

Contribution of low-frequency modes to the specific heat of Cu-Zn-Al shape-memory alloys

J. C. Lashley, F. R. Drymiotis,* D. J. Safarik, and J. L. Smith
Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

Ricardo Romero
*IFIMAT, Universidad del Centro de la Provincia de Buenos Aires and Comisión de Investigaciones Científicas
 de la Provincia de Buenos Aires, Pinto, 399, 7000 Tandil, Argentina
 and Departament d'Estructura i Constituents de la Matèria, Facultat de Física,
 Universitat de Barcelona, Avenida Diagonal, 647, E-08028 Barcelona, Catalonia*

R. A. Fisher
Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

Antoni Planes and Lluís Mañosa
*Departament d'Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona,
 Avinguda Diagonal, 647, E-08028 Barcelona, Catalonia
 (Received 20 July 2006; published 26 February 2007)*

We report a comparison of the specific-heat measurements on isoelectronic Cu-Zn-Al shape-memory alloys in the parent cubic phase ($L2_1$) and in the close-packed martensitic phase (18R). Measurements were made by thermal-relaxation calorimetry over the temperature range $1.9 \leq T \leq 300$ K. For the close-packed martensitic phase we find that the specific heat behaves similarly to that of pure copper which is also close packed. However, we observe deviations from Debye behavior for the cubic phase at low temperatures. This deviation is accounted for by the addition of $\sim 5\%$ of Einstein localized modes to the Debye modes. Although the microscopic origin remains unknown, it was anticipated that it is related to the well-known softening of the $TA_2[110]$ phonon branch. In order to address this hypothesis an analysis of the lattice heat capacity of the cubic phase was compared to the calculated lattice heat capacity of β -brass, as determined by integrating over the phonon density of states. A similar comparison was made between the close-packed phase and α -brass.

DOI: [10.1103/PhysRevB.75.064304](https://doi.org/10.1103/PhysRevB.75.064304)

PACS number(s): 63.20.Dj

I. INTRODUCTION

The Cu-based shape-memory alloys (SMAs) transform from a high-temperature bcc-based phase $L2_1$ to one of several possible martensitic phases, depending on composition. For the Cu-Zn-Al alloys that are the focus of the present study, the transition proceeds from an open $L2_1$ to a close-packed 18R phase.¹ The thermodynamic stability at high temperatures of open bcc-based phases is acknowledged to be a consequence of their large vibrational entropy.^{2–4} Zener's⁵ connection of the vibrational entropy in bcc materials with low $(110)[\bar{1}10]$ shear resistance led to the Voigt elastic stiffness relation $c' = (c_{11} - c_{12})/2$ and two additional findings. The first is that low c' values correspond to high vibrational mode entropy S , and they stabilize the bcc crystal structure at high temperatures through the TS term in the Helmholtz free energy $F = E - TS$. Second, at low temperatures the TS term yields to the energy term E , and the bcc structure transforms to a lower-symmetry structure. This picture has been largely confirmed and shown to be especially adequate for Hume-Rothery SMAs.¹ For these materials it has been suggested that low-energy TA_2 phonons^{6,7} provide the excess of entropy stabilizing the open phase at high temperature. It is interesting that these low-energy phonons correspond to high-amplitude atomic motions associated with the pathway that brings the system from the bcc-based phase to a close-packed structure. Measurements of the elastic

constants⁸ and the phonon-dispersion relations⁹ show the existence of anomalies in the high-temperature phases. In the bcc phases, the transverse acoustic phonon frequencies are observed to soften^{1,10} as the temperature is reduced toward the martensitic transition (MT) temperature, but generally the softening is incomplete since it is arrested by the phase transition before the phonon frequency reaches zero.¹¹

Recently¹² it has been suggested that Cu-based shape-memory materials show an excess of low-frequency modes similar to the boson peak (BP) in glasses that originates from the anomalous low-energy TA_2 acoustic modes. In general, the BP refers to an excess contribution to the usual Debye density of states observed below 10 meV (terahertz frequency range).^{13,14} It is commonly revealed by thermodynamic quantities such as the heat capacity (C), which shows a peak in the scaled C/T^3 vs T representation. This behavior is typically observed in amorphous solids¹⁵ and glasses¹⁶ of all bonding types in the range from 5 to 20 K where low-energy excitations have been suggested to result from resonant vibrational modes, which originate from disorder (including clustering or fragmentation).¹⁵ However, this behavior is not limited to structurally disordered solids, but rather a similar behavior has been reported in a number of crystalline materials¹⁷ including, for instance, ferroelectric materials¹⁸ and negative thermal expansion materials.¹⁹ In these cases the heat capacity was represented by a single Einstein mode. The frequencies obtained from these fits

