Excess modes and enhanced scattering in rare-earth-doped amorphous silicon thin films

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We report specific heat and thermal conductivity of gadolinium- and yttrium-doped amorphous silicon thin films measured using silicon-nitride membrane-based microcalorimeters. Addition of gadolinium or yttrium to the amorphous silicon network reduces the thermal conductivity over a wide temperature range while significantly increasing the specific heat. This result indicates that a large number of nonpropagating states are added to the vibrational spectrum that are most likely caused either by localized vibration of the dopant atom in a Si cage or softening of the material forming the cage structures. High-resolution cross-sectional electron micrographs reveal columnar features in Gd-doped material which do not appear in pure amorphous silicon. Scattering from both the nanoscaled columns and the filled-cage structures play a role in the reduced thermal conductivity in the rare-earth-doped amorphous semiconductor. The overall result is an amorphous solid with a large bump in C/T^3 and no plateau in thermal conductivity.

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I. INTRODUCTION

A wide range of amorphous materials have similar features in specific heat, thermal conductivity, and various spectroscopies that suggest a common physical origin. The most notable of these features are a linear term in the specific heat, C, observed below 2 K, thermal conductivity $k \propto T^{1.8}$ in the same temperature range, a broad peak in C/T^3 between 10 and 50 K which is larger than in the corresponding crystalline phase, and a plateau in k over the same temperature range.[1] The peak in C/T^3 is often correlated with excess vibrational density of states seen in neutron or Raman scattering, referred to either as a "boson peak"[2] or "excess modes."[3,4] Despite several decades of study, no microscopic theory exists that offers a complete explanation of these phenomena. The standard tunneling model is a widely accepted description of the behavior of C and k below 2 K. In this model the linear term in C is attributed to two-level tunneling systems (TLS), with the behavior of k explained by scattering from these states.[5,6] This model offers little explanation of the physical nature or origin of the very closely spaced energy levels. There have been several efforts to develop physical models which also explain the C/T^3 peak and k plateau. Examples are the soft-potential model,[7,8] the fracton model,[9,10] and a model relating dynamics at the glass transition to the low temperature phenomena.[11,12]

Amorphous silicon (a-Si) forms a tetrahedrally bonded continuous random network and can be made only in thin-film form by evaporation, sputtering, and various chemical vapor deposition techniques. Undercoordinated Si atoms form dangling bond defects, which can be reduced by introducing hydrogen either during deposition or after film growth. The hydrogenated material, a-Si:H, shows improved electronic properties and has several important industrial applications for large area microelectronic devices. a-Si is often studied theoretically, in part because of its relatively simple structure, but also due to several predicted and observed deviations from typical amorphous solids. Both theory and experimental evidence suggest a strikingly low density of two-level systems, a relatively large change in the Debye temperature between crystalline and amorphous silicon, and a relatively small peak in C/T^3 in a-Si, deviating less from the Debye model than does the crystalline phase.[4,5,13–15] Properties ranging from electrical conductivity to density of TLS also show a strong dependence on the a-Si film growth method.[16] Another example is the thermal conductivity plateau, though due to the difficulty of thermal measurements on thin-film samples, measurements of k in the expected temperature range of the plateau exist for only three samples: An ≈ 50 μm thick sputtered sample reported by Pompe and Hegenbarth[17] that shows a fairly well defined plateau, and much thinner 130 and 277nm thick films recently reported by our group grown by e-beam evaporation that show no evidence of the plateau.[15] Both results can be reasonably explained by the theory presented by Feldman and co-workers[4] with different treatment of the scattering of low energy, small wave vector vibrations.

