Probing quantum effects in lithium

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A B S T R A C T

In periodic table lithium is the first element immediately after helium and the lightest metal. While fascinating quantum nature of condensed helium is suppressed at high densities, lithium is expected to adapt more quantum solid behavior under compression. This is due to the presence of long range interactions in metallic systems for which an increase in the de-Boer parameter (\(\sigma\lambda\)) is predicted at higher densities \([1,2]\). Physics of dense lithium offers a rich playground to look for new emergent quantum phenomena in condensed matter and has been subject of many theoretical and experimental investigations. In this article recent progress in studying the quantum nature of dense lithium will be discussed.

1. Introduction

Lithium holds a special place among the elements. At ambient pressure lithium is the lightest metallic and superconducting element \([3]\). It is also the simplest solid that undergoes a martensitic type transition during cooling at ambient pressure \([4]\). While at ambient pressure and temperature lithium is an ideal metal with a symmetric structure, high pressure properties of lithium are highly counter-intuitive and lithium undergoes a series of symmetry breaking structural phase transitions \([5,6]\), metal-insulator transition \([7]\) and its superconducting transition temperature, \(T_c\), follows a very unusual pressure dependent path, which reaches the second highest \(T_c\)'s of any elemental superconductor at 20 K \([5,7–10]\). Properties of lithium under pressure both from the perspective of quantum solids and simple electronic systems are extremely important and have been attracted many studies since the earliest days of development of modern condensed matter \([2,11–16]\).

One special feature of lithium that has attracted considerable interest is its similarities with hydrogen. Lithium is iso-electronic to hydrogen which is the most abundant element of the visible universe. Over 80 years ago, Wigner and Huntington predicted that hydrogen will become metallic under pressure \([17]\). Metallic hydrogen is predicted to be a quantum material with properties beyond our understanding of condensed matter. The predicted properties include two-component superconductivity and superfluidity, fluid ground state, superconductivity at room temperature and many more e.g. \([18–23]\). Metallic hydrogen has been recently observed in laboratory at pressures near 5 Mbar and at 77 K \([24]\). However these conditions are within the upper limits of the current experimental high pressure static methods which make studies on the metallic hydrogen formidable difficult. Lithium on the hand is a metal at ambient conditions with considerable zero-point energy in the order of \(\sim 40\) meV \((500 K)\). Studying lithium at easily accessible pressures in laboratory would allow better understanding of the physics of metallic systems of low atomic mass at high densities.

While compared to metallic hydrogen, lithium is a much easier subject for studying quantum effects in light metallic systems; lithium on its own is a very difficult material for high pressure studies. Lithium readily reacts with most materials including diamonds that are the main component of diamond anvil cell (DAC). DACs can achieve the highest possible static pressure conditions and are one the best-suited devices for variety of high pressure measurements at variable temperatures. The high reactivity of lithium with diamonds especially at high pressure and temperature makes experiments in DAC very difficult. In addition, lithium is very poor scatterer of both X-ray and neutron and Raman studies at high pressure on metals are in general very difficult. Therefore studying the lattice dynamics of lithium remains a challenge. Recent developments of high pressure methods and possibility of synchrotron and neutron studies on small samples at high pressure allowed new measurements that will be presented in this article.

Several approaches are being used to quantify the quantumness of lithium lattice and its dependence on density. These include studies on broad range of properties of lithium including pressure dependence of its electronic conductivity \([7,25]\), melting \([6,26]\), vibrational studies \([27]\) and structures \([6]\) as well as few comparative isotope effect studies on elastic \([12]\), vibrational \([13]\) and superconducting properties of...
lithium [28]. Since isotope effects directly depend on the nuclei mass, these studies are best suited for quantitative determination of the lattice quantum effects. In this article I will discuss some of the recent high pressure studies on lithium.