agreed well with phonon anomalies determined by scattering experiments.⁶

It was therefore anticipated that the excess of low-frequency modes in the specific heat observed in Cu-based shape-memory alloys is related to a Van Hove singularity associated with the zone-boundary frequency of the soft TA_2 acoustic branch. In these materials low-frequency modes should be favored by a strong anisotropy of the vibrational properties. Here we report specific-heat measurements for different Cu-Zn-Al shape-memory alloys in the temperature range $1.9 \leq T \leq 300$ K. Single crystals were prepared in such a way that in one composition, $Cu_{61.98}Zn_{28.04}Al_{9.98}$, the high-temperature $L2_1$ phase is thermodynamically stable over the range $1.9 \leq T \leq 300$ K. Similarly, in a crystal of another composition, $Cu_{68.91}Zn_{13.17}Al_{17.92}$, the low-temperature 18R phase is stable over the measured temperature range. In a third composition, $Cu_{67.93}Zn_{16.14}Al_{15.93}$, the MT occurs at 234 K. For the sake of comparison, single-crystal copper was measured because its close-packed structure is close to the 18R structure and also because it is isoelectronic to all of the alloys. Through a detailed analysis of the specific-heat measurements described above we show that (a) there is a significant contribution to the specific heat from the low-frequency modes, (b) in order to evaluate thermodynamic functions it is necessary to account for these modes by fitting the specific heat to a fraction of Einstein modes, (c) the frequencies obtained to the fits for the $L2_1$ and 18R are significantly different, and (d) although the origin of the low-frequency modes remains unclear we are able to put an energy scale on them.

II. MODELING THE EXCESS HEAT CAPACITY IN SHAPE-MEMORY ALLOYS

We summarize an extension of the simple model introduced previously^{12,20,21} that will be applied to the specific-heat data. We assume localization over a narrow range of energies of the low-energy TA_2 modes. Therefore, these modes can be described by a sum of Einstein terms. Essentially these are peaks in the density of states related to Van Hove singularities in the reduced phonon spectra. Because there are a total of $3N$ modes, the Debye contributions are reduced when Einstein modes are introduced. The Einstein heat capacities used to represent these soft modes are labeled C_{Ei} with characteristic temperature θ_{Ei} . The Debye contribution to the specific heat is designated C_D with characteristic temperature Θ_D . The total number of vibrational modes is p , which is the sum of three contributions: $p = p_D + \sum p_{Ei} + \sum p_{ELi}$, where p_D are Debye modes, p_{Ei} low-temperature Einstein modes, and p_{ELi} higher-temperature Einstein modes that we add empirically to achieve a better fit to the high-temperature data. These high-frequency Einstein terms have a specific heat C_{ELi} and a characteristic temperature θ_{ELi} . These modes have θ_{ELi} over 300 K, so they are easily distinguished from C_{Ei} used to represent the soft modes and do not affect the fit to the low-temperature data. With these three different contributions, the isobaric heat capacity is represented by

TABLE I. Atomic composition and martensitic transition temperature of the studied alloys.

Cu	Zn	Al	T_M (K)	γ (mJ K ⁻² mol ⁻¹)	θ_D (K)
61.98	28.04	9.98	<2	0.75	269
67.93	16.14	15.93	234.5	0.78	310
68.91	13.17	17.92	>RT ^a	0.80	325
100	0	0	no MT	0.69	330

^aRoom temperature.

$$C_p = R \left(p_D C_D(\theta_D/T) + \sum p_{Ei} C_{Ei}(\theta_{Ei}/T) + \sum p_{ELi} C_{ELi}(\theta_{ELi}/T) \right) + \gamma T, \quad (1)$$

where R is the gas constant and γT the electronic heat capacity. The Debye heat capacity is given by

$$C_D = 3(T/\theta_D)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (2)$$

and the Einstein heat capacity is

$$C_E = (\theta_E/T)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2}. \quad (3)$$

III. EXPERIMENT

Three Cu-Zn-Al alloys of selected compositions were used for the experiments. Single crystals were grown in sealed quartz tubes by the Bridgman method using high-purity (99.999%) elements. The actual composition of each sample was checked by means of electron-dispersion analysis. The compositions of the samples are given in Table I. Resistivity measurements confirm that $Cu_{61.98}Zn_{28.04}Al_{9.98}$ remains cubic ($L2_1$) down to <2 K. The sample $Cu_{67.93}Zn_{16.14}Al_{15.93}$ undergoes a martensitic transformation from $L2_1$ to a monoclinic 18R structure below room temperature, and the sample $Cu_{68.91}Zn_{13.17}Al_{17.92}$ transforms martensitically to the same structure above room temperature. Transition temperatures (T_M) of the studied samples are also given in Table I. In the absence of an externally applied stress, a single crystal of the high-temperature phase splits into a number of energetically equivalent martensitic variants. Therefore, a single-variant martensite was obtained by training the sample $Cu_{68.91}Zn_{13.17}Al_{17.92}$. This training consisted in thermal cycling the sample through the transition under a small uniaxial stress that favors one of the variants with respect to the others. Specific-heat measurements²² were made on small ~ 3 -mm-diameter disks of about 1.5 mm thickness. Samples were cut from the single crystals by spark erosion, and the crystallinity was checked by back-reflection Laue.

IV. RESULTS AND DISCUSSION

Results of specific-heat measurements for the three Cu-Zn-Al alloys described above are shown in Figs. 1–3, and