Amorphous rare-earth-silicon alloys (a-RE_xSi_{1-x}, with RE=Gd, Y, Tb, etc.) prepared by e-beam codeposition have shown many phenomena related to the interaction between local RE magnetic moments and conduction electrons including a very large negative magnetoresistance at low temperatures.[18,19] A negative Hall coefficient[20] and thermopower[21] indicate that introducing the large, heavy RE adds carriers to the electron band, with the Gd ions contributing localized $S=7/2$ magnetic moments, while Y provides a nonmagnetic counterpart with nearly identical ionic radius and valency. Recent computational and experimental results shed some light on the structure of a-Gd_xSi_{1-x} and its nonmagnetic analog a-Y_xSi_{1-x}. Local density functional theory simulations of a-Y_xSi_{1-x} suggest that Y^{3+} ions are surrounded by low-coordinated Si, leaving them in a "cage" of dangling bonds.[22] X-ray absorption fine structure (XAFS) experiments on a-Gd_xSi_{1-x} using both the Si and Gd absorption edges give a similar picture, with Si atoms as nearest neighbors to the Gd ions and no clustering.[23] The XAFS studies also indicate that neither the Si coordination number

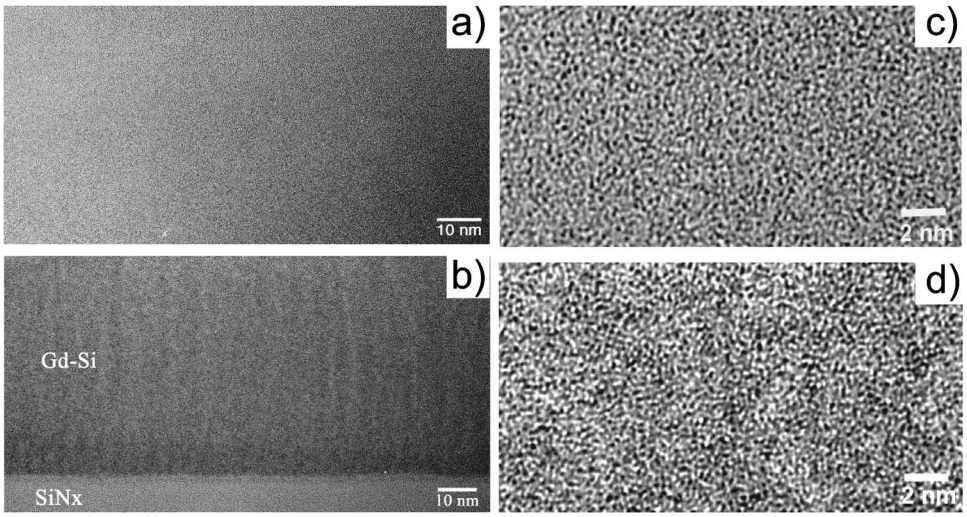

FIG. 1. XTEM images comparing *a*-Si and *a*-$Gd_{18}Si_{82}$ thin films. At low magnification (a) *a*-Si is featureless and shows no sign of crystallinity, while (b) *a*-$Gd_{18}Si_{82}$ is clearly amorphous but with columnar structures with approximate spacing of 3–4 nm. Higher magnification images confirm the amorphous nature of both (c) *a*-Si and (d) *a*-$Gd_{18}Si_{82}$.

nor the Gd–Si distance changes with Gd composition, suggesting a Si cage but no dangling bonds. Electron spin resonance measurements indicate that the addition of even small amounts of Gd to the Si matrix eliminates the dangling bonds.[24] Cages in *a*-Gd_xSi_{1-x} are further supported by calculations using the full potential linearized augmented plane wave method.[25]

This filled-cage structure is reminiscent of the filled skutterudite antimonides, such as $CeFe_4Sb_{12}$ (Ref. 26) or $RE_{1-y}Fe_{4-x}Co_xSb_{12}$ (RE=La,Ce),[27] or Sr or Eu doped Ge clathrates,[28] where the heavy La, Ce, Sr, or Eu dopant atoms fill cages in the host crystal structure. Slack originally proposed that "rattling" movement of the heavy dopant atom in the anharmonic potential of the cage would strongly scatter phonons but not charge carriers, resulting in a material with a high thermoelectric figure of merit.[29] Although there is some debate about the detailed mechanism of the phonon scattering,[30–32] it is clear that the filled-cage structures in these materials dramatically alter the vibrational spectrum, reducing the thermal conductivity over a wide temperature range (at least 2–300 K), and increasing the specific heat.[30,33,34]

