Localized vibrational mode analysis of the resistivity and specific heat of LaB_6

D. Mandrus,* B. C. Sales, and R. Jin
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
(Received 22 December 2000; published 14 June 2001)

LaB_6 and other hexaborides are inclusion compounds in which the rare earth or other metal ion is weakly bound and sits in an oversized ''cage'' of boron ions. Here we show that a simple model that treats the La ions as independent harmonic (Einstein) oscillators embedded in a Debye framework of boron ions successfully accounts for the anomalies in the specific heat and resistivity of LaB_6. One of the nice features of the model is that the Einstein temperature of the La atoms and the Debye temperature of the boron framework are derived from room-temperature x-ray crystallography data. This feature makes the model easy to apply to other hexaborides and other materials that can be treated as inclusion compounds. The results from this work imply that local modes are likely to be important for understanding the physical properties of all the hexaborides.

DOI: 10.1103/PhysRevB.64.012302 PACS number(s): 63.20.Kr, 63.20.Pw, 65.40.Ba

The discovery of unexpected ferromagnetism in samples of $Ca_{1-x}La_xB_6$ (Ref. 1) has brought renewed attention to the anomalous physical properties of CaB_6, LaB_6, and hexaborides in general. Although it has long been recognized that hexaborides are cryptoclathrates or inclusion compounds,[2] there has been little effort devoted to understanding how some of the anomalous physical properties of the hexaborides derive from their clathratelike structure. In this paper we show that neither the resistivity nor the specific heat of LaB_6 can be understood without taking into account the localized vibrations of the La ions.

The structure of LaB_6 is illustrated in Fig. 1. In this cubic structure the La is at the center of an oversized ''cage'' consisting of 24 boron atoms. The radius of the sphere encompassing the La ion is about 3 Å; this can be compared to 1.95 Å atomic radius, the 1.4–1.9 Å metallic radius, and the approximately 1.2 Å ionic radius of La. The La ion, therefore, is weakly bound and can be expected to undergo large excursions from its equilibrium position. The boron framework, on the other hand, is rigid and makes the hexaborides hard, with high melting points and low coefficients of thermal expansion.

Electronically, many properties of LaB_6 can be understood from simple electron counting arguments. The boron valence band formed from the 6 boron atoms per unit cell requires a total of 20 electrons per unit cell to fill the bonding orbitals; the 6 boron atoms contribute 18 electrons, and the La ion contributes 3 electrons. Thus, there is effectively 1 conduction electron per unit cell. Hexaborides containing divalent metal ions are semiconductors or semimetals in accordance with this picture.[2]

The above structural considerations suggest a simple model of LaB_6 in which the rigid boron framework is treated as a Debye solid and the La ions are treated as independent harmonic oscillators (Einstein oscillators). This model is clearly oversimplified in that we expect at least some hybridization between the La and boron modes as has been observed in inelastic neutron scattering.[3,4] Nevertheless, this model successfully captures the physics of the situation and has the virtue of great simplicity.

A good estimate for the Einstein temperature of the La ions and the Debye temperature of the boron framework can be obtained from room temperature crystallography data, specifically the atomic displacement parameters (ADP's) that measure the mean-square displacement amplitudes of an atom about its equilibrium position in a lattice. Crystallograpers typically report ADP information as a 3×3 matrix U_{ij} that allows for anisotropic displacements. Often an isotropic ADP value U_{iso} is given for each site. U_{iso} corresponds to the mean square displacement averaged over all directions and is given by one third of the trace of the diagonalized U_{ij} matrix. In the case of LaB_6 (space group $Pm3m$), the La ions are in position (1a) and cannot have an anisotropic U; the B ions occupy (6f) and have two independent ADP's: U_{11} and $U_{22}=U_{33}$. For a monatomic cubic crystal, U_{iso} vs T can be solved exactly within the Debye approximation[5,6] and is given by

$$U_{iso}=[3h^2T/(4\pi^2mk_B\Theta_D^2)][\Phi(\Theta_D)+0.25\Theta_D/T], \tag{1}$$

where

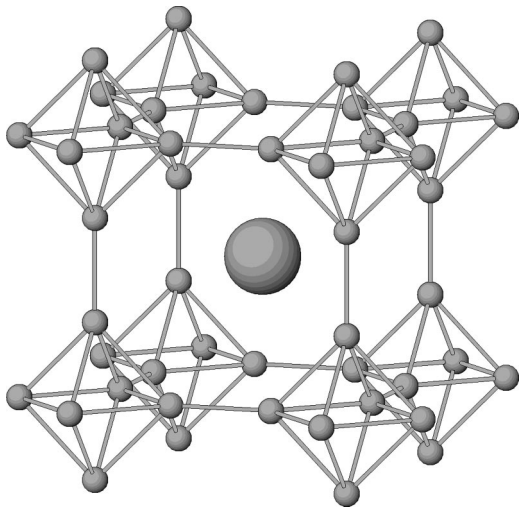

FIG. 1. Structure of LaB_6. The La ion is weakly bound and sits in a rigid three-dimensional boron ''cage.''