2. Experimental methods

2.1. Melting studies

From studies on the melting temperature of inert gases and especially helium it is known for a long time that quantum effects can contribute significantly to the melting temperature. While by virtue of short range type of interactions in helium at high densities helium becomes more classical and solidifies [29], lithium which has long range coulomb type interactions may experience quantum cold melting. First principle molecular dynamics calculations suggest a minimum in the melting line of lithium which is caused by increased core-valence electron interactions that lead to symmetry breaking structural phase transitions from face centered cubic structure (fcc) to lower symmetry structures in the region around 20 GPa and is followed by sharp decrease in the melting line between 50–60 GPa [30–32].

Experimentally the melting curve of lithium has been studied by several groups [6,11,16,26] as summarized in Fig. 1. Since lithium becomes exceedingly reactive under pressure especially at higher temperature only the latest two studies could reach pressure regimes where the minimum in melting was predicted by theoretical calculations. The first measurements used X-ray diffraction in diamond anvil cell in a very wide range of pressures up to 120 GPa and in temperatures between 77 K to room temperature. In these measurements the disappearance of diffraction lines, observed during isothermal pressurization, in a pressure range of 40–60 GPa at temperatures as low as 190 K has been interpreted as melting [6]. This observation together with earlier high pressure melting measurement of up to 15 GPa using differential thermal analysis method in a multi anvil cell [15,33], suggested a very sharp drop between 15–40 GPa in qualitative agreement with molecular dynamic calculations. A later series of studies used a different approach. Because of low melting temperature of lithium in the pressure region of interest, measurements of melting that required remote sensing of temperature by black body radiation could not be employed to determine the melting of lithium in a DAC. A rarely used method to determine melting of metals is based on well-documented abrupt drop in electrical conductivity of metals at their melting temperature [34–36]. This method is particularly useful in high pressure measurements of low melting temperature metals and the melting of lithium between P = 0–65 GPa [26] was determined using this method. While the melting behavior of lithium was qualitatively similar between different studies, it was found by electrical measurement method that the minimum melting temperature measured during isobaric warming paths, does not fall below 300 K which was considerably higher than that interpretation of the X-ray results. The electrical measurements therefore suggested that melting behavior of lithium adheres to classical thermodynamic melting. Due to presence of several pressure-induced structural phase transitions, interpretation of the melting behavior of lithium and the role of the zero point effects remains elusive. While these results did not illustrate signature of zero-point effects in lattice quantum dynamics of lithium, they paved the way for the next steps.

2.2. Superconducting isotope effects in dense lithium: quantum solid effects?

From the melting studies, it became clear that for pressures below 65 GPa, where lithium is still a metal, temperature plays the dominant role in lattice dynamics. Therefore, reducing temperature effects by studying a property of lithium at low temperature was a reasonable step. A follow up study on the vibrational properties of natural lithium under pressure at 100 K revealed the role of the zero point effects in stabilizing the oc88 structure above 65 GPa [27].

However in these pressures lithium is already transitioning from a metallic state to semiconducting state [7]. For studying the evolution of lattice quantum effects in metallic lithium, low temperature studies below 60 GPa would be most revealing. Since zero-point energy is related to the mass, studying isotope effects were compelling. Based on these considerations, the isotope effects in the pressure-induced superconductivity of lithium were studied. Since lithium is a simple metal, it was expected that the isotope effect in its superconducting transition to follow BCS prediction. BCS-type superconductor composed of one atomic species, with a static lattice, the superconducting transition temperature (Tc) and the ionic mass follow the simplified relationship, Tc ∝ M−0.5. Lithium has two stable isotopes with atomic mass of 6 and 7, and natural lithium is mainly composed of the heavier isotope. This relation is mainly attributable to differences in the Debye temperature for different ionic masses of different isotopes. Based on BCS theory the isotopic shift in superconducting transition temperature of 6Li and 7Li is expected to be less than 1 K in the known superconducting pressure region. Static pressures required for superconducting studies of lithium could be achieved in a DAC. However, uncertainties in reproducing the exact experimental conditions would challenge proper comparative studies on superconducting transitions of lithium isotopes. A method of simultaneous transport measurement in a DAC was developed which allowed accurate comparative measurements [37]. Using this method, the superconducting phase diagrams of lithium isotopes between 16–26 GPa were measured. The resulting isotope effects observed, however, were highly anomalous. Below 21.5 GPa, Li exhibited a direct, but unusually large isotope effect, while between 21.5–26 GPa, lithium showed an inverse superconducting isotope effect.

