Adiabatic Electron-Phonon Interaction and High-Temperature Thermodynamics of $A15$ Compounds

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Inelastic neutron scattering was used to measure the phonon densities of states of the $A15$ compounds V_3Si, V_3Ge, and V_3Co at temperatures from 10 to 1273 K. It was found that phonons in V_3Si and V_3Ge, which are superconducting at low temperatures, exhibit an anomalous stiffening with increasing temperature, whereas phonons in V_3Co have a normal softening behavior. First-principles calculations show that this anomalous increase in phonon frequencies at high temperatures originates with an adiabatic electron-phonon coupling mechanism. The anomaly is caused by the thermally induced broadening of sharp peaks in the electronic density of states of V_3Si and V_3Ge, which tends to decrease the electronic density at the Fermi level. These results show that the adiabatic electron-phonon coupling can influence the phonon thermodynamics at temperatures exceeding 1000 K.

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At cryogenic temperatures, the electron-phonon interaction (EPI) underlies the well-established effects of superconductivity and electron mass renormalization [1]. Anomalous phonon softenings with decreasing T have been observed (for $T < 300$ K) in V- and Nb-based superconducting $A15$ compounds and were related to nonadiabatic EPI effects (scattering of electronic states by phonons whose wave vectors span the Fermi surface) [2,3]. Measurements in cuprate superconductors at low T have also revealed anomalous softenings of specific phonons and have attracted much attention [4]. At high temperatures, however, the importance of the EPI for thermodynamics remains controversial [1,5]. Recent calculations have predicted that the adiabatic component of the EPI, which corresponds to averages of electronic properties over thermal nuclear displacements, could have a contribution to the free energy comparable to that of the bare electrons up to melting [6], but systematic measurements above the Debye temperature have not been available. In this Letter, we present measurements of the phonon density of states (DOS) of three $A15$ compounds from 10 to 1273 K, which show that the adiabatic EPI can have an effect on high-temperature thermodynamics comparable to that of electrons and thermal expansion. First-principles simulations show that sharp peaks in the electronic DOS near the Fermi level cause an anomalous stiffening (increase in energy) of the phonons with temperature. The magnitude of this effect at high temperature may be a useful measure of the electron-phonon coupling strength in superconductors.

Central to high-temperature thermodynamics is the behavior of phonon frequencies as T increases and more phonons are created [1,5]. The expansion of the lattice at high T usually leads to softer (lower energy) phonons and extra vibrational entropy. In the standard quasiharmonic model (QH), the decrease of the average phonon energy $\langle E \rangle$ is related to the change in volume V of the crystal as $\Delta\langle E\rangle/\langle E\rangle = -\bar{\gamma}\Delta V/V$, where the average Grüneisen parameter is $\bar{\gamma} = 3\alpha V B_S/C_P$, with α the coefficient of thermal expansion, B_S the isentropic bulk modulus, and C_P the constant-pressure heat capacity [5]. Typically, $\bar{\gamma} > 0$. In contrast with this picture, we show in this Letter that the adiabatic EPI causes a stiffening of phonons at high T in superconducting V_3X compounds, exceeding the effects from thermal expansion in the QH theory even as high as $T \sim 1000$ K.

All samples were prepared by arc-melting V slugs of 99.8% purity and pieces of Co, Si, and Ge of 99.9% or higher purity under a high-purity argon atmosphere. The ingots were melted three times to ensure a homogeneous composition. The ingots were crushed to form coarse powders, which were annealed in vacuum at 800 °C for 5 days. X-ray diffraction (XRD) measurements on powder samples showed a single phase $A15$ structure. *In situ* XRD at high temperatures was used to measure the lattice thermal expansion of all materials. Inelastic neutron scattering spectra were collected using the Pharos time-of-flight chopper spectrometer at the Los Alamos Neutron Science Center. The polycrystalline samples were mounted in an AS Scientific furnace, which was kept under high vacuum during all measurements. No oxidation was detected on the samples after the measurements. For measurements at low temperatures, the samples were encased in a thin-walled Al pan and mounted into a Cu frame cooled by a closed-cycle He refrigerator. The incident neutron energy was $E_i = 75$ meV, and the energy resolution was about 0.8 meV at 40 meV neutron energy loss, increasing to about 3.0 meV at the elastic line. The measurements between 523 and 750 K were performed with a custom, low-background furnace. Details of the data analysis are given in [7]. Additional inelastic neutron scattering spectra on V_3Co were measured on the HB2 3-axis spectrometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory, with the experimental conditions described in [8]. The curves

