Solving the LK-99 puzzle

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Summary

The claim of room-temperature, ambient-pressure superconductivity in copper-doped lead apatite, LK-99, was both sensational and puzzling. I describe how this puzzle was solved. An entirely different property, superionicity, of a byproduct produced by copper doping was mistaken to be superconductivity.

Keywords: room-temperature superconductor; lead apatite; superionic; copper sulfide; high-temperature superconductivity; phase transition

The backstory

Earlier this year, on July 22, two preprints from Lee et al. of the Quantum Energy Research Center appeared on the arXiv reporting the discovery of room-temperature, ambient-pressure superconductivity in the mineral lead apatite modified by copper doping.[1,2] The purported superconductor had a composition $Pb_{10-x}Cu_x(PO_4)_6O$ and was termed LK-99 because the earliest observations by the two primary discoverers, Lee and Kim, dated back to 1999. Within days, the reports went viral on social media and caused a sensation in science and technology circles. A room-temperature, ambient-pressure superconductor would enable lossless electrical transmission under practical, technoeconomically-viable conditions unlike the cryogenic conditions needed for operating existing commercial superconductors, such as rare-earth barium copper oxide (ReBCO). The implications for technology would be revolutionary ranging all the way from magnetic resonance imaging (MRI) to plasma-based fusion energy generation where a major challenge is the sustainable generation of large toroidal magnetic fields. At the same time, if LK-99 were to be verified as a room-temperature, ambient pressure superconductor, it would in all likelihood form a new class of superconductors—distinct from the existing high-temperature superconductors such as cuprates, which includes mercury barium copper oxide with a record-high T_c of 133 K or –140 ˚C below which it is superconducting at ambient pressures—and invoke the need for new models of electron pairing needed to form the superconducting state. Naturally, this prompted a flurry of theoretical and computational studies in search of an electronic structure basis and mechanism for the claimed superconductivity. The apparent simplicity of the chemical composition and reported synthesis further boosted the excitement and appeal of LK-99. Within days, experimental replication efforts began, with the first report from Awana and coworkers appearing on arXiv at the end of July.[3]

Yet, the claim was met by skepticism from the condensed matter physics community. After all, there is a long history of claims of high-temperature and room-temperature superconductivity, which later proved to be false or irreproducible. In fact, the community terms these as unidentified superconducting objects (USOs), which includes oxidized polypropylene. There was also wariness due to the lack of the Lee and Kim's track record in superconductivity research, the tentative nature of the preprints and the data therein, and the recent reports of fraud and retracted publications on high-pressure superconductivity in hydrides.

The puzzle

Considerable social media attention was focused on the levitation of a flake of LK-99 by a permanent magnet.[1] However, this was not a compelling signature of superconductivity; it could be best described as partial levitation rather than full levitation characteristic of the Meissner-Ochsenfeld effect shown by superconductors and easily explained as the result of a balance between repulsion of diamagnetic domains and attraction of ferromagnetic domains by the magnet.

However, Lee et al. reported multiple signatures of superconductivity in the 100 ˚C range.[1,2,4] Most striking was a sharp drop in resistivity of an LK-99 ingot as the temperature was decreased below 105 ˚C, which is reminiscent of a normal-to-superconducting phase transition.[1] Although the resistivity at room temperature was not zero—and was in fact, larger than copper, a mere conductor—one could not rule out the presence of domains of a superconducting phase embedded inside an otherwise lower-conductivity matrix. A series of electrical transport measurements[1,2] also showed that the application of a critical current and/or a critical magnetic field induced a transition from the low-resistivity state to the high-resistivity state, which could be interpreted as a disruption of a superconducting gap. Last but not the least, Lee et al. reported in a lesser-known April publication[4] a λ-shaped feature at ~100 ˚C in the temperature-dependent heat capacity of LK-99. This signature closely resembled the λ-transition of superfluids and superconductors and could be viewed as compelling evidence of superconductivity. Yet, Awana and coworkers had failed to observe superconductivity in their replicated samples of LK-99.[3] This dissonance prompted me to find an explanation for this puzzle.