In this paper, we present specific heat and thermal conductivity measurements of gadolinium- and yttrium-doped amorphous silicon thin films from 3–100 K, as well as high-resolution cross-section transmission-electron microscope (XTEM) observations of the films. We compare these measurements to data on *a*-Si films grown by the same technique and literature values for crystalline silicon to probe the nature of vibrational states and scattering in rare-earth-doped amorphous silicon.

II. EXPERIMENT

Thin film *a*-Y_xSi_{1-x} and *a*-Gd_xSi_{1-x} samples were *e*-beam coevaporated from separate Y, Gd, and Si crucibles onto amorphous Si–N membrane-based microcalorimeters and amorphous Si–N coated Si substrates. The microcalorimeters and substrates were held near room temperature throughout the deposition, promoting the growth of amorphous films. Typical deposition pressures were $\leqslant 2\times10^{-8}$ Torr. The films on substrates were used to measure the film thickness via profilometry, the composition by Rutherford backscattering (RBS), the sound velocity as described below,[35] and for XTEM imaging. Both XAFS (Ref. 23) and RBS measurements indicate atomic densities consistent with pore-free films. A picosecond ultrasonic measurement[35] of the longitudinal sound velocity in a *a*-Gd_xSi_{1-x} film gave $v_L=(5.39\pm0.44)\times10^5$ cm/s, lower than the value measured in our *a*-Si, $v_L=(7.51\pm0.30)\times10^5$ cm/s. Detailed description of the microcalorimetry techniques for measuring C and k, including the determination and subtraction of background contributions, appear elsewhere.[36–38] For the k measurements presented here, the microcalorimeter background was approximately 85% of the total signal. For the C measurement, the background or addenda heat capacity was ~50% of the total heat capacity at 100 K and ~85% at 5 K. In both k and C measurements, the background subtraction dominates the estimated experimental error shown below.

III. RESULTS AND DISCUSSION

Figure 1 compares XTEM images for *a*-Si and *a*-$Gd_{18}Si_{82}$ films. The low magnification images show a featureless *a*-Si film [Fig. 1(a)], whereas the *a*-$Gd_{18}Si_{82}$ film grown under identical conditions shows a vertically streaked appearance indicative of a columnar structure [Fig. 1(b)]. This type of columnar microstructure is a common outcome of the vapor deposition process for evaporated films when atomic mobility at the growth surface is low. The higher magnification images [Figs. 1(c) and 1(d)] confirm that both films are dense, pore-free, and clearly amorphous at the atomic level.

Figure 2 compares k of *a*-Y_xSi_{1-x} and *a*-Gd_xSi_{1-x} films to Pompe and Hegenbarth's sputtered 50 μm thick *a*-Si film[17] and *e*-beam evaporated thin-film *a*-Si.[15] The top axis indicates the estimated wavelength of the vibrations which carry the most heat in the dominant phonon approximation,[40] calculated for *a*-$Y_{12}Si_{88}$. The *e*-beam *a*-Si shows a lower k than the extremely thick sputtered film and no plateau. Addition of Y or Gd to the material further reduces k over the entire temperature range measured, and the three alloy films all