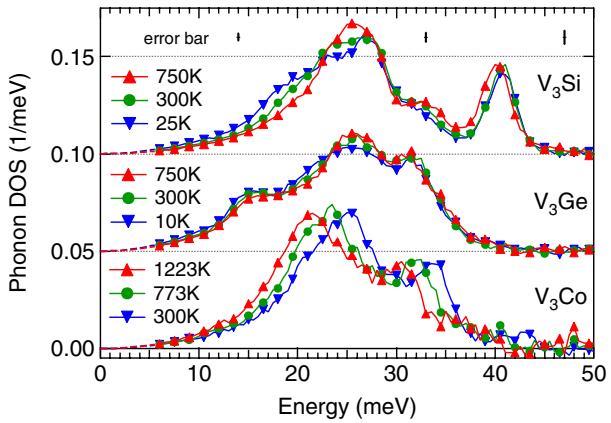

FIG. 1 (color online). Phonon DOS of V_3X compounds (X = Si, Ge, and Co), measured with inelastic neutron scattering, at different temperatures. Curves are extrapolated below 6 meV according to the long-wavelength limit.

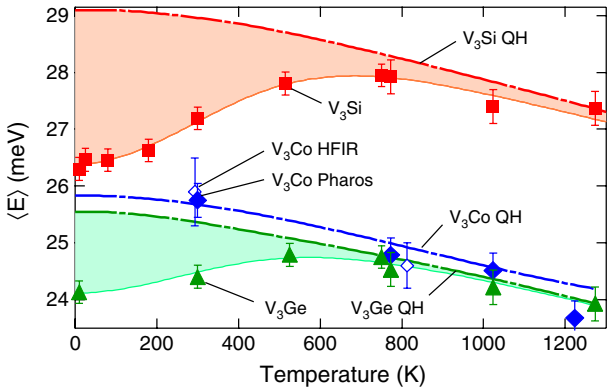

FIG. 2 (color online). Average phonon energy of V_3X compounds as a function of temperature. Markers are results from INS measurements, and dashed-dotted lines correspond to QH behavior, for the values of the Grüneisen parameters listed in the text. The QH curves were offset vertically to match the INS data at the highest T measured.

shown in Fig. 1 are generalized phonon DOS, owing to neutron-weighting of different elements. The neutron weights, given by the ratios of neutron cross section over mass σ/M are $(0.100, 0.096, 0.077, 0.118)$ barns/amu for (V, Co, Si, Ge), respectively. The neutron weighting is fortunately small for all V_3X compounds, and any effect on thermal trends is expected to be minimal. Differences in Debye-Waller factors between species were estimated from first-principles calculations (see below) and found to be small over the entire temperature range.