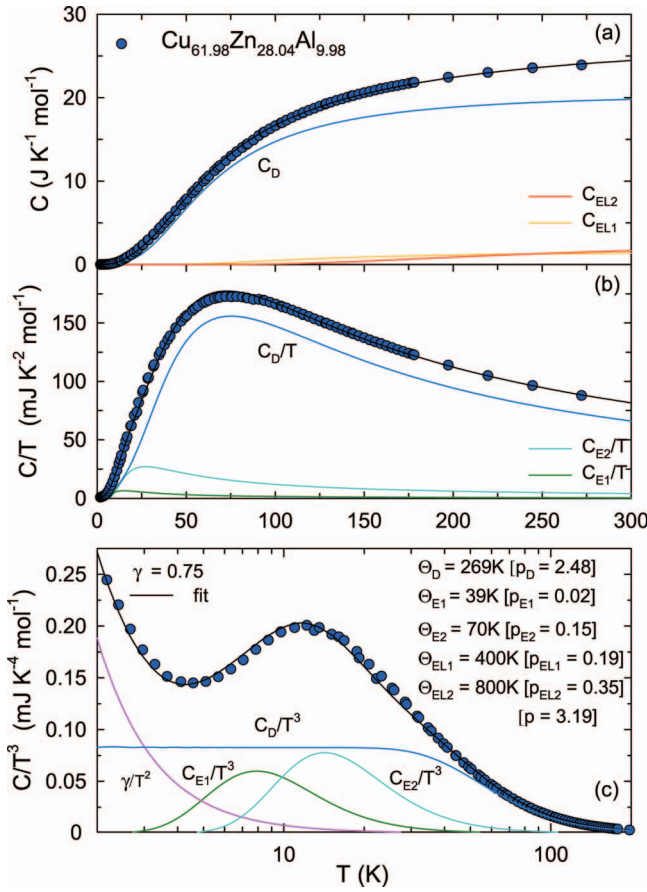


FIG. 1. (Color) Heat capacity as a function of temperature plotted as (a) C versus T ; (b) C/T versus T ; and (c) C/T^3 versus $\log_{10} T$. Each of the three panels emphasizes a different temperature region and demonstrates the validity of the fit using Eq. (1). The fit parameters are given in (c). Two Einstein modes, shown in (c), are necessary to represent the peak centered near ~ 12 K. The average of θ_{E1} and θ_{E2} is very close to the peak observed in spectroscopic measurements. The sum of the contributions (the fit) is represented by the black curve; the Debye contribution (C_D) by the blue curve; and, the low-temperature Einstein contributions by green C_{E1} and cyan C_{E2} curves. In (a) the red and orange curves denote the two Einstein heat capacities C_{EL1} and C_{EL2} needed to fit the high-temperature data.

copper in Fig. 4. The fits yielded γ and θ_D values for the three alloys and copper that are listed in Table I. The values of γ and θ_D are consistent with previously published data for the same alloy family.²³ In particular the composition dependence of θ_D is reproduced. In Fig. 5 we show a detail of the heat capacity of $\text{Cu}_{67.93}\text{Zn}_{16.14}\text{Al}_{15.93}$ in the region of its martensitic transition. Interestingly, a single fit is obtained through the transition. This is consistent with the common point of view²⁴ that, at this transition temperature, the change of heat capacity at the transition is, if any, very small.²⁵ The baseline is fitted through the lattice in each phase to illustrate this point. The values found for γ are very small, which indicates that these alloys are essentially isoelectronic with copper. Relative to one another the γ value for the cubic phase is slightly lower than in the martensitic phase, and therefore the electron contribution to the entropy of the mar-

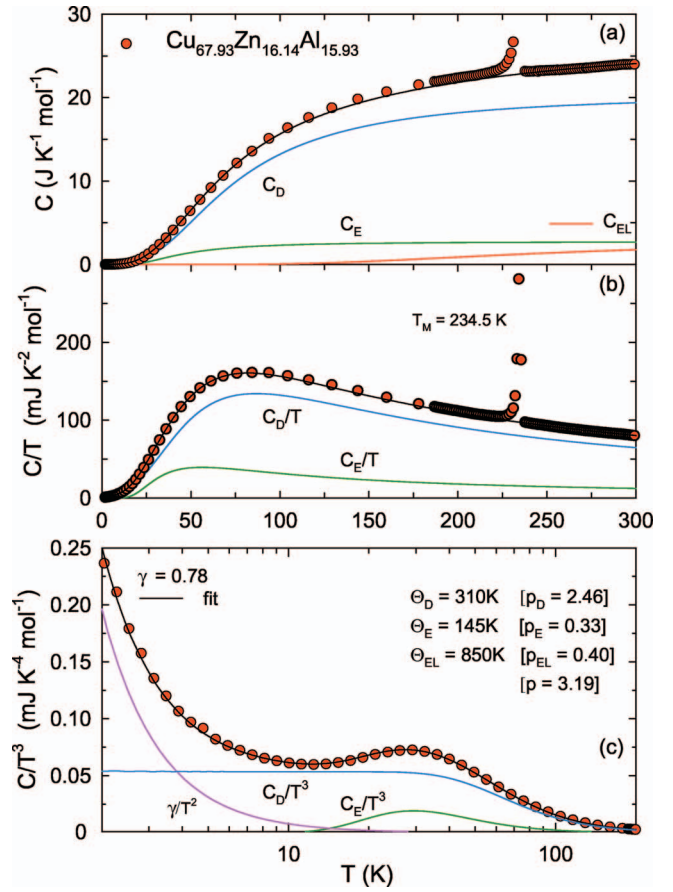


FIG. 2. (Color) Specific-heat data above and below the first-order martensite transition at $T_M = 234.5$ K for $\text{Cu}_{67.93}\text{Zn}_{16.14}\text{Al}_{15.93}$. A single, smaller Einstein contribution is needed to fit the BP peak centered at ~ 30 K.

tensite is slightly higher than that of the cubic phase. This finding is in agreement with a previous estimation of the electronic contribution to the transition entropy change in Cu-based shape-memory alloys based on magnetic susceptibility measurements.²⁶

