs better for more accurate data. The simulated data error shown here is achievable using standard laboratory equipment.

In order to simulate data consistent with acoustic phonons, the simple Debye model was used ($D(\epsilon) = 3\omega^2/\omega_D^3$). Although this is a crude DOS, it has many of the features of the

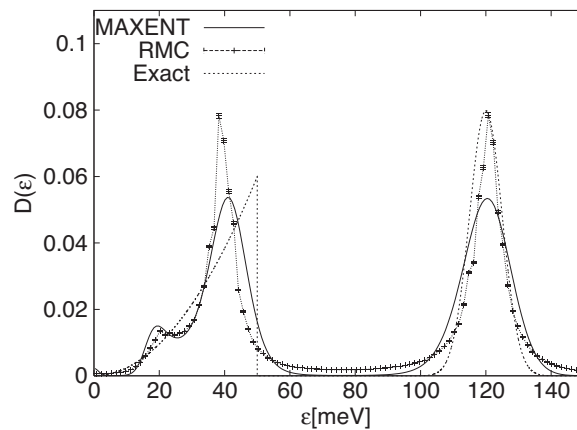


Figure 5. A more realistic simulated phonon DOS with one optical mode (represented as a Gaussian centred about 120 meV with a half-width of 5 meV) and one acoustic mode (represented by a Debye model with $\omega_D = 50$ meV). Data error is set to 0.1%. Both Bryan's algorithm and RMC were used. The method is able to distinguish between optical and acoustic modes which are on different energy scales without recourse to alternative models. The current method therefore represents a major improvement on existing techniques.

acoustic phonons, including the ω^2 behaviour at low frequencies, and a sharp cut-off consistent with the effects of the zone boundary, i.e. the cut-off can be thought of as representing a van Hove singularity. Results for the analysis are shown in figure 4. The low frequency behaviour is recovered; however, Bryan's algorithm was less successful for the high frequency behaviour because the discontinuity in the phonon DOS leads to ringing. This suggests that decomposition into a non-Gaussian basis might be more appropriate. Also shown is the result from a reverse Monte Carlo calculation. RMC is quite general; however, calculations take a few hours, in contrast to a few seconds for the MAXENT algorithm. I use a Cauchy scheme, where the half width of the distribution is modified to ensure 70% acceptance. The Cauchy update has changes on all scales, ensuring that the whole parameter space can be spanned. In both cases, the general features of the spectrum are recovered. It can be seen that as few as 100 data points are necessary to determine the spectrum, although they should be measured as accurately as possible. In particular, the RMC result shows that the correct form for the entropy has been used in the maximum entropy algorithm. Ringing is clearly inherent to both of the techniques shown here, although RMC performs slightly better. In reality, such a sharp cut-off in the DOS is not expected, and the spectrum is most likely to vary continuously to zero, which will remove some of the errors. The ringing is a limiting factor to the resolution of this technique, and means that the specific details of the van Hove singularities cannot be determined.

A more realistic simulated phonon DOS represents one optical and one acoustic mode. Data error is fixed at 0.1%, and Bryan's algorithm and RMC are used. Results are shown in figure 5. The acoustic phonon is represented as a Debye mode with $\omega_D = 50$ meV. The optical mode is modelled as a Gaussian centred about 120 meV with half-width 5 meV. As before, there is some ringing associated with the acoustic mode. However, the method is capable of dealing with densities of states on all energy scales, which is not possible with existing methods. As before, it is apparent that the RMC algorithm gives a more accurate answer. In particular, RMC is much better at determining the height of the high energy peak. Again, there are some anomalous states present between the modes and at very high energy, and the RMC clearly has some error in the continuity of the curves. It would take a very large but