As seen in Fig. 1, the phonon DOS of V_3Si and V_3Ge do not soften with increasing temperature, while that of V_3Co does. In V_3Si, the DOS actually stiffens, despite the thermal expansion of the lattice. The largest effect is for the low-energy transverse modes from 10 to 25 meV, involving mostly V atoms. The different behaviors of the three materials are seen in the mean phonon frequencies $\langle E \rangle$, plotted in Fig. 2. The measured softening of $\langle E \rangle$ for V_3Co is in excellent agreement with the effect of thermal expansion predicted by the QH model, for $\bar{\gamma} = 1.8$. On the other hand, V_3Si and V_3Ge show a large deviation from the predicted QH softening (we used $\bar{\gamma} = 1.46$ and 1.63, respectively, for V_3Si and V_3Ge, as determined by Carcia, Barsch, and Testardi [9]). A correlation can be drawn between the anomalous stiffening of phonons in V_3Si and V_3Ge (and lack thereof in V_3Co) and their superconducting transition temperature T_C or EPI coupling constant λ. In Table I, we compare the magnitude of anomalous stiffening (shaded areas in Fig. 2), T_C, and λ for the three compounds. It can be seen that the integral of the anomalous stiffening provides an estimate of the strength of the EPI (assessed with T_C or λ).

The heat capacity at constant pressure of V_3Si was measured from 400 to 1473 K, using a Netzsch DSC-404c differential scanning calorimeter with Pt crucibles, Al_2O_3 liners, a heating rate of 20 K/ min , and an ultrapure argon gas flow. The reference sample was a synthetic sapphire disk, of mass comparable to the sample. Minimal oxidation was detected on the samples after runs up to 1673 K. Results are shown in Fig. 3. Heat capacity components were obtained as described in [11]. The measured heat capacity C_P of V_3Si is much below the expected sum of contributions from harmonic phonons ($C_{\mathrm{ph,H}}$), lattice dilation (C_D), and electrons renormalized by the EPI ($C_{\mathrm{el},e\text{-}p}$). This suppression represents an extra negative component from the increase of phonon energies with T [12] and corroborates our inelastic-neutron-scattering (INS) measurements. The EPI also decreases the electronic density at the Fermi level, causing a reduced C_P (the difference between $C_{\mathrm{el},e\text{-}p}$ and $C_{\mathrm{el,bare}}$ in Fig. 3), as explained below. The suppression in C_P can be ascribed to the adiabatic EPI at high T, since all other components are already accounted for. It is striking that, at 1200 K, this EPI component is larger than the electronic or dilation components (but of opposite sign). At low T, our measurements are in good agreement with the results of Knapp *et al.* [13]. The high-T XRD data were fitted to obtain the thermal expansion: $\Delta a/a_{300} = K_1(T - 300) + K_2(T - 300)^2$. Fit results are listed in Table I. A reduced quadratic term (K_2) in the thermal expansion of V_3Si and V_3Ge is consistent with the phonon stiffening effect, which reduces the phonon entropy, suppressing thermal expansion.

TABLE I. Superconducting and expansion properties. Values in parentheses are the ratio to the V_3Si value.

	V_3Si	V_3Ge	V_3Co
$T_c(K)$[a]	17	6.5 (0.38)	<2.7 (<0.15)
$\lambda(\mu^* = 0.13)$[b]	1.07	0.71 (0.66)	<0.3 (<0.3)
$\int\langle E\rangle_{\mathrm{QH}} - \langle E\rangle dT$[c]	0.97	0.54 (0.56)	0.0 (0.0)
K_1 (K^{-1})	8.58×10^{-6}	9.74×10^{-6}	8.13×10^{-6}
K_2 (K^{-2})	1.43×10^{-9}	2.07×10^{-9}	4.47×10^{-9}

[a]Measured with Quantum Design magnetometer system.
[b]Using the formula of [10].
[c]In (eV K). Integrals correspond to shaded areas in Fig. 2.