The vibrational contribution to the heat capacity has been obtained by subtracting the electronic heat capacity from the measured heat capacity, i.e., $C_{\text{vib}} = (C - \gamma T)$. In order to reveal the deviations in C_{vib} from pure Debye behavior we have plotted in Fig. 6 $\Sigma C_{Ei}/(C - \gamma T)$ versus $\log_{10} T$ for the three alloys. Data for pure copper,²² which has a fcc structure closely related to the structure of the martensite, have also been included for comparison. For $\text{Cu}_{61.98}\text{Zn}_{28.04}\text{Al}_{9.98}$, the structure remains cubic down to the lowest temperature measured and an excess heat capacity contribution is clearly observed with a maximum at ~ 12 K. A much smaller and broader peak is also observed at ~ 30 K in $\text{Cu}_{67.93}\text{Zn}_{16.14}\text{Al}_{15.93}$ and $\text{Cu}_{68.91}\text{Zn}_{13.17}\text{Al}_{17.92}$. Copper also has a peak near the same temperature and serves as a favorable comparison for the martensite phase.

From Fig. 6 the different behavior of the low-temperature heat capacity of parent and martensitic phases in Cu-Zn-Al is evidenced. While the martensitic phase shows the typical behavior of close-packed metallic phases,^{27,28} strong deviations from pure Debye behavior are observed in the open-

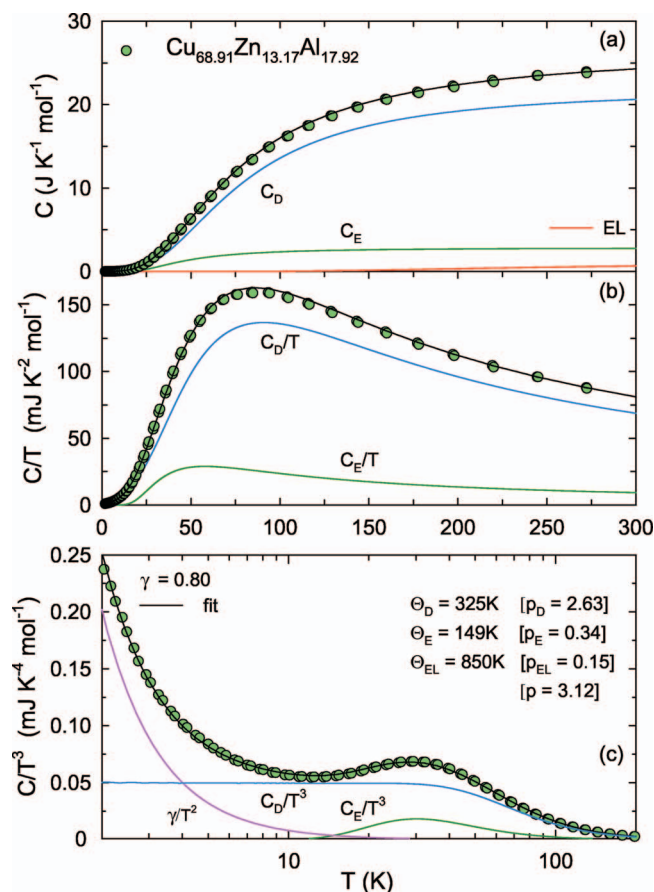


FIG. 3. (Color) Specific-heat data for $\text{Cu}_{68.91}\text{Zn}_{13.17}\text{Al}_{17.92}$. This composition remains in the close-packed martensite phase over the measured temperature range.

structure phase, especially in the low-temperature region where the Debye prediction is in principle expected to apply. This anomalous behavior is essentially related to the weak restoring forces for displacements on the $\{110\}$ planes along $\langle 1\bar{1}0 \rangle$. These weak restoring forces result in the appearance of Van Hove singularities at low frequencies in the phonon density of states. This is illustrated in Fig. 7 where we compare the $g(\omega)/\omega^2$ versus ω in β -brass (open structure), α -brass (close-packed structure), and pure copper. The figure has been produced by digitizing published data. Data for the density of states were obtained by digitizing the data of Ref. 29 for copper, from Ref. 30 for α - $\text{Cu}_{0.75}\text{Zn}_{0.25}$, and from Ref. 31 for β - $\text{Cu}_{0.53}\text{Zn}_{0.47}$. The data obtained from this digitization procedure were of poor quality below 4 meV. Thus, for each material we assumed a Debye density of states in the range 0–4 meV. The Debye temperatures used were $\theta_D = 342$ K for copper, $\theta_D = 305$ K for α -brass, and $\theta_D = 270$ K for β -brass. Strong deviations from Debye behavior ($g \sim \omega^2$) are observed in β -brass in a low-frequency region (a sharp peak is located at about 6 meV). In contrast, α -brass behaves very similarly to pure Cu, showing smaller deviations from the Debye model prediction in the low-frequency region.