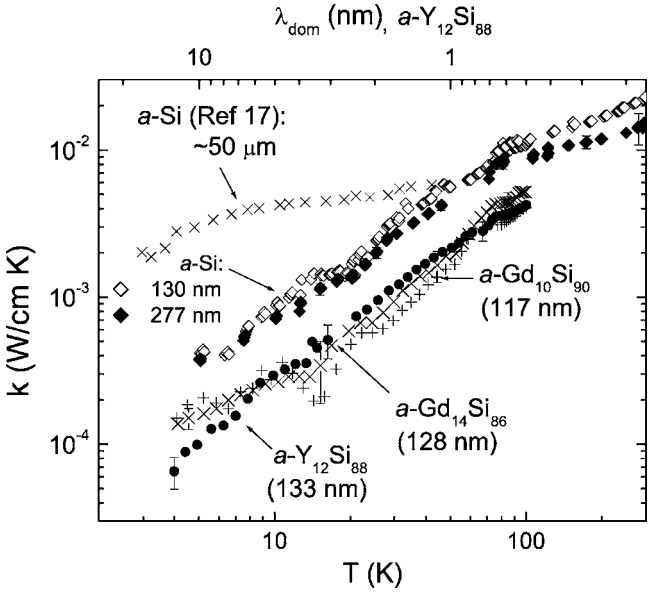

FIG. 2. k vs T plot comparing a-$Y_{12}Si_{88}$, a-$Gd_{10}Si_{90}$, and a-$Gd_{14}Si_{86}$ to thin e-beam evaporated a-Si films (Ref. 15) and previously published values for a-Si in the plateau regime (Ref. 17). The top axis is explained in the text.

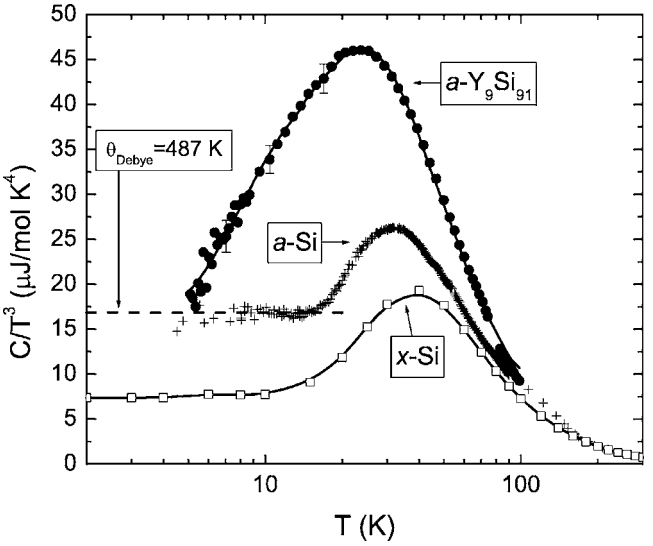

FIG. 3. C/T^3 vs T plot showing a-Y_xSi_{1-x}, a-Si (Ref. 15), and x-Si (Ref. 39). The dashed line indicates the measured Debye contribution in a-Si (Ref. 15) and the solid line through the a-Y_xSi_{1-x} data is a fit described below.

have the same k within error bars at all T. This reduction occurs despite the addition of electrons to the material, which increases the electrical conductivity dramatically; for example, at 4 K the electrical conductivity of a-$Gd_{15}Si_{85}$ is nearly 500 times larger than a-$Gd_{13}Si_{87}$.[18] However, this is not surprising, since a Wiedemann-Franz law estimation of the electronic contribution gives values at least an order of magnitude smaller than the measured values of k shown in Fig. 2. This suggests that k is totally dominated by vibrational excitations. In addition to the lack of composition dependence, k of a-Gd_xSi_{1-x} (which shows a huge negative magnetoresistance at low T, e.g., for $x=11$ a factor of 100 at 4 K in 8 T) showed no measurable change in applied magnetic fields up to 8 T.