The unusual dependence of the superconducting phase diagram of lithium on its atomic mass could only be related to the differences in their lattice properties or their nuclear statistics (which is unlikely to be relevant at the temperatures of the studies in discussion). In a non-static lattice and in the presence of large quantum zero point motion of ions, electrons do not see the lattice as a perfect crystal (this is the case even if these displacements do not affect the structures of the isotopes) and thus, in total, deviations from conventional isotope effects in a

![Fig. 1. Phase diagram of 7Li based on available data from several research groups. Showing the boundaries of the solid structures of lithium (solid black lines) [5,6,45,47], superconducting region (red shaded area) [8–10] and melting temperature (symbols) [6,11,15,26]. The gray shaded area represents the approximate liquid region where various measurements agree. Striped blue shaded region shows the area that interpretation of x-ray (crosses) [6] and resistivity data (pluses) [26] are not in agreement. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
superconducting quantum solid can be expected [38,39].

In addition to the electronic effects mentioned above, large lattice quantum dynamics can cause structural differences between isotopic species. In a solid with static lattice, isotope effects in the structures are not expected. Whereas, in the presence of large lattice quantum dynamics, the large zero point energy can have an impact on the equilibrium structures [40,41]. Since BCS assumes identical structures for isotopes, the BCS superconducting isotope relation is not applicable in systems with a structural isotope effect. These observations strongly recommended examining the low temperature structures of lithium isotopes that have not been performed previously.

2.3. Low temperature structural phase diagram of lithium isotopes

Current advances in synchrotron X-ray and neutron diffraction of small size samples, made new attempts on finding the high pressure and low temperature structures of lithium promising. Since lithium is a very weak scatterer of x-rays, neutron studies have played a major role in determining the low temperature structures of lithium; e.g. [42–44]. Since BCS assumes identical structures for isotopes, the BCS superconducting isotope relation is not applicable in systems with a structural isotope effect. These observations strongly recommended examining the low temperature structures of lithium isotopes that have not been performed previously.

Until recently, the high pressure structures of lithium at low temperatures remained unknown. Recent developments in neutron diffraction and synchrotron X-ray studies, allowed determining the boundaries of the martensitic transition of lithium and also examine the energy landscape of lithium low temperature structures [45,47]. The result of these studies showed that unlike bcc, fcc is stable down to the lowest temperature and furthermore even if decompressed, lithium would not transform back to a martensite. This observation together with theoretical calculations showed that martensitic transition lithium is solely there for kinetic reasons and the actual ground state of lithium is a very simple fcc structure.

2.4. Simultaneous studies

The structures of lithium are found, both experimentally and theoretically, to be very close in energy and kinetic effects in the phase transitions of lithium are found to play an important role. The thermal path dependence of the transitions can be large and hysteresis can be present. Therefore, to correlate different properties of lithium, the studies have to be done under very similar conditions. One of the significant properties of materials is the relation between their electronic and structural properties. For proper comparison and excluding the effect of hysteresis we have performed simultaneous synchrotron X-ray studies together with four probe Kelvin resistance measurements on lithium samples under pressure in DAC. The results of some of these preliminary measurements are shown in Fig. 2. These studies are currently being developed to reach the P-T conditions deep within the superconducting region of lithium isotopes.

Fig. 2. Simultaneous X-ray and resistivity measurements of 6Li under pressure. a) P-T path of sample. The inset table shows the structural parameters of sample at each data point. The image inset is the X-ray image of the sample (dark red) in the gasket with the platinum leads (yellow) arranged to measure the resistance simultaneously. Lighter lines show the cooling and warming path across which resistivity data is recorded in part b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
4. Conclusions

Studies on lithium show the importance of zero point effects in its properties. Lithium is the lightest metal at moderate pressure to exhibit detectable quantum solid effects. Correlation between the electronic and structural properties and understanding the evolution of quantum solid effects as function of pressure offers exciting direction for future research.

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