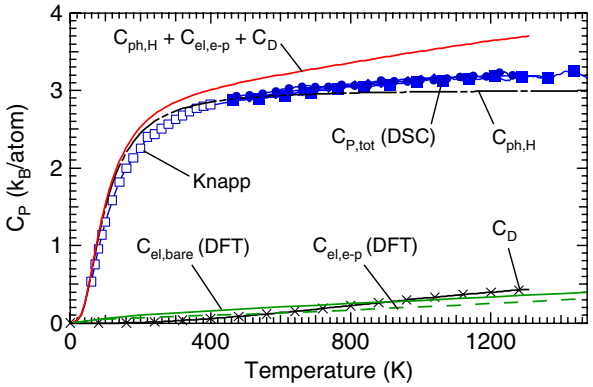

FIG. 3 (color online). Heat capacity at constant pressure C_P for V_3Si, measured by DSC (several data sets), and contributions calculated from harmonic phonons ($C_{ph,H}$), bare electrons ($C_{el,bare}$), electrons with EPI effect ($C_{el,e-p}$, see text), and thermal dilation (C_D). Open squares are data from Knapp *et al.* [13].

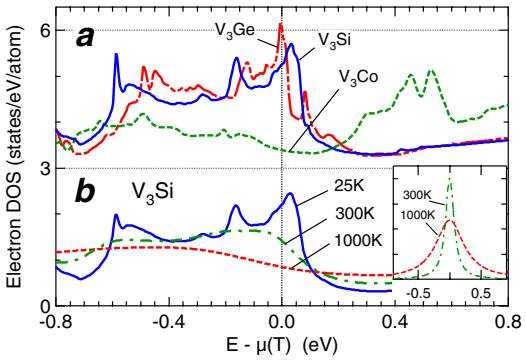

FIG. 4 (color online). (a) Electronic DOS for V_3Si, V_3Ge, and V_3Co, computed from first principles. (b) Electronic DOS for V_3Si broadened by EPI at 25, 300, and 1000 K, using $\lambda = 1.0$ at all T. Energies are with respect to $\mu(T)$. Inset: Broadening function at 300 and 1000 K.

The electronic DOS for $A15$ V_3Si, V_3Ge, and V_3Co were calculated from first-principles using density functional theory (DFT). Computations used VASP [14], with the projector-augmented wave method [15,16], and the generalized gradient approximation of Perdew, Burke, and Ernzerhof [17]. We used cubic unit cells in all cases. (Experimentally, V_3Ge and V_3Co are cubic at all T, and V_3Si is cubic above the cubic-tetragonal martensitic transformation temperature $T_M = 22$ K.) The volume was optimized, and the convergence with respect to kinetic energy cutoff and sampling of k points in the Brillouin zone was checked in all cases. The calculated electron DOS curves $N(E)$ are shown in Fig. 4(a).

Both V_3Si and V_3Ge have very sharp peaks at the Fermi level, whereas the Fermi level of V_3Co lies in a valley. We expect the peak in V_3Si and V_3Ge to broaden and decrease in height as phonons disrupt the periodicity of the lattice at high T and cause finite lifetimes for the electronic states. We calculated the resulting broadened electron DOS by convoluting the DFT result with a Lorentzian function $\mathcal{L}_\Gamma$ of full width at half maximum (FWHM) $2\Gamma = 2\pi\lambda k_B T$, as derived by Grimvall [1]. The shift in electron chemical potential $\mu(T)$ was calculated consistently. Results for $N(E)$ and the broadened $\tilde{N}(E)$ are shown in Fig. 4(b) for V_3Si ($\lambda = 1.0$). The broadening of the DOS results in a monotonic decrease of $N(E_F)$ to temperatures of 1000 K or higher for V_3Si and V_3Ge. On the other hand, there is a small increase of $N(E_F)$ in V_3Co. The suppression of $N(E_F)$ in V_3Si and V_3Ge is expected to decrease the ability of the conduction electrons to screen the nuclear motions, resulting in stiffer phonons and a reduction in phonon entropy and heat capacity, as observed (Figs. 1 and 3). The decrease in $N(E_F)$ also suppresses the electronic entropy and heat capacity (see $C_{el,bare}$ and reduced $C_{el,e-p}$ in Fig. 3), although this contribution appears smaller. The anomalous phonon stiffening effect may occur whenever a sharp peak is present at the Fermi level, and we have observed a similar effect in dilute V-based solid solutions [11]. Electron lifetime considerations were previously used to estimate the maximum superconducting temperature in $A15$ compounds, but consequences on high-T thermodynamics were not investigated [18]. As pointed out in [18], the broadening of the electronic levels by the EPI should be self-limiting, since it tends to decrease λ at higher T [λ scales approximately with $N(E_F)$], so a more accurate self-consistent result should lie between the unbroadened and broadened DOS in Fig. 4.