In Fig. 8, we show a comparison of our data for the lattice heat capacity of $\text{Cu}_{68.91}\text{Zn}_{13.17}\text{Al}_{17.92}$ (close-packed structure) with the computed lattice heat capacity of Cu and of

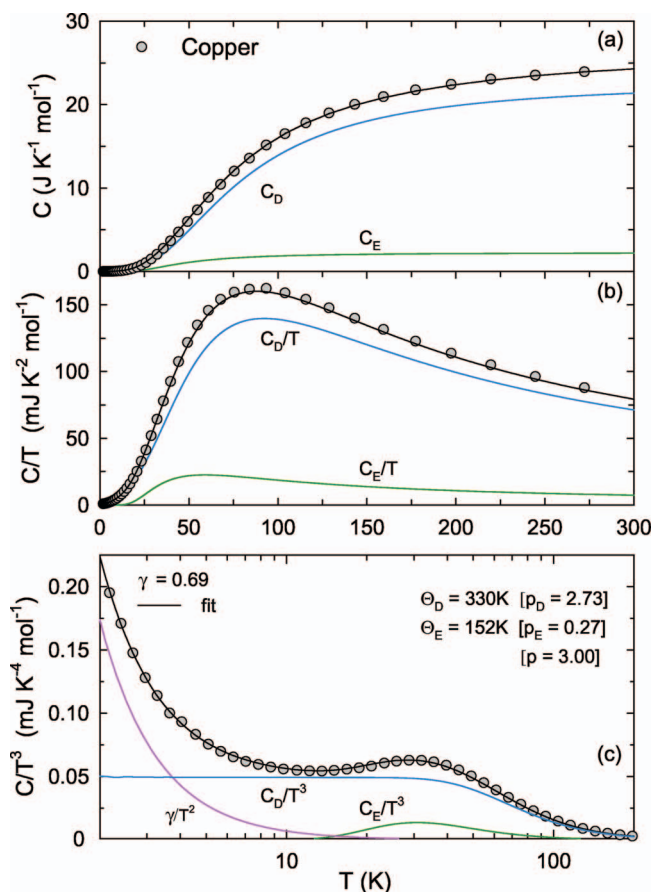


FIG. 4. (Color) Specific-heat data for single-crystal copper. Copper was chosen as a comparison to the close-packed martensite phase. The fit parameters and BP are comparable for the two materials although C_E for copper is smaller.

α - $\text{Cu}_{0.75}\text{Zn}_{0.25}$. In Fig. 9 we show the same comparison for $\text{Cu}_{61.98}\text{Zn}_{28.04}\text{Al}_{9.98}$ (open structure) and β - $\text{Cu}_{0.53}\text{Zn}_{0.47}$. The lattice heat capacity of pure copper, α -brass, and β -brass was

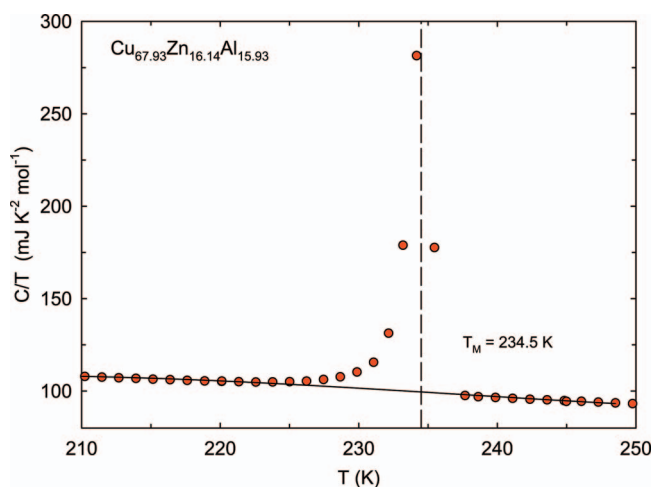


FIG. 5. (Color) Expanded plot of C/T in the vicinity of the first-order MT at $T_M = 234.5$ K. The polynomial background curve C_{bkg} through the points above and below T_M clearly demonstrates that there is little or no change in the lattice heat capacity associated with the transition. The full height of C/T for the MT is not shown.

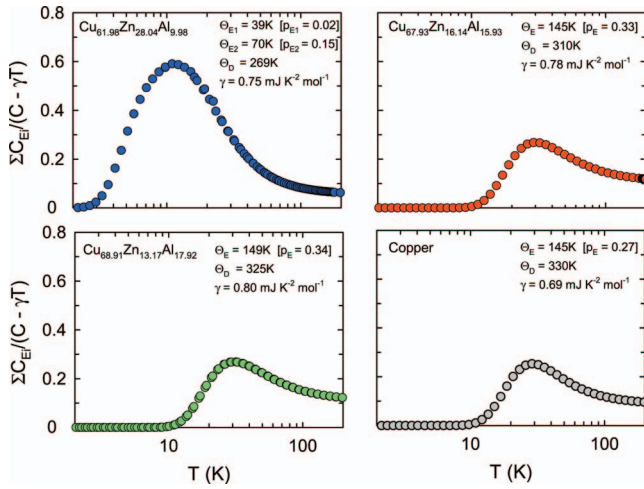


FIG. 6. (Color) $\Sigma C_{Ei}/(C - \gamma T)$ plotted versus T to show the Einstein contributions associated with the peaks relative to the total lattice specific heat. The quantity $\Sigma C_{Ei}/(C - \gamma T)$ is a convenient way to express the excess contribution relative to the total C . The peaks in $\Sigma C_{Ei}/(C - \gamma T)$ are about twice larger for $\text{Cu}_{61.98}\text{Zn}_{28.04}\text{Al}_{9.98}$ than for either $\text{Cu}_{67.93}\text{Zn}_{16.14}\text{Al}_{15.93}$ or $\text{Cu}_{68.91}\text{Zn}_{13.17}\text{Al}_{17.92}$, which are nearly identical. It is also about twice larger than that for copper.