Figure 3 compares C/T^3 vs T (in J/g K^4) for a-Y_9Si_{91} to thin-film a-Si (Ref. 15) and bulk crystalline silicon.[39] The dashed line is the Debye specific heat function, C_D, for θ_D =487 K, which we previously measured for a-Si.[15] C/T^3 for a-Y_9Si_{91} shows a much larger bump than that seen in either a-Si or crystalline Si. a-Y_xSi_{1-x} for a broad range of x have very similar specific heat above 60 K, and all show a large maxima in C/T^3 equal to or greater than that shown here. Samples with larger x have electronic terms, γT (which appear as γ/T^2 on a C/T^3 plot), and an additional contribution to C occurs in samples near the metal-insulator transition.[41] We have previously reported the specific heat of a-Gd_xSi_{1-x}, which is similar to values for a-Y_xSi_{1-x} above 60 K, but is dominated at lower temperatures by large contributions from magnetic degrees of freedom.[41–43]

Figure 4 compares k vs T below 100 K for a-Si and a-Y_xSi_{1-x} to two porous glasses, a porous silica (Vycor) sample with 29% porosity[44] (dashed line) and a glassy borosilicate material formed by fusing an array of capillaries (▽).[45] The data for both porous materials have been corrected for the missing volume of the pores. Neither of these materials have a k plateau in the typical temperature range, though Vycor shows an apparent plateau at much lower temperature. The reduction of k in these porous materials is due to enhanced damping or scattering of long-wavelength modes caused by the pores.[45,46] The addition of Gd and Y to a-Si reduces k by a quantitatively similar factor as does the addition of pores to a-SiO_2, but must rely on a different mechanism for scattering of heat carriers.

The structural evidence from XTEM (shown in Fig. 1), XAFS measurements, and simulations suggests two likely

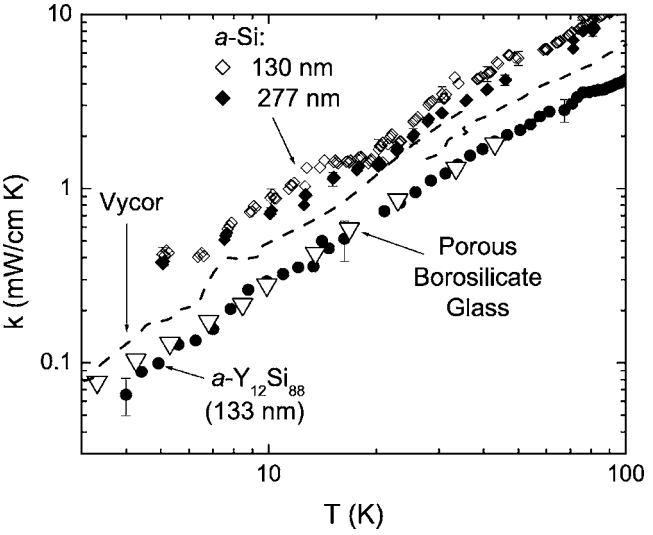

FIG. 4. k vs T for dense, pore-free a-Si (◇, ◆) and a-Y_xSi_{1-x} (•) thin films compared to data for Vycor, a silica glass with 29% porosity (dashed line) (Ref. 44) and a borosilicate glass sample (▽) with artificially structured arrays of pores (Ref. 45). k of a-SiO_2 is not shown but is only slightly higher than a-Si values at 10 K (Ref. 1). At this temperature, k for these two porous materials is 2–4 times lower than for a-SiO_2, while adding Y to a-Si reduces k by approximately a factor of 3.