As discussed by Bock, Coffey, and Wallace [6], one must distinguish the adiabatic and nonadiabatic contributions of the EPI to the free energy. The nonadiabatic component represents the action of the nuclear kinetic energy operator on the electronic part of the many-body wave functions [1,5]. It is expected to vanish at high temperatures, as it is a purely quantum mechanical effect. The adiabatic component, on the other hand, represents the effect of thermal disorder on the electronic states. It can be described in the Born-Oppenheimer approximation, with the electrons "seeing" the ions in their instantaneous, distorted, configuration. As the phonon displacement amplitudes increase with T, this contribution is expected to increase, and Bock, Coffey, and Wallace have found a scaling with T^3 up to melting.

The effect of the adiabatic EPI on the phonon spectrum was calculated within the framework of finite-temperature DFT. The discrete electronic eigenenergies obtained by solving the Kohn-Sham Hamiltonian were broadened to have a finite energy width. The phonon density of states of V_3Si was obtained from first principles, by calculating Hellmann-Feynman forces resulting from explicit atomic displacements, as implemented in [19]. The phonon DOS was computed for different electronic broadenings, using the Fermi smearing scheme implemented in VASP [14]. We used electronic broadenings $25 \leq \sigma \leq 200$ meV. The broadening energy scale can be related to a temperature scale, by matching the FWHM of the Fermi-function derivative to the FWHM of $\mathcal{L}_\Gamma$, $3.5\sigma = 2\pi\lambda k_B T$, giving $170 \leq T \leq 1300$ K (using a constant $\lambda = 1.0$). A more

accurate estimate would require a self-consistent calculation of $\lambda(T)$, which is beyond the scope of the present study. We also investigated the dependence on volume by calculating the phonon DOS at a volume V_{low}, corresponding to the equilibrium DFT volume, and for an expanded volume $V_{\mathrm{high}} = 1.03 \times V_{\mathrm{low}}$.

Figure 5 shows that the broadening of electronic levels induces a stiffening of phonons in V_3Si (and also in V_3Ge, not shown), in particular, for the low-energy modes involving predominantly motions of the V atoms. Conversely, in V_3Co, electronic broadening results in a slight softening of phonons, in agreement with an increase in $N(E_F)$. These behaviors are very similar to our experimental observations, and the calculated and measured phonon DOS are in good agreement. On the other hand, volume expansion alone yields a softening of the phonons corresponding approximately to a rescaling of the energy axis. This is as expected with the QH model but is inconsistent with the experimental trend, ruling out anharmonicity of the interatomic potentials as the source of the anomalous temperature dependence. At the bottom of Fig. 5 are phonon DOS curves with the effects of both thermal expansion and adiabatic EPI, which agree well with the experimental trends. It is striking that the broadening of electronic levels implemented in finite-T DFT captures so well the adiabatic EPI at high temperature.