computed by convoluting the phonon densities of states shown in Fig. 7 with the heat capacity of an Einstein oscillator, as earlier shown in Eq. (3). As shown in Fig. 8, the temperature and amplitude of the modes calculated from the phonon density of states for copper are in favorable agreement with those measured for the $\text{Cu}_{61.98}\text{Zn}_{28.04}\text{Al}_{9.98}$ SMA. Although an excess heat capacity contribution at the proper

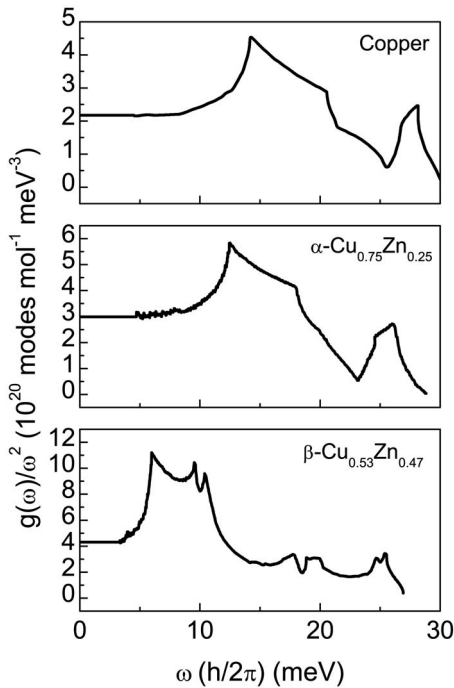


FIG. 7. Comparison of phonon spectra. Copper and $\alpha\text{-CuZn}$ have been added because they are close packed and similar to the martensite phase. The Debye temperatures used were $\theta_D = 342\text{ K}$ for copper, 305 K for $\alpha\text{-brass}$, and 270 K for $\beta\text{-brass}$.

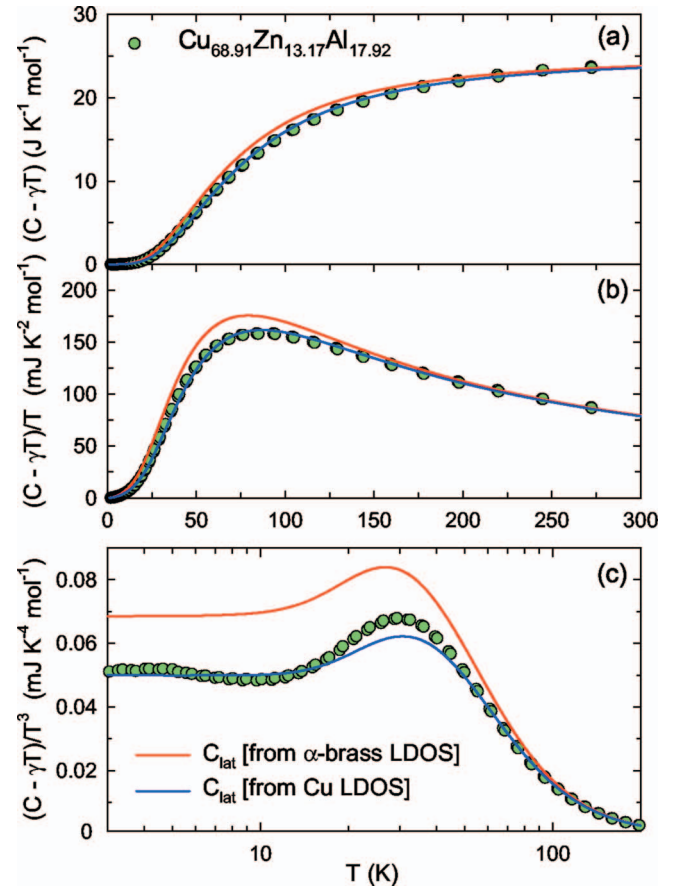


FIG. 8. (Color) Lattice heat capacity $(C - \gamma T)$ as a function of temperature plotted as (a) $(C - \gamma T)$ versus T ; (b) $(C - \gamma T)/T$ versus T ; and (c) $(C - \gamma T)/T^3$ versus $\log_{10} T$. The symbols are our data for $\text{Cu}_{68.91}\text{Zn}_{13.17}\text{Al}_{17.92}$ (martensite phase), whereas the curves were calculated for $\alpha\text{-Cu}_{0.75}\text{Zn}_{0.25}$ and pure Cu by integrating over the phonon densities of states shown in Fig. 7. The temperature and amplitude of the peak calculated from the phonon density of states for copper are in favorable agreement with the measured one. A similar calculation for $\alpha\text{-brass}$ produces a BP at the proper temperature but the heat capacity below $\sim 40\text{ K}$ is much greater. Quantitatively for copper and qualitatively for $\alpha\text{-brass}$, all three materials have a similar phonon density of states at low frequencies.

temperature is obtained using the $\alpha\text{-brass}$ phonon density of states the heat capacity below $\sim 40\text{ K}$ is much greater. This fact suggests that the low-frequency phonon density of states of the close-packed SMA is quantitatively similar to that of copper, but only qualitatively similar to those for $\alpha\text{-brass}$. Likewise, Fig. 9 shows that the excess contribution computed from the density of states of $\beta\text{-brass}$ is comparable to that measured for the SMA, suggesting that the two materials have a similar density of states at low frequencies. However, it is clear that an excess appears at an even lower temperature and has a larger amplitude in the SMA than in $\beta\text{-brass}$. Thus the soft modes in the SMA must extend to even lower frequencies than the soft modes in $\beta\text{-brass}$.

