

# Isotope effect on the heat capacity of the monatomic and diatomic semiconductors diamond and zinc oxide

R.K. Kremer, M. Cardona, G. Siegle and R. Lauck; S.K. Estreicher (Texas Tech University, USA); A.H. Romero (Unidad Querétaro, Mexico); M. Sanati (Texas Tech University, USA); J. Serrano (ESRF, France); T.R. Anthony (GE Corporate Research and Development, USA)

The availability of semiconductor crystals with different isotopic abundances has triggered profuse investigations of the effect of isotopic composition on thermodynamic, vibrational, and electronic properties [1]. Most of this work is concerned with monatomic semiconductors, i.e. diamond, Si, Ge, and  $\alpha$ -Sn. The effect of the isotopic masses in multinary compounds on the thermodynamic properties should essentially depend on which mass is being considered. We have determined the effect of isotope variation on the heat capacity at constant pressure,  $C_p$ , for a monatomic example, namely diamond, and for the diatomic system zinc oxide and compare our results with first-principles calculations.

Historically, the low-temperature heat capacity of diamond has played a central role in the development of the quantum theory of the thermal properties of solids. Natural diamond is composed of two stable isotopes,  $^{12}\text{C}$  ( $\approx 99\%$ ) and  $^{13}\text{C}$  ( $\approx 1\%$ ). Meanwhile, artificial diamonds with different isotopic compositions which cover the range  $^{12}\text{C}_{1-x}^{13}\text{C}_x$  ( $0 \leq x \leq 1$ ) grown by a high-pressure high-temperature technique became available.

Zinc oxide is a wurtzite-like semiconductor with an electronic band gap of 3.4 eV that makes it suitable for fabrication of optoelectronic devices in the ultraviolet range. Therefore an appropriate characterization of the thermodynamic properties, such as the thermal conductivity and the heat capacity, is essential for the development of high-quality devices. Recently, small single crystals of ZnO with a wide range of isotopic abundances (highly enriched  $^{64}\text{Zn}$ ,  $^{68}\text{Zn}$ ,  $^{18}\text{O}$ ) have been grown by chemical vapor transport. The Zn mass affects mainly the acoustic phonons, thus leading to isotopic effects on the heat capacity mostly at low temperatures, whereas the O mass affects mainly the optic phonons, which become thermally active at higher temperatures.

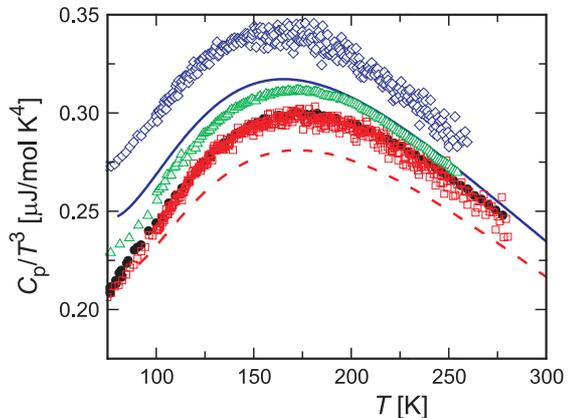


Figure 1: Temperature dependence of  $C_p/T^3$  measured for three samples with different isotopic compositions (red  $\square$   $^{12}\text{C}$ ; green  $\triangle$   $^{12}\text{C}_{58}^{13}\text{C}_{42}$ ; blue  $\diamond$   $^{13}\text{C}$ ). We have added to the figure the literature data reported for natural diamond ( $\bullet$ ) and the theoretical results based on self-consistent, first-principles molecular-dynamics simulations based on local density-functional theory [3] for  $^{12}\text{C}$  and  $^{13}\text{C}$  (red dashed and blue solid curves, respectively).

Figure 1 displays the specific heat of a natural diamond, a crystal with isotopic composition  $^{12}\text{C}_{0.58}^{13}\text{C}_{0.42}$  and a  $^{13}\text{C}$  sample. We have added the data of Desnoyers and Morrison for natural diamond which agree with ours to within the scatter ( $\pm 1\%$ ). The solid curves represent the calculations for  $^{12}\text{C}$  and  $^{13}\text{C}$  [3]. Whereas calculations fall, at the maxima of  $C_p/T^3$ , about 7% short of the measurements, they reproduce rather well the general trend of  $C_p/T^3$  vs.  $T$ . The 7% difference can be attributed to deficiencies of the fully *ab initio* model of the lattice dynamics, which uses a rather small 128 atom periodic supercell. It is worth pointing out, however, that the relative change observed at the maximum of  $C_p/T^3$ , between  $^{12}\text{C}$  and  $^{13}\text{C}$  (13%), is the same for the measured as for the calculated data.