 ©2001 The American Physical Society

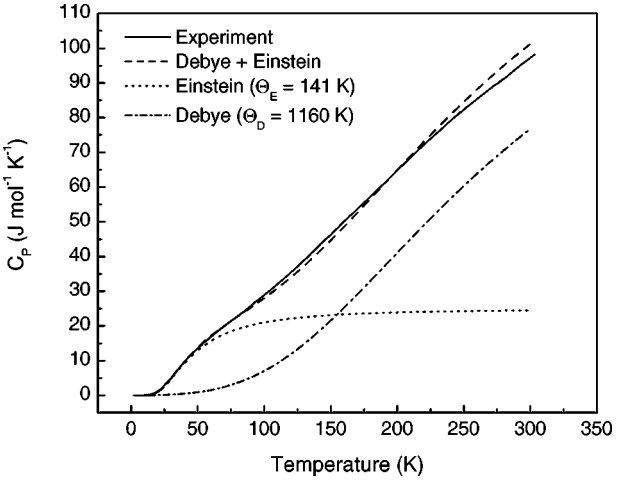

FIG. 2. Specific heat per mole of LaB_6 vs temperature and model calculations performed as described in the text. The unusual shoulder in the data near 50 K is due to the local mode vibrations of the La ions.

$$\Phi(x)=\frac{1}{x}\int_0^x dy\,\frac{y}{e^y-1}. \tag{2}$$

Here h is Planck's constant, k_B is Boltzmann's constant, m is the atomic mass, and Θ_D is the Debye temperature of the lattice. For LaB_6, a careful x-ray refinement gives U_{iso} (boron) = 0.0040(1) Å^2 (Ref. 7) and from Eq. (1) $\Theta_D = 1160$ K.

For an Einstein oscillator, the mean square displacement amplitude is given by[6,8]

$$U_{iso}=\frac{h^2}{8\pi^2 m k_B \Theta_E}\coth\left(\frac{\Theta_E}{2T}\right). \tag{3}$$

For La, $U_{iso}=0.00537(2)$ Å^2 (Ref. 7), which, from Eq. (3), implies an Einstein temperature of $\Theta_E=141$ K. It is now possible to calculate the specific heat implied by the model and compare with experiment. For the calculation, 1 mol of La ions are treated as Einstein oscillators and 6 mol of B ions are treated as a Debye solid. The results are shown in Fig. 2. A commercial heat-pulse calorimeter manufactured by Quantum Design was used for the measurements. The crystal was grown by the floating zone method.[3] As is evident from Fig. 2, the agreement is remarkable considering that the input parameters are derived from x-ray data and that there are no adjustable fitting parameters. Previous studies of the heat capacity of LaB_6 (Refs. 9–11) were restricted to low temperatures, and the Debye temperatures obtained ($\approx$250 K) mainly reflect the contribution of the La local mode. Little thought seems to have been given to reconciling these low Debye temperatures with the high melting points and low coefficients of thermal expansion characteristic of the hexaborides.

We now consider the resistivity. For an apparently simple metal such as LaB_6 one would expect that the Bloch-Grüneisen (BG) formula would be a good starting point for

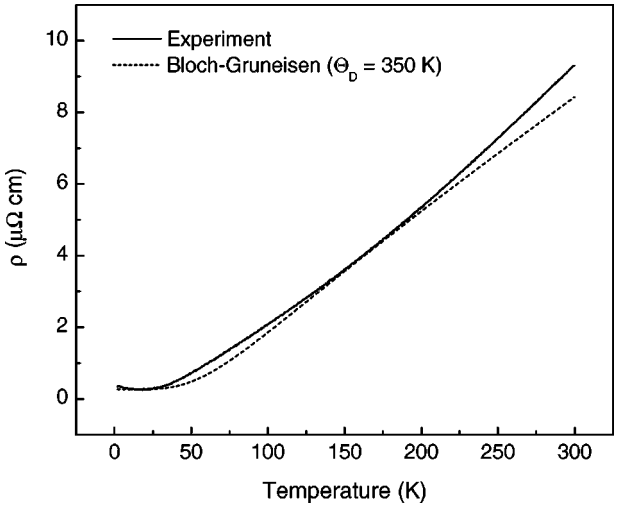

FIG. 3. Resistivity of LaB_6 and a model calculation using the Bloch-Grüneisen formula [Eq. (4)] and an (unrealistic) Debye temperature $\Theta_D=350$ K. This formula qualitatively fails to describe the resistivity of LaB_6.

