A Determination of the Zero-Point Energy of Lithium Under Pressure

M.I. McMahon, E.E. McBride, and R.J. Husband

SUPA, School of Physics & Astronomy, and Centre for Science at Extreme Conditions, The University of Edinburgh, Kings Buildings, Mayfield Road, EH9 3JZ, Edinburgh, U.K.

Lithium is a "simple" metal at ambient conditions, with an electronic structure well explained by the nearly-free electron model. For decades, it was believed that such metals would remain simple at high densities, and indeed would become *more* free-electron like as a result of the relative increase in the electron kinetic energy. The outcome would be a high-symmetry close-packed array of ionic cores in a "sea" of pressure-ionised electrons. However, in their seminal paper, Neaton and Ashcroft [1] showed that at high densities, the overlap of core electrons on neighbouring atoms might lead to low-symmetry, low-coordination structures. Using a novel combination of low-temperature single-crystal x-ray diffraction and *ab initio* random structure searching [2, 3], we have recently determined the structures of the three very complex phases that emerge in Li above 60 GPa. These structures – with 88, 40 and 24 atoms/cell – arise as a result of core-valence and increased core-core interactions, and are either semiconductors or poor metals. These high-pressure diffraction studies of Li were conducted mostly at low temperature, since above 20 GPa at 300 K lithium readily diffuses into the diamond anvils of the pressure cell, leading to their failure. However, the remarkable melting curve of Li unveiled by our studies meant that it was possible to locate the liquid phase at temperatures as low as 200 K at 50 GPa.

But there is a still more exotic density-driven phenomenon predicted to occur in Li. As materials are compressed, the atoms become increasingly localised and, via the Heisenberg Uncertainty Principle, their momentum and kinetic energy increase. In Coulombic systems, compression leads to an enhancement of the zero-point energy, with the result that the melting temperature at extreme pressures can drop to 0 K, resulting in a liquid ground state [4]. This phenomenon – so-called "cold melting" – has not been observed in any material at high pressure to date, but a metallic liquid ground state is predicted to occur in solid hydrogen at pressures above 400 GPa [5], and there is indeed evidence to suggest a broad maximum occurs in the hydrogen melting curve at ~100 GPa and ~1000 K [6, 7], consistent with the liquid ground state above 400 Gpa.

Lithium is an obvious low-Z system in which to look for the same phenomenon, particularly as compression experiments to only modest pressures have already highlighted the increasing role of quantum effects with increasing pressure [4, 9]. The search for a broad melting maximum indicative of the existence of the liquid ground state at still-higher pressures forms the basis of our long-term dynamic compression campaign at the JANUS, OMEGA and NIF laser platforms in the US.

Crucially, in order to provide an estimate of the location of a melting maximum, we need to determine the magnitude of the quantum-isotope effects in Li at high pressure. In particular we need a determination of the pressure dependence of the zero-point energy.

This can be obtained from the difference in the compressibility of the two lithium isotopes Li6 and Li7 [4, 9], and, as said, quantum effects have already been observed to increase with pressure in Li [9]. However, in this study, the compressibilities of the two isotopes were measured to only 1.7 GPa – very much lower than the same effects have been successfully measured in H2/D2 (~110 GPa – ref. [10]). The resulting uncertainty in the magnitude of the quantum effects at higher pressures is greatly hindering our ability to estimate the location of a melting maximum. In this

proposal we were awarded 3 days of beam time on beam line P02.2 to determine the relative compressibilities of Li6 and Li7, initially to 20 GPa at 300K, and then to 60 GPa at 180 K.

More than 8 DACs loaded with Li6, Li7 and a Ta calibrant were brought to Petra. The DACs were cooled to 150 K using P02.2's cryostat and were pressurised using the beamline's gas membrane controller. We collected diffraction data in small (~1 GPa) steps to a maximum pressure of ~30 GPa in both Li6 and Li7. The quality of the diffraction data from the weakly-scattering Li was excellent as a result of the extremely high intensity on P02.2. However, much time was spent trying to find the very small (few micron) pieces of Ta calibrant within the much larger samples. Thin (0.5-micron) foils will be used in future studies. Difficulties experienced during the experiment prevented us from obtaining data to the highest pressures. In particular, our membrane device jammed at the lowest temperatures, preventing us from increasing the pressure further. Attempts to overcome this problem resulted in breakage of the diamonds, and the premature end of the experiment. Initial analysis of the compressibilities to 16 GPa shows a small, but clear, difference in the two isotopes (see Figure 1), with Li7 being slightly more compressible – in agreement with the earlier work of Gromitsykya *et al* [9]. Further analysis of the data to higher pressures, with the aim of extracting information on the zero-point energy, is still in progress.

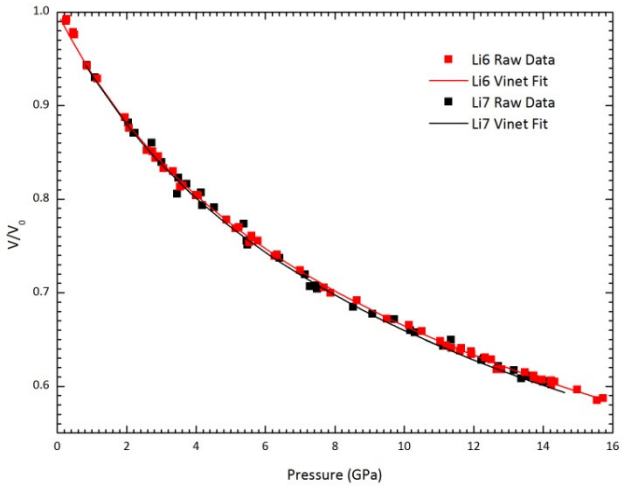

Figure 1: The compressibilities of Li6 and Li7 to 16 GPa.

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