

cay of the enhanced amplitude.

(iii) After exposure of the W surface to  $\sim 7$  L ( $1 \text{ L} = 10^{-6} \text{ Torr sec}$ ) of oxygen, the  $\langle 100 \rangle$  surface-peak intensity increases by  $\sim 20\%$ . This could be due to a lateral translation of the W surface atoms, as suggested by Bauer *et al.*<sup>14</sup> In any case this observation illustrates the importance of clean surfaces for comparison of surface-peak measurements with theory.

In conclusion, we have shown that the intensity of the surface peak behaves predictably as a function of energy or  $\rho/R$ . For  $\rho/R < 0.4$  in W the interaction is almost entirely with the first exposed monolayer. In general, MeV scattering from single crystals in the region of  $\rho/R < 1$  will be a useful surface tool.

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<sup>1</sup>E. Bøgh, in *Channeling*, edited by D. V. Morgan (Wiley, London, 1973), p. 435.

<sup>2</sup>J. A. Davies, D. P. Jackson, J. B. Mitchell, P. R.

Norton, and R. L. Tapping, *Phys. Lett.* **54A**, 239 (1975), and *Nucl. Instrum. Methods* **132**, 609 (1976).

<sup>3</sup>W. C. Turkenburg, thesis, University of Amsterdam, 1976 (unpublished).

<sup>4</sup>B. R. Appleton, D. M. Zehner, T. S. Noggle, J. W. Miller, O. E. Schow, III, L. H. Jenkins, and J. H. Barrett, in *Ion Beam Surface Layer Analysis*, edited by O. Meyer, G. Linker, and F. Kappeler (Plenum, New York, 1976), Vol. 2, p. 607.

<sup>5</sup>J. Lindhard, *K. Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **34**, No. 14 (1965).

<sup>6</sup>G. H. Wheatley and C. W. Caldwell, Jr., *Rev. Sci. Instrum.* **44**, 744 (1973).

<sup>7</sup>L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber, *Handbook of Auger Electron Spectroscopy* (Physical Electronics Industries, Inc., Edina, Minnesota, 1976), 2nd ed.

<sup>8</sup>J. A. Davies, in *Channeling*, edited by D. V. Morgan (Wiley, London, 1973), p. 391.

<sup>9</sup>J. F. Ziegler and W. K. Chu, *At. Data Nucl. Data Tables* **13**, 463 (1974).

<sup>10</sup>R. M. Nicklow, private communication, calculated from a publication of S. H. Chen and B. N. Brockhouse [*Solid State Commun.* **2**, 73 (1964)].

<sup>11</sup>J. H. Barrett, *Phys. Rev. B* **3**, 1527 (1971).

<sup>12</sup>B. W. Lee, A. Ignatiev, S. Y. Tong, and M. Van-Hove, *J. Vac. Sci. Technol.* **14**, 291 (1977).

<sup>13</sup>D. P. Jackson, *Surf. Sci.* **43**, 431 (1974).

<sup>14</sup>E. Bauer, H. Poppa, and V. Viswonath, *Surf. Sci.* **58**, 517 (1976).

## Linear Specific Heat of Disordered Solids at Low Temperatures

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It is shown that a linear specific heat in amorphous systems at low temperatures is a general consequence of the nonapplicability of the third law of thermodynamics. A hydrodynamic formula relating the pair density of states of Anderson *et al.* to diffusive and mechanical coefficients, determinable under favorable conditions by Rayleigh light scattering is also proposed.

Much interest has rightly been aroused by the observation of a low-temperature specific heat which is linear with temperature in amorphous solids<sup>1</sup> and also in spin-glasses.<sup>2</sup> In particular Anderson, Halperin, and Varma<sup>3</sup> have presented a model in which the linear temperature dependence is interpreted in terms of Schottky excitation between two levels; the two-level density of states at zero excitation energy determines the coefficient of this linear term.

In this Letter, we draw attention to the fact that for disordered systems in which the third law of thermodynamics is not obeyed, i.e., the entropy

$S(T)$  is nonzero as  $T \rightarrow 0$ , one must have a linear specific heat. The argument utilizes the following thermodynamic equations:

$$C_P - C_V = T\alpha^2 V / K_T, \quad (1)$$

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = - \frac{1}{V} \left( \frac{\partial S}{\partial P} \right)_T, \quad (2)$$

$$K_T / K_S = C_P / C_V, \quad (3)$$

where  $K$  represents the compressibility and  $C$  the specific heat. We see immediately from (1) that if  $C_P - C_V \propto T$  as  $T \rightarrow 0$ , then  $\alpha$ , the thermal expansion must tend to a constant as  $T \rightarrow 0$ , since

$K_T$  clearly remains finite in this limit.