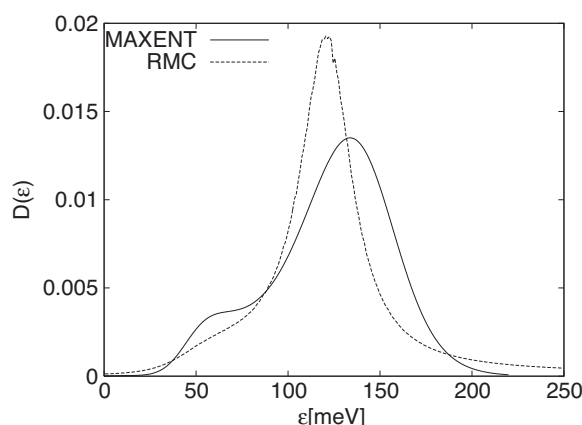


Figure 6. The phonon DOS extracted from the heat capacity of diamond.

not impractical number of Monte Carlo measurements to reduce those errors. With increasing computational power, spectral RMC calculations will clearly become more feasible.

It is typical to use the specific heat capacity of diamond as a benchmark for new techniques. To finish, I apply the maximum entropy and RMC techniques to the data from [11, 12]. The MAXENT analysis is very quick, taking only a few seconds on a modern PC (~ 1 GHz). The RMC analysis took a few hours and is typically run overnight. A data error of 0.5% is taken according to [11, 12]. For the maximum entropy algorithm, a flat default model, normalized to unity, and spread between 0 and 220 meV, was used.

Figure 6 shows the results from the fitting. First, Einstein's expression for the specific heat was fitted to the available data using Gnuplot's least squares refinement. The energy of the corresponding Einstein phonon was found to be 111 ± 1.3 meV. Next, the maximum entropy and spectral RMC procedures were applied. The results show that the general form of the DOS is very similar to that of Debye, which is reassuring, since the variation of the measured 'Debye temperature' with decreasing temperature is small, indicating a form very similar to the Debye model [13]. In order to determine the DOS in greater detail, either more data points or higher accuracy data are required. Typically, neutron scattering studies where the DOS is obtained indirectly using e.g. a shell model to determine the phonon dispersion have additional structure. However, it should be noted that in a typical neutron scattering experiment the dispersion is measured along the symmetry directions only, so most of the DOS is obtained by interpolation and some of the additional structure is spurious.

4. Conclusion

I have introduced a general maximum entropy approach for the computation of the phonon DOS of materials directly from specific heat measurements. The method is model independent, as opposed to standard methods of determination such as fitting to Debye or Einstein modes, or a specific form of the phonon DOS. The Bayesian nature of MAXENT ensures that the best fit to the data is found, without the over-fitting often associated with least squares approaches. This method will be of general benefit to the experimental condensed matter physics community, since the measurement of the phonon dispersion using neutron scattering is expensive, and Raman scattering is limited to zone centre modes. The method is better than existing heat-capacity methods, because it can deal with phonons on all energy scales, can treat acoustic

and optical phonons on an equal footing, and does not suffer from the unphysical negative densities of states that are reported in [5].

There are some caveats to this approach. The specific heat at constant volume (c_v) is required. Such measurements are slightly more difficult to carry out than the specific heat at constant pressure. However, at moderate temperatures, the specific heat at constant volume and pressure converge³. Details of the conversion between c_v and c_p measurements can be found in [11]. Also, it should be noted that in materials with very strong electron–phonon interaction the phonon DOS is likely to change with temperature. In this case, the MAXENT derived DOS should be considered to be an approximation to the true result.

It is for these reasons that the method should not be considered as a replacement for techniques such as neutron and Raman scattering, but as a complementary method, either for the quick extraction of parameters (for example when it is required to separate phonon and magnetic contributions to the specific heat), when the phonon DOS is averaged through an integral transform (such as applying the Eliashberg theory of superconductivity [14]) or when it is necessary to have a good idea where to look for excitations (such as in neutron scattering experiments). It is certainly expected to be a good way to determine which materials might be interesting enough for further study.

Acknowledgments

I would like to thank Emma Chung for useful discussions and the Condensed Matter Physics group at the University of Leicester for hospitality.

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³ For high temperatures c_p is linear, since c_v saturates to a constant and $c_p - c_v = \alpha T$ (from thermodynamics— α is a constant related to the compressibility). Therefore it is also possible to determine c_v directly from c_p .