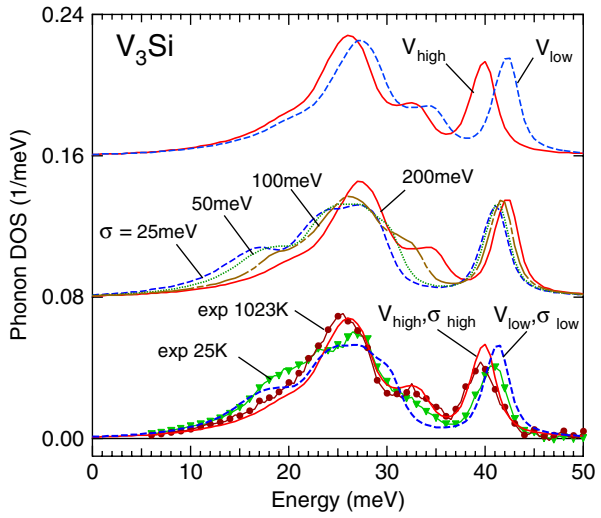

FIG. 5 (color online). Top: Phonon DOS for V_3Si calculated from first principles for two different volumes ($V_{\mathrm{high}} = 1.03 \times V_{\mathrm{low}}$). Middle: Calculated DOS for different electronic broadenings σ. Bottom: The same as above for two different (V and σ) combinations ($\sigma_{\mathrm{low}} = 50$ meV and $\sigma_{\mathrm{high}} = 200$ meV). Computations used a $2 \times 2 \times 2$ supercell (64 atoms) and a $4 \times 4 \times 4$ k-point grid. The calculated DOS was obtained from the neutron-weighted contributions of V and Si species and convolved with the experimental instrument resolution. The markers are experimental results for V_3Si at 25 and 1023 K.

A thermodynamically significant effect of the EPI exists to 1000 K in $A15$ V_3Si and V_3Ge, a surprising result considering common assumptions and many calculations of the effect of the EPI on the free energy of metals [1,5]. Such a possibility was suggested by a few early theoretical papers considering EPI effects on the heat capacity [12], and by more recent calculations of the free energy in free electron metals [6], but had not been observed experimentally. These results suggest that studies of phonons at high temperatures may provide useful information on the EPI. More generally, we expect that a thermodynamic description reliant on independent phonons and electronic excitations may be inadequate for materials whose electronic DOS has sharp features close to the Fermi level.

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[1] G. Grimvall, *The Electron-Phonon Interaction in Metals* (North-Holland, Amsterdam, 1981).
[2] B. P. Schweiss, B. Renker, E. Schneider, and W. Reichardt, in *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglass (Plenum, New York, 1976), p. 189.
[3] L. Pintschovius, H. Takei, and N. Toyota, Phys. Rev. Lett. **54**, 1260 (1985).
[4] D. Reznik *et al.*, Nature (London) **440**, 1170 (2006).
[5] D. C. Wallace, *Statistical Physics of Crystals and Liquids* (World Scientific, Singapore, 2002).
[6] N. Bock, D. Coffey, and D. C. Wallace, Phys. Rev. B **72**, 155120 (2005); **73**, 075114 (2006).
[7] M. G. Kresch, O. Delaire, R. Stevens, J. Y. Y. Lin, and B. Fultz, Phys. Rev. B **75**, 104301 (2007).
[8] P. D. Bogdanoff, B. Fultz, J. L. Robertson, and L. Crow, Phys. Rev. B **65**, 014303 (2001).
[9] P. F. Carcia, G. R. Barsch, and L. R. Testardi, Phys. Rev. Lett. **27**, 944 (1971).
[10] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[11] O. Delaire, M. Kresch, J. A. Muñoz, M. S. Lucas, J. Y. Y. Lin, and B. Fultz, Phys. Rev. B **77**, 214112 (2008).
[12] P. B. Allen and J. C. K. Hui, Z. Phys. B **37**, 33 (1980).
[13] G. S. Knapp, S. D. Bader, H. V. Culbert, F. Y. Fradin, and T. E. Klippert, Phys. Rev. B **11**, 4331 (1975).
[14] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
[15] P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994).
[16] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[18] K. M. Ho, M. L. Cohen, and W. E. Pickett, Phys. Rev. Lett. **41**, 815 (1978).
[19] D. Alfè, http://chianti.geol.ucl.ac.uk.