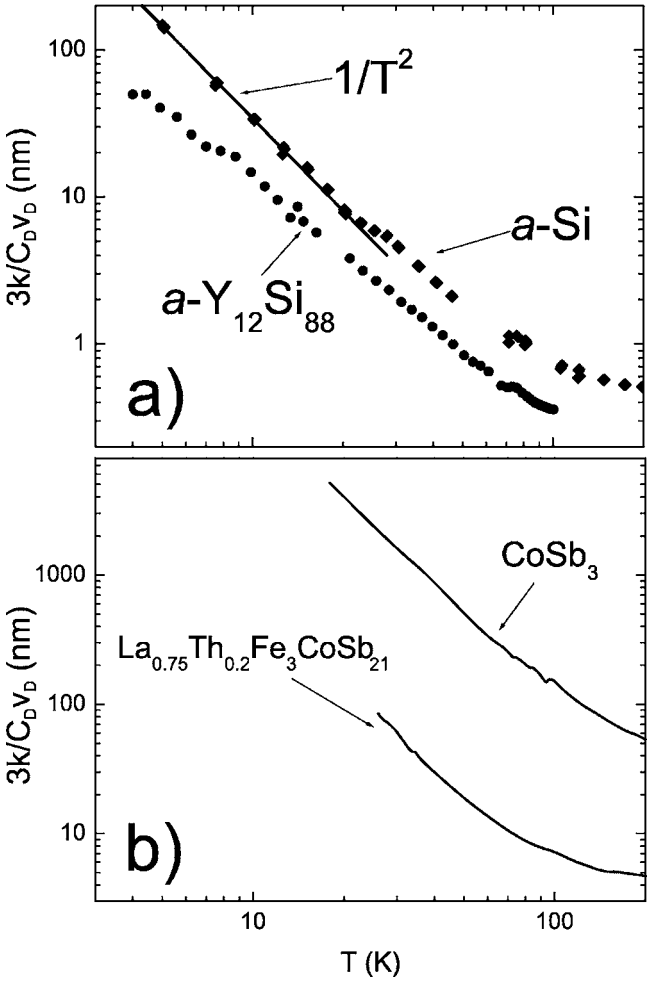

FIG. 5. Estimated mean free path (MFP) ($3k/C_Dv_D$, as described in the text) for vibrations vs T. (a) a-$Y_{12}Si_{88}$ (heavy solid line) compared to a a-Si film (dashed line) grown by the same technique. Adding Y to a-Si reduces MFP at all T measured here. (b) Filled ($La_{0.75}Th_{0.2}Fe_3CoSb_{12}$) and unfilled ($CoSb_3$) skutterudite antimonides (Ref. 27). Filling the skutterudite cage structures with La causes a similar reduction in the estimated MFP over the whole measured temperature range.

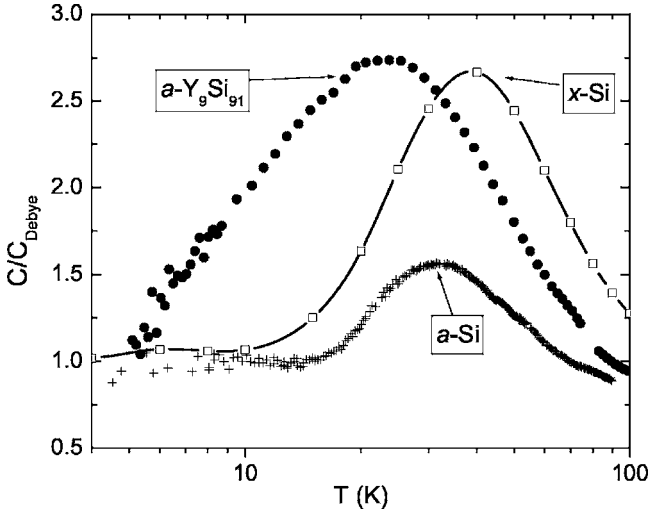

FIG. 6. C/C_D plot compares contributions to C in excess of the Debye model for crystalline Si (Ref. 39), a-Si, (Ref. 15), and a-Y_9Si_{91}. The line through the crystalline Si data is a guide to the eye. The low C/C_D for a-Si compared to crystalline Si is atypical for amorphous systems, where the peak in C/T^3 is typically larger than in the corresponding crystal. The larger C/C_D in a-Y_9Si_{91} is closer to expectedbehavior for amorphous systems.

mechanisms for enhanced scattering of propagating vibrational excitations in a-RE_xSi_{1-x} compared to a-Si: Effects of the columnar structural features, and rattling of the caged Y or Gd dopants. While our measurements of C confirm that the rattling dopants play an important role in the thermal properties of the rare-earth-doped amorphous silicon, the k measurements we present here cannot clearly distinguish whether the rattling cage modes themselves or the columnar structure caused by the added rare-earth dopants cause the reduced thermal conductivity.

