Experiment III [1]

High Temperature Superconductors. Solid State Synthesis and Demonstration of the Meissner Effect.

Perhaps the most exciting scientific advancement of our lifetimes was the discovery of high temperature superconductivity. In early 1987, a research group at the University of Houston discovered a ceramic material which displays the two diagnostics of superconductivity, resistanceless current flow and perfect diamagnetism.[2] The remarkable feature of this material, was that the superconductivity onset, T_c, was above 77 K. This allowed liquid nitrogen (bp 77 K), which is cheap and easily handled, to be used as a coolant in superconductive devices and research. The discovery of this material created an ongoing maelestrom of research activity in chemistry, physics, and materials science.

The ceramic material which started all the excitement has the chemical formula $YBa_2Cu_3O_{7-x}$ ($x < 0.1$) and is often referred to as the "1-2-3" compound because of the Y:Ba:Cu stoichiometry. It is worthwhile to assign formal oxidation states to the elements of the 1-2-3 compound. Based on the normal oxidation states of -2 for the oxide oxygen atom, +3 for the yttrium atom, and +2 for each barium atom, the resulting average oxidation state for each copper atom is 7/3 (for x =0). We can interpret this nonintegral oxidation state for Cu to mean that, on average, two-thirds of the Cu is present as Cu^{2+} and the other third is present as Cu^{3+}. The structure of the 1-2-3 compound has been determined by x-ray crystallography and is shown in Figure 1. The structure of this superconductor belongs to the perovskite family. If the 1-2-3 compound had an idealized perovskite structure it would possess nine oxygen atoms in its formula. Why doesn't the 1-2-3 compound have the formula $YBa_2Cu_3O_9$? Probably because this would require an average copper oxidation state of 11/3, which implies contributions from Cu^{3+} and Cu^{4+} oxidation states. Both these oxidation states are extremely rare for Cu. These materials achieve a lower oxidation state for Cu by expelling oxygen atoms from the lattice.

While the mechanism for superconductivity in these materials remains unknown, the mixed-valence form of Cu is believed to be important. The oxygen vacancies in the 1-2-3 structure create sheets and chains of Cu atoms, linked through the remaining oxygen atoms, Figure 1. Since the discovery of the 1-2-3 compound a large family of

Perovskite Structure $YBa_2Cu_3O_{7-x}$ Structure

Figure 1.

high T_c superconducting ceramic materials have been prepared. All the new materials have in common a mixed valence Cu-O backbone in agreement with the notion that this feature is key to high temperature superconductivity. However, much more information is needed before the remarkable properties of this particular 1-2-3 oxide can be explained.

In this laboratory experiment you will prepare the 1-2-3 superconductor using solid state synthetic techniques. You will then demonstrate one of the two diagnostics of superconductivity, perfect diamagnetism, by levitating a magnet over your superconductive material. This almost magical quality of superconductivity was discovered in 1933 by Meissner and now carries his name.

Hazards

Acetone (CAS No. 67-64-1): Acetone is an extremely flammable liquid. It is not normally considered dangerous, but normal precautions should be employed. ORL RAT LD50: 5800 mg/kg.

Barium Carbonate (CAS No. 513-77-9): This compound may be fatal if inhaled, swallowed or absorbed through the skin. Barium compounds are known to cause heavy metal poisoning. Wash repeatedly with water if skin is contacted. ORL-HMN LDLo: 17 mg/kg, ORL-RAT LD50: 418 mg/kg.

In preparing the superconductor pellets avoid inhalation of the ceramic powders. This is particularly important during the grinding procedures. Do this in a hood, at arms distance, with gloves, a dust mask, and safety goggles.

The most serious danger in this experiment is the potential for burns from both extreme cold and heat. When using the tube furnace or when handling hot objects always use heat-proof gloves and tongs. Do not place hot objects in areas where someone else might touch them. Leave them to cool on the heat-proof pad. Skin contact with liquid nitrogen can cause severe frostbite. The protective cryogenic gloves should be worn whenever liquid nitrogen is used. Do not handle the ceramic materials when they are in the superconducting state.

Experimental Procedure

A. 1-2-3 Superconductor Preparation

Weigh 0.60 g of yttrium oxide, Y_2O_3. Weigh out a stoichiometrically equivalent amounts of barium peroxide, BaO_2, and cupric oxide, CuO. In a hood, grind these powders together until a homogenous and uniform colored material is formed. This should take about twenty minutes.

Divide the solid into three equal parts and press into pellets. The pellets will be placed in an alundum (a form of Al_2O_3) boat and heated in a furnace. The furnace will be heated slowly to 930 C over a period of eight hours, held at 930 C for 12-16 hours, cooled to 500 C and held for 12-16 hours. The samples are then stored in a desiccator until use.

B. Demonstration of the Meissner Effect.

Place the 1-2-3 superconducting pellet in a Styrofoam cup. Pour liquid nitrogen into the cup and allow the 1-2-3 compound to cool for a few minutes. Invert a second Styrofoam cup. Carefully place the superconductor on the inverted cup using the protective cryogenic gloves. Using plastic tweezers place the samarium-cobalt magnet over the center of the pellet. It should levitate a few mm above the superconductor. Use a plastic ruler to measure the height. You may need to occasionally add more liquid N_2 to the shallow depression formed by the base of the cup. You may keep one of the pellets as a souvenir.

Current Research Efforts

The discovery of high temperature superconductivity sparked an ongoing industrial and academic research surge. It is safe to state that every major university has superconductivity research teams in either physics, materials science, or chemistry. The goals of this research include: 1) fabrication of wires, thin films and devices, 2) preparation of new materials with higher T_c's, and 3) attempts to understand the mechanism of superconductivity in these fascinating materials.

Another class of materials which deserve special attention are organic solid state superconductors. The first organic superconductor was prepared at The Johns Hopkins Chemistry Department in Dunning Hall by chemistry Professor Cowan and his students in

1974.[3] These compounds have much lower T_c's than the 1-2-3 material you prepared today. However, the unique one-dimensional conductivity behavior the organic materials display may lead to novel new applications. This science continues to be an active area of research.[4]

References

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