Critical clues

The chemical reaction described by Lee et al.[1] for the synthesis of copper-doped lead apatite yields an unbalanced equation:

$$Pb_2(SO_4)O + Cu_3P \rightarrow Pb_{10-x}Cu_x(PO_4)_6O + S \text{ where } x = 0.9\text{–}1.1$$

A proposed balanced equation for $x = 1$:

$$5\ Pb_2SO_4O + 6\ Cu_3P \rightarrow Pb_9Cu(PO_4)_6O + 5\ Cu_2S + Pb + 7\ Cu$$

suggested that 5 moles of copper sulfide (Cu_2S) would be formed for every mole of the Cu-doped lead apatite phase, $Pb_9Cu(PO_4)_6O$. In fact, this conjecture is supported by Lee et al.'s own finding of Cu_2S in the X-ray diffraction pattern (XRD),[2] further verified by Awana and coworkers.[3] Thus, LK-99 is far from a simple material; rather it is a multicomponent, multiphase material consisting of Cu_2S—among other potential ingredients—mixed with the claimed superconductor, $Pb_{10-x}Cu_x(PO_4)_6O$. Once this was realized, it seemed too much of a coincidence that the transition in the resistivity of LK-99 occurs sharply at 105 ˚C, glaringly close to the temperature of a phase transition of Cu_2S.[5] This phase transition originates from a property of Cu_2S known as superionicity. Could it be that the apparent signatures of superconductivity in LK-99 were in fact due to an entirely different "super" property in a byproduct of the synthesis?

What is superionicity?

Superionicity is a phenomenon involving fast, liquid-like conduction of ions in a crystalline solid. Typically, in a crystalline ionic solid at room temperature, ions vibrate about their mean lattice positions but otherwise have little to no mobility even under an applied bias. Table salt, sodium chloride (NaCl), and Cu_2S are both crystalline ionic solids, but the latter has a peculiar property. When NaCl is heated up, at 801 ˚C, the solid melts to form a molten salt, i.e., a liquid phase. But when Cu_2S is heated up, well below its melting temperature of 1130 ˚C, at 104 ˚C, the Cu^+ cationic sublattice melts while the S^{2-} sublattice maintains its rigid hexagonal crystalline structure. In the state above 104 ˚C, the cations exhibit a liquid-like mobile, disordered network constantly hopping from one interstice to another inside the rigid anionic cage. This is observed in XRD or electron microscopy, where the diffraction peaks or lattice fringes associated with the ordered arrangement of the cations disappear at the transition temperature. The high-temperature structural form of the material conducts electricity under an applied bias except the carriers are cations rather than electrons or holes. This is a superionic conductor, which has the mechanical properties of a solid, but ionic diffusivities typical of a liquid. This is a useful property for moving cations around rapidly, as in a rechargeable battery where fast charging/discharging is desired. In principle, superionic phases can be ideal electrolytes for rechargeable batteries because they circumvent the problems associated with a flammable liquid electrolyte. Although fundamental understanding of superionicity is incomplete, it is thought to be realizable in ionic solids where cations and anions are mismatched in size, which accommodates the presence of many interstitial sites for cations (or anions) to hop to and from within a rigid cage of the anions (or cations).

Role of oxygen, vacancies, and holes

The structural transition of Cu_2S induced by heating across 104 ˚C is accompanied by a large jump in the conductivity.[5] This is because the low-temperature, fully ordered phase has negligible ionic conductivity, whereas the high-temperature, superionic phase has a large ionic conductivity. In other words, Cu_2S undergoes upon heating a sharp drop in resistivity at 104 ˚C. Although this coincides with the sharp transition observed for LK-99,[1,2,4] the trend is exactly the opposite. This discrepancy is resolved by recognizing the structural richness of copper(I) sulfide and the role played by oxygen exposure known to us from mineralogy literature.[6]