Due to the lack of a sufficient experimental basis for the isotopic-mass dependence of the specific heat, a quantitative comparison of the calculated isotopic-mass dependence on the

heat capacity with experimental data thus far was carried out by relating the derivative with respect to the isotopic mass with the derivative with respect to temperature. In the harmonic approximation (but otherwise exact) the following equation can be derived [3]:

$$\frac{d \ln(C_p/T^3)}{d \ln M} = \frac{1}{2} \left\{ 3 + \frac{d \ln(C_p/T^3)}{d \ln T} \right\}. \quad (1)$$

Our measurements on six different diamond samples with varying isotopic compositions (see Fig. 2) enabled us for the first time to obtain rather good experimental values for the l.h.s. of Eq.(1). The agreement between measured and calculated results is excellent for  $T > 170$  K. The upturn in the experimental results at lower temperatures is assigned to the presence of inclusions of metals used as catalyst for the crystal growth (for more details cf. Ref. [2](a)).

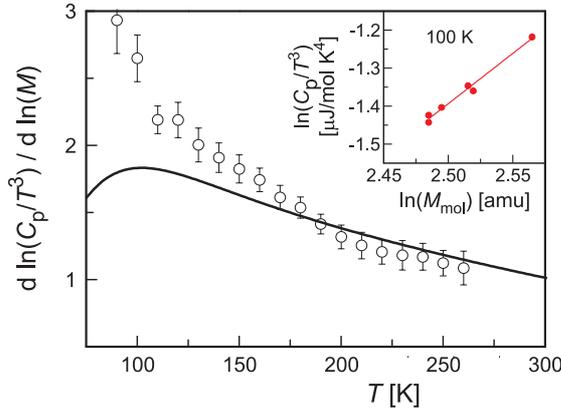


Figure 2: Logarithmic derivative of  $C_p/T^3$  vs. isotopic mass gained from six diamond samples with isotopic compositions  $^{12}\text{C}_{1-x}^{13}\text{C}_x$  ( $0 \leq x \leq 1$ ) ( $\circ$ ). The solid line represents the calculated temperature dependence [3]. Agreement is good above 170 K. Below this temperature, the experimental points deviate from the calculated curve, possible reflecting the presence of iron inclusions. The inset illustrates the procedure used to obtain the logarithmic derivative from the experimental data.

Figure 3 displays the logarithmic derivative of  $C_p/T^3$  with respect to the mass of zinc isotope for all measured samples of ZnO grouped into blocks with different oxygen mass. A sharp peak is observed at  $\approx 22$  K that corresponds to acoustic vibrations, associated mainly to displacements of zinc atoms. The larger mass of zinc with respect to that of oxygen explains the presence of this peak at low temperatures. The *ab initio* calculations agree well with the experi-

mental data at temperatures larger than 100 K. At low temperatures the peak position is described in a qualitative way by the calculations, although the latter yield the maximum at 4 K lower temperature than the experimental data (see inset Fig. 3).

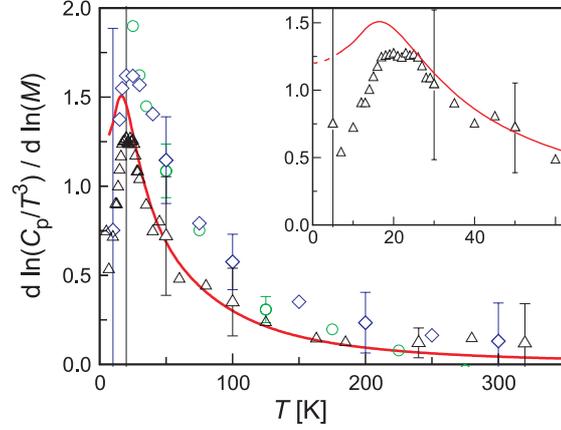


Figure 3: The logarithmic derivatives  $d \ln(C_p/T^3) / d \ln M$  with respect to the mass of the Zn isotope. Solid (red) line: Result of the *ab initio* calculation. Experimental data: (black  $\triangle$ )  $^p\text{Zn}^{16}\text{O}$  ( $p = 64, 65.4, 68$ ); (green  $\circ$ )  $^p\text{Zn}^{16/18}\text{O}$  ( $p = 64, 65.4, 68$ ); (blue  $\diamond$ )  $^p\text{Zn}^{18}\text{O}$  ( $p = 64, 66, 66, 68$ ). The inset shows the data for  $^p\text{Zn}^{16/18}\text{O}$  in an enlarged scale, together with the calculation.

The temperature dependence of the logarithmic derivative of  $C_p/T^3$  with respect to the oxygen mass (Fig. 4) shows two distinct maxima at  $\approx 20$  K and 160 K. The first maximum corresponds to transverse acoustic vibrations of  $\omega$  close to zero, which behave as sound waves and the atomic displacements depend on the total mass. Therefore they are also slightly affected by the oxygen mass. This maximum depends on the possible inhomogeneity of the isotopic distribution of the Zn atoms and overlaps with the maximum observed in Fig. 3. This is demonstrated in Fig. 4 by the difference between the solid line, corresponding to an average between four derivatives with respect to the oxygen isotope, and the open circles, corresponding to the set  $^{64}\text{Zn}^q\text{O}$  ( $q = 16, 16/18, 18$ ). Besides this low temperature peak, there is a broad asymmetric band with a maximum at 160 K. This band is related to the activation of lattice vibrations that predominantly involve displacements of oxygen atoms. The much lighter mass of oxygen as compared to that of zinc is responsible for the higher frequency of these modes, which in turn requires a higher activation temperature.

