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Specific Heats of Solid Natural Neon at Five Molar Volumes and of the Separated Neon Isotopes at $P = 0$

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Direct measurements of the constant volume specific heat C_V *are reported for solid natural neon at several molar volumes (13.39–12.39 cm³/mole) at temperatures from 1 K to the melting line. All samples were solidified in a high-pressure bomb at the melting line (maximum conditions of 53 K and 2.5 kbar) and molar volumes for the melting line are given. The extrapolations of these data to 0 K result in a* $\Theta_0(V)$ *relation for which* $\Theta_0(P = 0, T = 0) = 75.1 \pm 0.1$ *K and an average Grüneisen parameter* $\gamma_0 = 2.51 \pm 0.03$*. These data can be represented at all temperatures and for all volumes by a single reduced curve as* $C_V[T/\Theta_0(V)]$*, with a maximum deviation of* $\pm 0.8\%$ *near* $T/\Theta_0 = 0.12$*. The deviations are systematic with volume and consistent with a temperature-dependent contribution to the Grüneisen parameter of* $1 \pm 1\%$*. The melting line parameters are used to test the Lindeman melting relation, and systematic deviations are found. Much less complete measurements of* C_V *for the separated neon isotopes* ^{20}Ne *and* ^{22}Ne *are consistent with the reduced curve for natural neon, and with an* $M^{-0.5}$ *dependence for* Θ_0*, where M is the isotopic mass.*

1. INTRODUCTION

The thermodynamic properties of the weakly bound rare gas solids are of particular interest because of large anharmonic contributions to their lattice dynamics. Solid helium represents an extreme case where short-range correlation effects become very important, while conventional perturbation techniques may be used to treat the effects of anharmonicity in the heavier solids (argon, krypton, and xenon) at low temperatures.[1] For neon, the amplitude of the zero-point vibrations (approximately 6% of the nearest-neighbor distance) is sufficiently great so as to make the use of perturbation techniques questionable even near 0 K.[2] The three-body triple–dipole interactions which are important for argon,[3] krypton,[4] and xenon probably are not important for neon, although the commonly used Lennard–Jones 6–12 potential[2] very likely is not correct.[5] The very factors which cause neon to be of considerable theoretical interest also result in a solid which is very compressible and which has large thermal expansions and relatively low melting temperatures.

The present experiments were undertaken to provide direct measurements of the constant–volume heat capacity C_V for solid natural neon at several molar volumes and for the separated isotopes ^{20}Ne and ^{22}Ne near the equilibrium volume. C_V data can be correlated directly with the density of states function for the lattice and hence with inelastic neutron scattering data,[6] while the limiting value of the Debye temperature Θ_0 represents an average over the elastic constants of the solid.[7–9] The volume dependence of Θ_0 can be used to understand, to first order, the volume dependence of C_V in terms of a reduced temperature, $C_V(T/\Theta_0)$, where the only volume dependence occurs through $\Theta_0(V)$. In effect, this model assumes that the shape of the density-of-states function is independent of volume, so deviations from such a reduced temperature dependence can be interpreted in terms of the actual volume dependence of the frequency spectrum. The combined volume and temperature dependences of C_V can be related directly to the Grüneisen parameter γ, the volume thermal expansion coefficient, and to the equation of state $P(V, T)$ if a single pressure–volume relation (such as that along the melting line) is known.[10]

Constant-pressure specific heat C_P measurements on natural neon by Fagerstroem and Hollis–Hallet[11] and Fenichel and Serin[12] have been summarized by Batchelder *et al.*[7] These data are in basic agreement, and earlier uncertainties in the conversion of C_P to C_V can be removed through the use of recent elastic constant data.[8,9] The most direct comparisons of C_V data and theoretical calculations are made for constant volume conditions, so the 4.4% volume expansion of solid neon between 0 K and the triple point 24.5 K requires that a rather large correction be made to C_V values which have been obtained from a constant-pressure experiment. This correction can be made relatively much smaller in an experiment which is conducted under almost constant-volume conditions.

Previous direct measurements of C_V at constant volume have been reported for helium (Ref. 13 is typical of work with this solid, which exists only under pressure), for hydrogen,[14] and more recently for argon and xenon.[15] In all of these experiments, the calorimeter which contains the solid is in the form of a high-pressure bomb which must be filled at the melting line under conditions where the molar volume of the solid is at least as small as the equilibrium volume at absolute zero, V_0. The heat capacity of the relatively massive bomb (which must be designed to withstand at least 2 kbar pressure) is not a serious factor for helium where the heat capacities and