Copper(I) sulfide has a Cu_2S composition only under oxygen-free conditions. This form is called chalcocite. But any oxygen exposure induces the formation of Cu vacancies.[6] A copper-deficient form with ~3% Cu vacancies, termed djurleite, is a structural local minimum in the Cu–S composition space. Each Cu vacancy, if ionized, forms a hole carrier in the lattice. Therefore, djurleite, has holes in the valence band at a density of 10^{21} cm^{-3}. That is one hole for every nm^3, which is a large enough carrier density to make the material electronically conductive. So, whereas the fully stoichiometric form (Cu_2S), is a poor electronic conductor, the copper-deficient form ($Cu_{2-\delta}S$, where δ represents the Cu-deficiency level) is a p-type electronic conductor due to the hole carriers and has a low resistivity at room temperature. The copper(I) sulfide in LK-99 can be conjectured to be in the electronically conductive $Cu_{2-\delta}S$ form. After all, Lee et al. report inadvertent oxygen exposure of their successful LK-99 samples: "While studying the superconductivity phenomenon...the quartz tube was destroyed due to internal pressure during rapid cooling or reaction" (Korean-to-English translation).[4]

$Cu_{2-\delta}S$ upon heating undergoes the same ordered-to-superionic structural transition as Cu_2S around 100 ˚C. No different from Cu_2S, there is a sharp jump in the ionic conductivity at this transition. But the exact opposite trend is exhibited by the electronic conductivity due to the hole carriers. Cationic disorder is detrimental for the mobility of electronic carriers. The hole mobility is markedly lower in the high-temperature phase of $Cu_{2-\delta}S$. Because the electronic conductivity dwarfs the ionic conductivity, the total (electronic + ionic) conductivity of $Cu_{2-\delta}S$ undergoes upon heating a sharp drop at the transition temperature.[5] In other words, the electrical resistivity jumps upon heating across the superionic transition temperature. This is precisely the trend[7] observed for LK-99[1,2,4] and mistaken as a signature of superconductivity.

This deduction[7] is supported by the experimental measurements of Zhu et al.[8] Furthermore, the opposite transition signatures in the resistivities of Cu_2S (which needs to be made without air exposure) and $Cu_{2-\delta}S$ (formed when there is air exposure) are likely reflected in their results. Zhu et al. find for a sample made by vacuum annealing a drop in resistivity going from low to high temperature.[8] This is attributable to the Cu_2S form. On the other hand, for a sample made by air annealing, Zhu et al. observe a sharp jump in resistivity going from low temperature to high temperature.[8] This is attributable to the $Cu_{2-\delta}S$ form.

A consistent picture

The structural transition of copper(I) sulfide is a first-order phase transition that is accompanied by a latent free energy. This is the origin of the peak at ~100 ˚C in the temperature-dependent heat capacity plot of LK-99, a feature misinterpreted as a λ-transition signature of a superconducting gap.[7]

In the absence of superconductivity, why did Lee et al.[1,2,4] observe critical currents? I conjectured[7] that the application of a current caused Joule heating and raised the internal temperature of the ingot inducing the structural phase transition of copper(I) sulfide at a lower apparent temperature, as later verified by measurements of Liu et al.[9] The higher the applied current, the lower the apparent transition temperature. This gave the appearance of a superconducting gap being disrupted by the application of a critical current. However, Lee et al.'s observation of critical magnetic fields[1,2,4] is not fully explainable by the properties of copper(I) sulfide and would require a constituent of LK-99 possessing large magnetoresistance.

Cautionary tale for materials science

Thus, LK-99 serves as a cautionary tale of a known structural phase transition masquerading as a signature of a superconducting transition across multiple properties. Perhaps, consideration of alternative explanations—in the vein of the refutation method advocated by Popper—would have prevented this misattribution. In fact, in their pathbreaking discovery of high-temperature superconductivity of lanthanum barium copper oxide (LBCO), Bednorz and Muller[10] were sure to consider and eliminate an alternative explanation based on a metal-to-metal structural transition.

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