But Eq. (2) shows us that this is a consequence of the fact that  $S(T=0) \neq 0$ , and therefore we can change  $S$ , or the total number of configurations, by compression. Thus, quite generally, we deduce from (1) and (2) that

$$C_P - C_V \propto T, \quad (4)$$

as a consequence of thermodynamics, which stems from nonzero thermal expansion as  $T \rightarrow 0$  in disordered systems.

Equation (3) now completes the argument. Normally, with the third law obeyed,  $K_T \rightarrow K_S$  as  $T \rightarrow 0$  and hence  $C_P \rightarrow C_V$ . But this is not true when the third law is no longer applicable. Hence (4) leads to  $C_P$  and  $C_V$  separately proportional to  $T$  at low temperatures.

Anderson, Halperin, and Varma<sup>3</sup> write that

$$C \simeq (\pi^2/6)k_B^2 n(0)T, \quad (5)$$

where  $n(0)$  is the density of pair states at zero excitation energy. If we assume the coefficients of  $T$  in  $C_P$  and  $C_V$  differ by a factor  $\gamma$  [note that formula (1) involves  $\alpha^2$  so that an order of magnitude cancellation would only lead to a factor  $\sim 3$  in  $\alpha$ ] then we find

$$(\gamma - 1)k_B^2 n(0) \sim \alpha^2(T=0)V/K_T. \quad (6)$$

By use of the Anderson, Halperin, and Varma<sup>3</sup> estimate of  $n(0)$  we get an estimate of the zero-temperature thermal expansion for fused silica as  $\sim (\gamma - 1)^{1/2} 10^{-6} \text{ K}^{-1}$  while the room-temperature value is  $1.5 \times 10^{-6} \text{ K}^{-1}$ . Obviously the deviation of  $\gamma$  from unity as  $T \rightarrow 0$  is all important in determining whether the low-temperature thermal expansion lies within the range of present experimental methods.

A little further information can be obtained from the thermodynamic relation

$$(\partial C_V / \partial V)_T = T(\partial / \partial T)(\alpha / K_T). \quad (7)$$

Since  $(\partial C_V / \partial V)_T \propto T$  at low temperatures, we must have  $\alpha / K_T \simeq \text{const} + O(T)$  at low temperatures, showing that either one or both of  $\alpha$  and  $K_T$  must be linear in  $T$  for disordered systems at low temperatures.

As is the case for specific models,<sup>3</sup> this line of argument implies that the configurations of interest for the specific heat at a low temperature  $T$  will be those which (a) are separated by sufficiently small barriers that tunneling between them can take place and thermal equilibration can occur during the time span of the relevant experiment, and (b) correspond to local minima which are ac-

cidental degenerate within an amount of order  $k_B T$ .

We turn next to what hydrodynamics can add to this discussion. Cohen, Fleming, and Gibbs<sup>4</sup> have given a set of hydrodynamic equations for a pure one-component amorphous solid. From these equations, we can derive the low-frequency part of the spectrum for configurational rearrangement. If we interpret the zero-frequency value of this spectrum as essentially  $n(0)$  of Anderson, Halperin, and Varma, then we find

$$n(0) \sim (\rho D / n_0^2) (\partial c / \partial \varphi_L)_{\rho, T}, \quad (8)$$

where  $\rho = mn$ , the mass density of the amorphous solid,  $D$  is the diffusion constant,  $c = 1 - n/n_0$  is to be interpreted<sup>4</sup> as the concentration of a free volume in the glass.  $\varphi_L$  is the longitudinal part of the variable which is thermodynamically conjugate to the strain. Thus  $(\partial c / \partial \varphi_L)_{\rho, T}$  is, essentially, telling us how mechanical properties change with degree of disorder. This will be a difficult quantity to measure directly; it is therefore worth remarking that  $D(\partial c / \partial \varphi_L)_{\rho, T}$  enters as a contribution to the Rayleigh intensity in light scattering, which may be separated from the thermal-fluctuation contribution under favorable conditions (see Ref. 4).  $D$  itself is, of course, then derivable from the half-width of the Rayleigh peak.

In summary, the nonapplicability of the third law has been shown to lead to a linear temperature dependence of the specific heat of disordered systems at low temperatures. The converse must *not* be assumed; for example, electrons in metals contribute a linear term to the specific heat but in metals  $C_P \rightarrow C_V$  as  $T \rightarrow 0$  and, of course, the thermal expansion therefore tends to zero at absolute zero. In a model such as that of Anderson, Halperin, and Varma,<sup>3</sup> it is shown that the density of pair states at zero excitation can be connected to thermodynamic and hydrodynamic quantities at least approximately. It would seem that the considerations of this Letter should prompt a careful experimental study at very low temperatures of the relation between specific heat, thermal expansion, and, if feasible, light-scattering properties of disordered systems of all kinds.