The excess heat capacity in the open structure of the shape-memory alloy originates from the low-energy vibrational modes, and the energy as determined from specific-heat data compares favorably to the energy of the TA_2

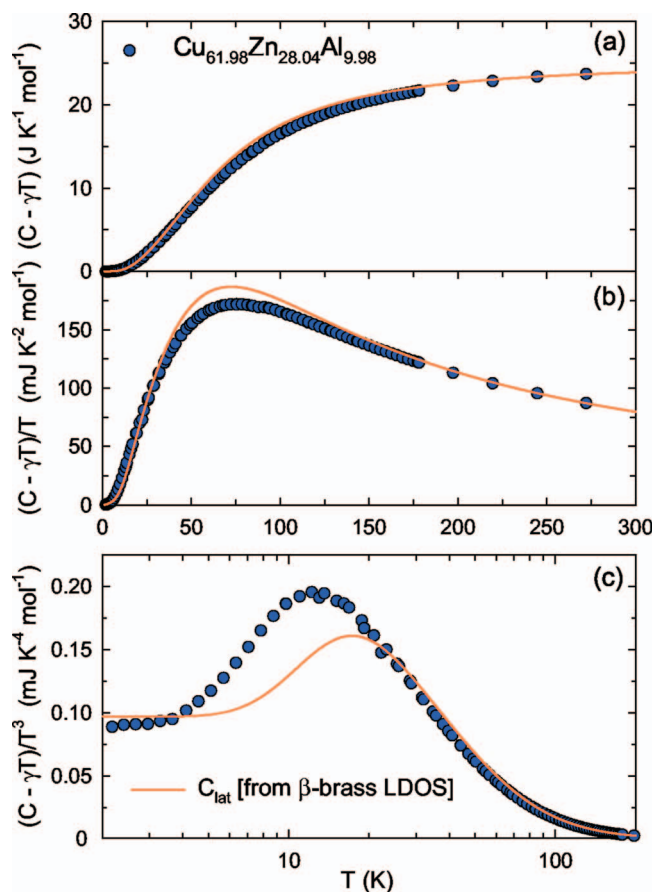


FIG. 9. (Color) Lattice heat capacity ($C - \gamma T$) as a function of temperature plotted as (a) $(C - \gamma T)$ versus T ; (b) $(C - \gamma T)/T$ versus T ; and (c) $(C - \gamma T)/T^3$ versus $\log_{10} T$. The symbols are our data for $\text{Cu}_{61.98}\text{Zn}_{28.04}\text{Al}_{9.98}$ (open-structure phase), whereas the curves were calculated for $\beta\text{-Cu}_{0.53}\text{Zn}_{0.47}$ by integrating over the phonon density of states shown in Fig. 7. The amplitude of the peak calculated from the phonon density of states for β -brass is comparable to the measured one but it occurs at a higher temperature. Qualitatively, the density of states for both materials is similar at low frequencies.

acoustic-phonon branch at the zone boundary.⁶ These low-energy modes represent a small fraction of all modes, with frequencies spanning a relatively small range. To a good approximation, they can be treated as low-energy Einstein modes, and they are responsible for significant deviations of the heat capacity from the expected Debye prediction at low temperatures. In fact, this apparently anomalous behavior seems to be common to a class of crystallographically open (bcc-based) materials that show an incipient instability with respect to $(110)[\bar{1}\bar{1}0]$ transversal displacements. In the present paper we have shown that a combination of Debye and Einstein expressions is suitable to reproduce the BP be-

havior in Cu-based shape-memory alloys. Soft modes are described by Einstein term(s), and we have shown that they represent $\sim 5\%$ of the total number of vibrational modes. Moreover, our results prove the suitability of the model proposed in Ref. 12 to account for the vibrational properties of Cu-based shape-memory alloys.

The small peak in $\Sigma C_{Ei}/(C - \gamma T)$ detected in the close-packed phase is reminiscent of the excess heat capacity in the open-structure phase. This result is in agreement with the fact that, in the martensitic state, the phonon branch that is derived from the TA_2 cubic branch has higher energies. However, such a branch is still lower than the other phonon branches in martensites.^{1,32} The Cu-based SMAs are composed of light mass elements and are free-electron-like. Therefore, it is likely that the vibrational entropy of the parent and martensitic phases could be related to geometrical features of open and close-packed structures, which impose different degrees of rigidity by underconstraining or overconstraining atom displacements.

V. CONCLUSIONS

We have measured the low-temperature specific heat in both cubic and martensitic phases of Cu-Zn-Al single crystals. The data have enabled us to compare the vibrational behavior of the two phases. Results show that the alloys behave mostly as free-electron phases in both phases although the vibrational contribution turns out to be very different. While the martensitic phase behaves very similarly to pure Cu, the cubic phase shows a significant concentration of low-frequency modes in the low-temperature region. Many neutron scattering experiments have been performed in Cu-based SMAs which show that the TA_2 branch is flat. From the analysis of the heat capacity the average Einstein temperature associated with the boson peak of the cubic phase (Fig. 1) is ~ 60 K. This temperature is in favorable agreement with the characteristic temperature deduced from the zone-boundary frequency of the TA_2 phonons. For Cu-based shape-memory alloys $\hbar\omega_{ZB} \approx 5$ meV and the corresponding characteristic temperature $\hbar\omega_{ZB}/k \approx 58$ K, which is perfectly comparable with the Einstein temperature obtained from specific-heat measurements.