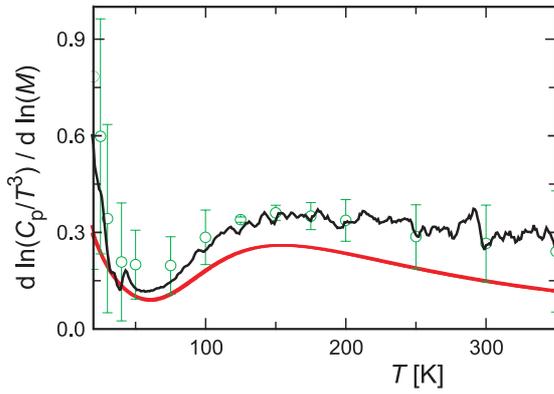


Figure 4: The logarithmic derivatives with respect to the mass of the oxygen isotope,  $d\ln(C_p/T^3)/d\ln M_O$ . Lower solid (red) line: Result of the theoretical calculation. Upper solid (black) line: Average of four derivatives with respect to the mass of the oxygen isotope. Open circles (green  $\circ$ ): Derivative with respect to the mass of the oxygen isotope for the set  $^{64}\text{Zn}^q\text{O}$  ( $q = 16, 16/18, 18$ ).

The calculations, displayed by the lower solid curve on Fig. 4, describe remarkably well the experimental behavior of  $d\ln(C_p/T^3)/d\ln M$  as a function of temperature, taking into account the magnitude of  $d\ln(C_p/T^3)/d\ln M$ , the limited accuracy of the calculation of the logarithmic derivatives, and the error bars present at low and high temperatures.

Equation(1) can be evaluated for monatomic crystals from the phonon DOS without any additional details about the lattice dynamics (e.g. the phonon eigenvectors). As illustrated in Fig. 5, this is not possible for binary or ternary materials. The r.h.s. of Eq.(1) calculated from an average of  $C_p$  of an 68/18 and 64/16 isotopic composition displays only one sharp peak at  $T \approx 18$  K. In the actual partial derivatives this peak splits into two, one for the  $M_{\text{Zn}}$  derivative, at  $\approx 20$  K, and a broader one for the  $M_{\text{O}}$  derivative at  $\approx 160$  K. In order to obtain these partial derivatives with an expression similar to Eq.(1), some knowledge about the corresponding phonon eigenvectors would be needed. A general argument to explain these differences between both partial derivatives is that the zinc components of the eigenvectors are larger for the phonons with lower frequencies, and viceversa, whereas the opposite situation happens for the oxygen components. The agreement found between measured and calculated curves of  $d\ln(C_{p,v}/T^3)/d\ln M_{\text{Zn,O}}$  shown in Figs. 3 and 4 also reflects the quality of our *ab initio* calculations.

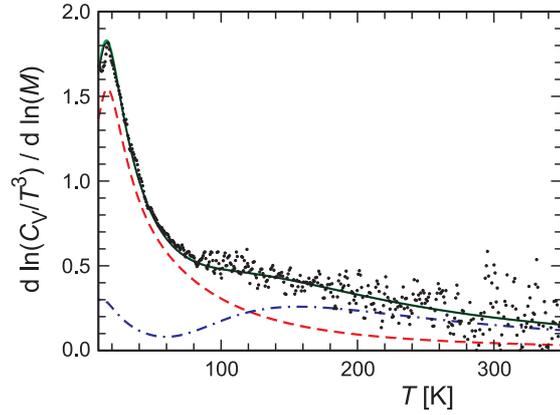


Figure 5: Calculated logarithmic derivatives  $d\ln(C_p/T^3)/d\ln M$  with respect to  $M_{\text{Zn}}$  (red, dashed) and  $M_{\text{O}}$  (blue, dot-dashed), sum of both curves (green, solid), and r.h.s. of Eq.(1) (black, solid), the latter obtained from an average of the calculated heat capacity for 68/18 and 64/16 isotopic compositions. The filled circles ( $\bullet$ ) correspond to the r.h.s. of Eq.(1) with the logarithmic derivative taken on the average of experimental data of two samples with isotopic composition 68/18 and 64/16. Note that the sum of the two dashed curves (green, solid) coincides with the solid black curve.

In summary, we have measured the heat capacity of diamond and zinc oxide on single crystals with a wide spread of isotopic compositions. Our data allow for the first time to obtain reliable values for the logarithmic derivatives of  $C_p/T^3$  with respect to the atomic masses. For ZnO there is a distinct temperature dependence of the logarithmic derivatives with respect to Zn and O masses, which stems from the contribution of Zn and O atomic displacements to the lattice vibrations and the activation of the latter at different temperatures. This behavior, as well as the heat capacity, are reasonably well-reproduced by *ab initio* calculations that we have performed within the harmonic approximation.

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- [3] Sanati, M., S.K. Estreicher and M. Cardona. Solid State Communications **131**, 229-233 (2004).