Specific Heat of Monoclinic Se at Low Temperatures*

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Specific heats of $\alpha$ monoclinic Se have been measured from 2 to 20 K. Excess specific heat was noted.

1. INTRODUCTION

There exist four different forms of solid Se known to date: the thermodynamically stable helical-chain hexagonal arrangement, the metastable ring-type $\alpha$- and $\beta$-monoclinic structures,1-3 and the amorphous form. Monoclinic and amorphous Se will convert to the hexagonal form when heated4 or pressurized.5 Since amorphous Se can readily be prepared in bulk and in film, the physical properties have been thoroughly investigated.6 However, little has been reported about the monoclinic phases, mainly because of the difficulties of growing monoclinic Se of suitable size for most experiments.4 Reported here are low-temperature specific heat measurements of $\alpha$-monoclinic Se.

2. EXPERIMENTAL

High-purity Se (99.999+ %) was obtained from American Smelting and Refining Co. Single crystals of $\alpha$-monoclinic Se were grown from a saturated solution of methylene iodide.7 The growth rate was rather slow. For 4–5 weeks the largest crystals grown were of the size $3 \times 2 \times 1 \text{ mm}^3$.

A thermal relaxation method with laser beam as a heat source was used for specific heat measurements.8 The thermal contact between samples and thermocouple leads was greatly improved with a thin-layer coating of gold, evaporated under high vacuum. The sample, attached to and supported by thermocouple wires, was inside a vacuum chamber and was thermally

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linked to a copper block as a heat reservoir through these wires. The adden-
dum heat capacity was calibrated from two standard copper samples. From
the thermal relaxation time constant and the addendum heat capacity data,
the specific heats of the unknown samples were determined. In the present
investigation, a beam splitter was used so that two specimens could be
measured during the same run.

3. RESULTS AND DISCUSSION

The specific heat of monoclinic Se is shown in Fig. 1 with $C/T^3$ as a
function of $T$, together with the literature data of hexagonal and amorphous
Se.\textsuperscript{9,10} It is clear that at high temperature the specific heats of different
forms of Se approach each other in magnitude as expected, since even
relatively large differences in the detailed shapes of the phonon frequency
distributions will result in only small variations in specific heat. However,
in the temperature range of the present measurements, several interesting
features are outstanding and appear in the definitely monotonic order—
from the hexagonal to the monoclinic to the amorphous:

1. The Debye temperature ($\Theta_D$) decreases from 152 K for hexagonal
Se,\textsuperscript{10} to 128 K for monoclinic Se, to $\sim$100 K for amorphous Se
(calculated from Refs. 9 and 10).

![Fig 1. Curves of $C/T^3$ vs. $T$ for amorphous, monoclinic, and hexagonal Se](image-url)