describing the temperature dependence of the resistivity. Following Allen[12] the BG formula can be written as

$$\frac{\rho_{BG}-\rho_0}{\lambda_{tr}\omega_D/\omega_p^2}=(4\pi)^2\left(\frac{2T}{\Theta_D}\right)^5\int_0^{\Theta_D/2T}dx\,\frac{x^5}{\sinh^2(x)}. \tag{4}$$

In this equation ρ_0 is the residual resistivity, Θ_D is the Debye temperature, ω_D is the Debye phonon energy, ω_p is the Drude plasma frequency, and λ_{tr} is the electron-phonon coupling constant. For our purposes we can treat the denominator on the left-hand side of Eq. (4) as an overall coupling constant that controls the strength of the scattering. In using Eq. (4) to fit experimental data, three fitting parameters are required: the residual resistivity ρ_0, which shifts the curve along the vertical axis, the Debye temperature Θ_D, which scales the curve on the horizontal axis, and an overall coupling constant to scale the curve on the vertical axis. Figure 3 shows an attempt to use Eq. (4) to describe the temperature dependence of the resistivity of LaB_6 using a Debye temperature of 350 K. This value of the Debye temperature was chosen to achieve a broad interval of agreement near the center of the temperature range studied. Other values of the Debye temperature fail even more dramatically to model the data. It is clear from Fig. 3 that a BG description of the resistivity is qualitatively wrong.

The effect of a local soft mode on the resistivity of a metallic solid was examined in the case of $Al_{10}V$ by Caplin, Grüner, and Dunlop,[13] and a more careful analysis was given by Cooper.[14] Cooper finds that the local mode contribution to the resistivity is given by

$$\rho_E=\frac{KN}{mT(e^{\Theta_E/T}-1)(1-e^{-\Theta_E/T})}, \tag{5}$$

where m is the atomic mass, N is the number of oscillators per unit volume, and K is a constant that depends on the electron density of the metal and on the electron-local-mode

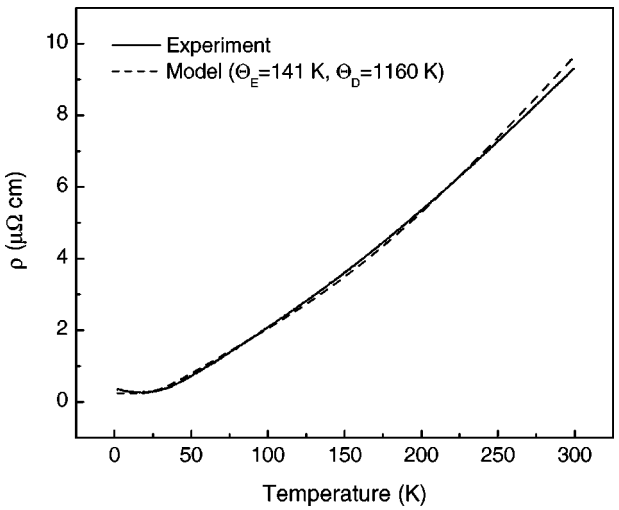

FIG. 4. Resistivity of LaB_6 and a model calculation that incorporates scattering from localized vibrations of the La ions ($\Theta_E = 141$ K) and a Bloch-Grüneisen contribution from the boron framework ($\Theta_D = 1160$ K). The characteristic energies used in the model calculation were inferred from ADP data given in Ref. 7.

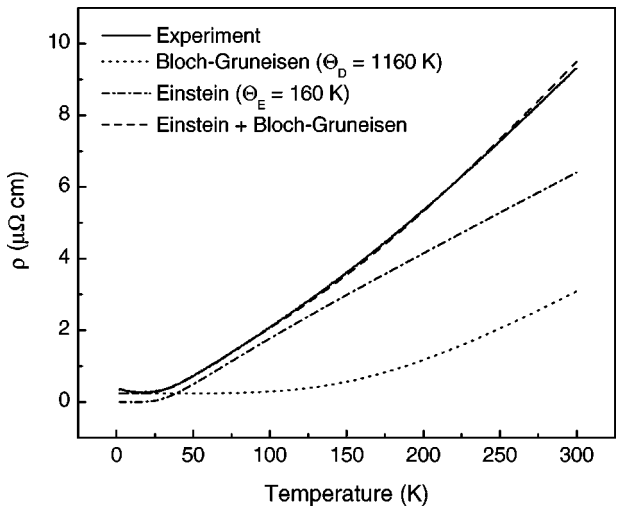

FIG. 5. Resistivity of LaB_6 and a model calculation that incorporates scattering from localized vibrations of the La ions ($\Theta_E = 160$ K) and a Bloch-Grüneisen contribution from the boron framework ($\Theta_D = 1160$ K). The small change in the Einstein temperature compared to Fig. 4 gives nearly perfect agreement with the data. The separate contributions of the Einstein and Bloch-Grüneisen terms are also shown.