ACKNOWLEDGMENTS

We thank Turab Lookman, Ricardo Schwarz, and Peter Riseborough for helpful discussions. Part of this work was carried out under the auspices of the United States Department of Energy. Part of this work was supported by CICYT (Spain) Project No. MAT2004-1291 and CIRIT (Catalonia) Project No. 2005SGR00969. R.R. acknowledges financial support from Secretaria de Estado de Universidades e Investigación (MEC, Spain).

*Present address: Department of Physics, Clemson University, Clemson, SC 29634, USA.

- ¹A. Planes and L. Mañosa, *Solid State Phys.* **55**, 159 (2001).
- ²J. Friedel, *J. Phys. (Paris), Lett.* **38**, 39 (1974).
- ³A. Zangwill and R. Bruinsma, *Comments Condens. Matter Phys.* **13**, 1 (1987).
- ⁴B. Fultz, L. Anthony, L. J. Nagel, R. M. Nicklow, and S. Spooner, *Phys. Rev. B* **52**, 3315 (1995).
- ⁵C. Zener, *Phys. Rev.* **71**, 846 (1947).
- ⁶L. Mañosa, J. Zarestky, T. Lograsso, D. W. Delaney, and C. Stassis, *Phys. Rev. B* **48**, 15708 (1993).
- ⁷A. Nagasawa and Y. Morii, *Mater. Trans., JIM* **34**, 855 (1993).
- ⁸G. Guénin, M. Morin, P. F. Gobin, W. de Jonghe, and L. Delaey, *Scr. Metall.* **11**, 1071 (1977).
- ⁹M. Mori, Y. Yamada, and G. Shirane, *Solid State Commun.* **17**, 127 (1975).
- ¹⁰W. Petry, A. Heiming, J. Trampenau, M. Alba, C. Herzig, H. R. Schober, and G. Vogl, *Phys. Rev. B* **43**, 10933 (1991).
- ¹¹S. M. Shapiro, B. X. Yang, G. Shirane, Y. Noda, and L. E. Tanner, *Phys. Rev. Lett.* **62**, 1298 (1989).
- ¹²M. Stipcich, J. Marcos, L. Mañosa, A. Planes, and R. Romero, *Phys. Rev. B* **68**, 214302 (2003).
- ¹³B. Frick and D. Richter, *Science* **267**, 1939 (1995).
- ¹⁴T. Nakayama, *Rep. Prog. Phys.* **65**, 1195 (2002).
- ¹⁵W. Schirmacher, G. Diezemann, and C. Ganter, *Phys. Rev. Lett.* **81**, 136 (1998).
- ¹⁶E. R. Grannan, M. Randeria, and J. P. Sethna, *Phys. Rev. B* **41**, 7799 (1990).
- ¹⁷D. J. Safarik, R. B. Schwarz, and M. F. Hundley, *Phys. Rev. Lett.* **96**, 195902 (2006); J. W. Lynn, H. G. Smith, and R. M. Nicklow, *Phys. Rev. B* **8**, 3493 (1973).
- ¹⁸W. N. Lawless, *Phys. Rev. B* **14**, 134 (1976).
- ¹⁹A. P. Ramirez and G. R. Kowach, *Phys. Rev. Lett.* **80**, 4903 (1998).
- ²⁰T. W. Darling *et al.*, *Philos. Mag. B* **82**, 825 (2002).
- ²¹J. C. Lashley, R. A. Fisher, J. Floquet, A. Huxley, and N. E. Phillips, *Physica B* **378-379**, 961 (2006).
- ²²J. C. Lashley *et al.*, *Cryogenics* **43**, 369 (2003).
- ²³D. Abbé, R. Caudron, and R. Pynn, *J. Phys. F: Met. Phys.* **14**, 1117 (1984).
- ²⁴R. Romero and J. L. Pelegrina, *Phys. Rev. B* **50**, 9046 (1994).
- ²⁵The difference of θ_D in cubic and martensitic samples cannot be considered as indicative of a possible difference in heat capacity between parent and martensitic phases due to the different composition of the two samples.
- ²⁶L. Mañosa, A. Planes, J. Ortín, and B. Martínez, *Phys. Rev. B* **48**, 3611 (1993).
- ²⁷E. S. R. Gopal, *Specific Heats at Low Temperature* (Heywood Books, London, 1966).
- ²⁸A. Tari, *The Specific Heats of Matter at Low Temperature* (Imperial College Press, London, 2003).
- ²⁹R. N. Nicklow, G. Gilat, H. G. Smith, L. J. Raubenheimer, and M. K. Wilkinson, *Phys. Rev.* **164**, 922 (1967).
- ³⁰E. D. Hallmann and B. N. Brockhouse, *Can. J. Phys.* **47**, 1117 (1969).
- ³¹G. Gilat and G. Dolling, *Phys. Rev.* **138**, A1053 (1965).
- ³²H. Chou, S. M. Shapiro, S. C. Moss, and M. Mostoller, *Phys. Rev. B* **42**, 500 (1990).