Figure 5(a) is a plot of $3k/C_Dv_D$ vs T for amorphous Si and a-Y_xSi_{1-x} films. Here v_D is the estimated Debye velocity and C_D is the corresponding specific heat contribution from propagating modes, estimated here using θ_D=487 K measured for a-Si.[15] Where k and C are dominated by propagating modes, $3k/C_Dv_D$ gives the mean free path. At temperatures where C and k have significant contributions from modes which are not simple propagating excitations, this quantity is at best an upper limit of the mean free path. For a-Si both C and k are dominated by propagating modes below 20 K.[4] At these temperatures, the mean free path in a-Si goes as T^{-2}, indicating that scattering of vibrations goes as Q^2.[15] In a-$Y_{12}Si_{88}$, $3k/C_Dv_D$ is shorter than in a-Si throughout the measured temperature range and is roughly $\propto T^{-1.65}$ below 20 K.

Figure 5(b) makes a similar comparison between filled and unfilled skutterudites, using k, v_D, and C_D values reported by Sales *et al.*[27] Filling the cage in the skutterudite crystal with the heavy La dopant reduces the estimated mean free path over the whole measured temperature range, as did adding Y to a-Si. This suggests the interpretation that the similar overall suppression of $3k/C_Dv_D$ in a-Y_xSi_{1-x} is due to the effect of the rattling of caged rare-earth dopants, but the cause of the change in temperature dependence at low T cannot be determined from our data alone. Further study of a range of films prepared by different deposition techniques could help clarify whether this is due to scattering from the columnar variations or from the nanoscale cage structures.

Figure 6 compares the ratio of the measured C to the Debye contribution, C_D, for crystalline silicon, a-Si, and a-Y_9Si_{91}. In typical amorphous solids such as a-SiO_2, C is significantly larger than C_D, as a result of the excess modes.[1] We previously reported that the situation is very different in a-Si, where C more closely matches the Debye model than does crystalline Si.[15] As shown in Fig. 6, the additional nonpropagating vibrational states introduced by adding Y to the matrix cause C/C_D for a-Y_9Si_{91} to slightly exceed the value for crystalline Si, approaching the expectation for a typical amorphous material. It is also interesting to note that for a-Y_9Si_{91}, a-$Y_{13}Si_{87}$, and a-$Y_{21}Si_{79}$, the height of the peak in C/T^3, P_c, scales with its position in temperature, T_{max}, as $P_c \propto T_{max}^{-1.6}$, which agrees with the scaling observed by Liu and

Lohneysen for a wide range of amorphous solids.[47] Our recent *a*-Si measurement does not match this scaling behavior particularly well, indicating again that *a*-Si is a somewhat atypical amorphous material, while the additional nonpropagating vibrational states cause *a*-Y_xSi_{1-x} to show more typical behavior.

The exact nature of these states is unknown, though it seems likely that excess modes are added due to locally softened Si cages around the heavy dopants or to rattling of the dopant in the cage or both. It is clear from the reduced k that these excess modes do not carry heat. Several authors have reported a similar increase in the specific heat of filled skutterudites when compared to the "empty" host crystal. In the case of the skutterudites, the excess C can be explained by the contribution of one or more Einstein modes, which each contribute a term $C_E=(\theta_E/T)^2e^{(\theta_E/T)}/(e^{(\theta_E/T)}-1)^2$, where θ_E is the Einstein temperature. The observation of these Einstein contributions provides direct evidence of the localized "rattling" of the filler atom, and is corroborated by inelastic neutron scattering data, resonant ultrasound spectroscopy, and simulations.[33,34] There is still ongoing debate on the nature of the dynamics in these materials, with recent evidence from lattice dynamical models indicating that the motion of the cage-filling atom is harmonic rather than anharmonic.[30,32] However, these models still include well-defined peaks in the vibrational density of states that are due to the filler atom and lead to additional scattering of heat carriers.