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<sup>1</sup>R. C. Zeller and R. O. Pohl, Phys. Rev. B 4, 2029

(1971).

<sup>2</sup>See P. W. Anderson, *Mater. Res. Bull.* **5**, 549 (1970).<sup>3</sup>P. W. Anderson, B. I. Halperin, and C. M. Varma,*Philos. Mag.* **25**, 1 (1972).<sup>4</sup>C. Cohen, P. D. Fleming, and J. H. Gibbs, *Phys. Rev. B* **13**, 866 (1976).

## Heavy-Ion-Induced Defect Production at Low Temperature in Superconducting Nb<sub>3</sub>Sn and Effects of Saturation

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Critical temperature  $T_c$  and transition width  $T_\phi$  of 5- $\mu$ m Nb<sub>3</sub>Sn samples (chemical vapor deposition) have been measured as functions of 25-MeV oxygen irradiation below 30 K and isochronal annealing up to 410 K. After the known strong reduction,  $T_c$  shows at high fluences leveling-off effects, a flat minimum followed by an increase revealing competing superimposed disorder mechanisms. Significant recovery of  $T_c$  and  $T_\phi$  to lower values is observed. Results are discussed in terms of atomic disordering and compared to  $n$  and He experiments at room temperatures.

It seems to be a property of A15 compounds  $T_3X$  containing a nontransition element  $X$  that it is quite difficult to change the long-range order parameter  $S$  ( $T$ -chain integrity) by thermal methods alone, as it can be varied to a greater extent in "atypical" A15 compounds. Irradiation with fast neutrons<sup>1-6</sup> and highly energetic ions (e.g., He<sup>7,8</sup> or oxygen<sup>9,10</sup> ions) is more successful in producing atomic disorder over a wide range.<sup>11</sup> Sweedler, Schweitzer, and Webb<sup>1</sup> were the first to observe a universal degradation of  $T_c$  after neutron-induced damage at ambient reactor temperatures correlating the density of antisite defects with the reduction in  $T_c$ . Similar results were obtained for A15 compounds when irradiated with highly energetic neutrons<sup>3,4,6,12</sup> and with heavy ions at low temperatures.<sup>9</sup> The antisite mechanism for the observed  $T_c$  depressions works well for Nb<sub>3</sub>Sn irradiated with neutrons<sup>1,6</sup> or with 25-MeV oxygen ions<sup>9,10,13-15</sup> at  $T \leq 30$  K; this agreement is remarkable although the data belong to various projectiles, irradiation temperatures, and sample types. The direct measurement of  $S(\text{Nb}_3\text{Al})$  supports this disorder mechanism.<sup>2</sup> However Poate *et al.*<sup>8</sup> found that  $T_c$  saturates at about 3 K after He bombardment at 50°C, an effect recently also reported after  $n$  irradiation.<sup>16</sup> In the region of saturation of  $T_c$ , the lattice constant continues to increase and the high-order x-ray lines show broadening and eventually weakening at very high fluences.<sup>7,17</sup> Furthermore, a correlation between  $T_c$  and the resistance ratio for several A15 compounds<sup>18</sup> has been found. This indicates that additional effects other than

the antisite mechanism may be of importance, e.g., the recently proposed smoothing-out of an unusually large energy-gap anisotropy.<sup>19</sup>

In this Letter we report on extensions of our previous irradiation experiments to confirm the existence of the saturation effect. It is of special interest whether this effect is observable also in bulk Nb<sub>3</sub>Sn with a complete different preparative prehistory in a low-temperature irradiation with different projectiles.

Our samples consist of a 5- $\mu$ m-thick Nb<sub>3</sub>Sn layer vapor-deposited onto 50- $\mu$ m Hastelloy tape used as commercial engineering material (for details of the chemical vapor-deposition preparation see Ziegler *et al.* and Pfister.<sup>20</sup> The atomic ratio Nb:Sn of  $3(\pm 0.1):1$  was measured by Rutherford backscattering analysis with 25-MeV <sup>16</sup>O ions.<sup>21</sup> The irradiations were carried out in the low-temperature irradiation facility using 25-MeV oxygen ions produced by a HVEC accelerator.<sup>13</sup> The pressure during the experiments was  $< 10^{-6}$  Torr. The range of the ion beam corresponds to about twice the thickness of the samples, thus a sufficiently homogeneous damage was produced without any doping with oxygen and, because of the high Coulomb barrier, without compositional changes by nuclear reactions. For a uniform irradiation, a suitable beam focus was scanned electrostatically by a triangle voltage over a defining collimator. The fluences were accurate within 5%. The temperature during irradiation was  $\leq 30$  K obtained from the linear temperature-fluence dependence.  $T_c$  was determined resistively with an accuracy of  $\pm 5$  mK by