coupling strength. In Fig. 4 we model the resistivity of LaB_6 by adding a local mode contribution ($\Theta_E = 141$ K) to a BG ($\Theta_D = 1160$ K) contribution. This calculation was performed by summing Eqs. (4) and (5). The model parameters were $\rho_0 = 2.4\times10^{-7}$ Ω cm, $\lambda_{tr}\omega_D/\omega_p^2 = 3.4\times10^{-7}$ Ω cm, and $(KN/m) = 4.1\times10^{-4}$ Ω cm K. Qualitatively, the agreement is seen to be excellent, especially considering that the Einstein and Debye temperatures are inferred from crystallography data. If we allow the Einstein temperature to increase to 160 K, the model calculation almost perfectly matches the data as shown in Fig. 5. In this case the model parameters used were $\rho_0 = 2.4\times10^{-7}$ Ω cm, $\lambda_{tr}\omega_D/\omega_p^2 = 2.7\times10^{-7}$ Ω cm, and $(KN/m) = 5.67\times10^{-4}$ Ω cm K. It is interesting that a superficially similar analysis of the resistivity, but one based upon very different physical assumptions, was performed by Tanaka *et al.*[15] It should be noted, however, that the analysis given in Ref. 15 is not consistent with either neutron scattering results[3] or heat capacity data to 300 K (this paper).

In conclusion, we have shown that the specific heat and the resistivity of LaB_6 can be described with a model that treats the La ions as independent Einstein oscillators embedded in a boron framework treated as a Debye solid. This model arises naturally from a consideration of the structure of LaB_6. Atomic displacement parameters obtained at room temperature were used to calculate the Einstein temperature of the La ions ($\Theta_E = 141$ K) and the Debye temperature of the boron framework ($\Theta_D = 1160$ K). These values were used to successfully predict the temperature dependence of the specific heat. An analysis of the resistivity reveals that it does not obey conventional Bloch-Grüneisen behavior, but requires an additional term describing the scattering from the localized vibrational mode of the La ions. The results from this work imply that local modes are likely to be important for understanding the physical properties of all the hexaborides.

We thank H. G. Smith for bringing our attention to Ref. 3 and for providing the single crystal used in this work. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

*Email address: mandrusdg@ornl.gov. Also affiliated with the Dept. of Physics, The University of Tennessee, Knoxville, TN 37996.

[1] D. P. Young, D. Hall, M. E. Torelli, Z. Fisk, J. L. Sarrao, J. D. Thompson, H. R. Ott, S. B. Oseroff, R. G. Goodrich, and R. Zysler, Nature (London) **397**, 412 (1999).

[2] F. R. Gamble and T. H. Geballe, in *Treatise on Solid State Chemistry*, edited by N. B. Hannay (Pergamon Press, New York, 1976).

[3] H. G. Smith, G. Dolling, S. Kunii, M. Kasaya, B. Liu, K. Takegahara, T. Kasuya, and T. Goto, Solid State Commun. **53**, 15 (1985).

[4] K. Takegahara and T. Kasuya, Solid State Commun. **53**, 21 (1985).

[5] B. T. M. Willis and A. W. Pryor, *Thermal Vibrations in Crystallography* (Cambridge University Press, London, 1975).

[6] B. C. Sales, B. C. Chakoumakos, D. Mandrus, and J. W. Sharp, J. Solid State Chem. **146**, 528 (1999).

[7] M. M. Korusukova, V. N. Gurin, T. Lundstrom, and L. E. Tergenius, J. Less-Common Met. **117**, 73 (1986).

[8] J. D. Dunitz, V. Schomaker, and K. N. Trueblood, J. Phys. Chem. **92**, 856 (1988).

[9] J. Etourneau, J. P. Mercurio, R. Naslain, and P. Hagenmuller, J. Solid State Chem. **2**, 332 (1970).

[10] J. P. Mercurio, J. Etourneau, R. Naslain, and J. Bennerot, C. R. Seances Acad. Sci., Ser. B **268**, 1766 (1969).
[11] T. Fujita, M. Suzuki, T. Komatsubara, S. Kunii, T. Kasuya, and T. Ohtsuka, Solid State Commun. **35**, 569 (1980).
[12] P. B. Allen, in *Quantum Theory of Real Materials,* edited by J. R. Chelikowsky and S. G. Louie (Kluwer, Boston, 1996).
[13] A. D. Caplin, G. Grüner, and J. B. Dunlop, Phys. Rev. Lett. **30**, 1138 (1973).
[14] J. R. Cooper, Phys. Rev. B **9**, 2778 (1974).
[15] T. Tanaka, T. Akahane, E. Bannai, S. Kawai, N. Tsuda, and Y. Ishizawa, J. Phys. C **9**, 1235 (1976).