Following the "rattling" atom analogy, we fit the measured specific heat of *a*-Y_9Si_{91} to the equation $C=C(a\text{-Si})+A_1C_{E1}+A_2C_{E2}+A_3C_{E3}$. A fit of this type assumes that the filling of the cages has little effect on the elastic properties of the host material, which we believe is true to good approximation for the *a*-Y_xSi_{1-x} sample. If this approximation does not hold, there are important implications for the physical interpretation of the resulting fit parameters.[30,32] The solid line in Fig. 3 represents the fit with $A_1=1.0$ J/mol K, $\theta_{E1}=194$ K, $A_2=0.83$ J/mol K, $\theta_{E2}=100$ K, and $A_3=0.086$J/mol K, $\theta_{E3}=52$ K. The data can be fit somewhat less well by two Einstein modes (~108 and 51 K), but is very poorly modeled with a single Einstein contribution.[48] As a comparison, Keppens *et al.* used Einstein modes at 70 and 200 K to explain the contribution of the rattling La atom in $La_{0.9}Fe_3CoSb_{12}$,[33] Feldman *et al.* modeled revised data on the same material with a more detailed lattice dynamics calculation but also noted the data could be fit using two Einstein modes,[30] while Hermann *et al.* needed only a single Einstein mode at 53 K to describe thallium rattling in similar antimony skutterudites.[34] The similarity of these results to the Y-doped amorphous Si data presented here suggests that similar physics drives the excess modes and reduced k in these two classes of materials.

Regardless of the exact nature of the contributions to C and k in *a*-Y_xSi_{1-x}, the combined effect of the addition of excess modes and the enhanced scattering is an amorphous material with a large bump in C/T^3 but no corresponding plateau in k. We conclude that the bump in C/T^3 and the plateau in k, which are often both observed in a given amorphous material, are not necessarily the work of the same physical mechanism. This suggests an interesting future experiment. It is currently a matter of debate whether the k plateau and C/T^3 bump and the related excess modes can be explained within a single theoretical framework with the TLS that dominate the low T properties of most amorphous insulators. Our work shows that addition of heavy Y dopants to *a*-Si, a material which has few excess modes and very low contributions from TLS, adds excess modes to the material. Study of *a*-Y_xSi_{1-x} below 2 K could indicate whether TLS have returned with the addition of Y, which would provide evidence of correlation between TLS and excess modes. This also suggests that addition of heavy dopants could provide a potentially tunable method for adding excess modes to *a*-Si, allowing systematic study of the vibrational excitations in amorphous insulators.

IV. CONCLUSIONS

In summary, we measured specific heat and thermal conductivity of Gd- and Y-doped amorphous Si thin films. Specific heat shows that a large number of excess vibrational modes are added, resulting in a bump in C/T^3 which is much larger than that in the pure amorphous material and also larger than in crystalline Si, in better agreement with expected behavior in amorphous insulators. This bump can be explained in a similar manner as the contribution of rattling modes to filled antimony skutterudites, suggesting that similar physics drives the thermal behavior of these rather different systems. Thermal conductivity shows that addition of the heavy dopant atoms introduces scattering which significantly reduces k below values measured for pure *a*-Si. Whether this reduction is caused directly by the rattling cage modes seen in the specific heat or indirectly by the columnar microstructure induced by the added rare-earth dopants cannot be distinguished by the present data. Furthermore, the ability to add excess modes to *a*-Si suggests that continuing study of heavy-atom doped amorphous silicon could enable a systematic probe of the correlation between tunneling systems and excess modes in amorphous materials.

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