Rare-earth Information Center INSIGHT

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Volume 8 | September 1, 1995 | No. 9

GMR Advances

A relatively new scientific discovery of the super giant magneto-resistance (GMR) in rare earth-manganese perovskite thin films, $R_{1-x}M_xMnO_{3-\delta}$ (where M = Ca, Sr, Ba, Pb or Cd), has generated much scientific and technological interest in the past year and a half. The scientific interest stems from the extremely large changes in the resistivity of these thin films in an applied magnetic field, i.e. over 10^5 percent, and a possible explanation for this phenomenon. Technologically, super GMR will have an impact on magnetic recording, memory and sensor devices. Several important papers have appeared in the literature since the last issue of **RIC Insight** indicating a great deal of interest and activity in this exciting field. One is about a new record for the super GMR, while the others deal with a simpler GMR material and an improved room temperature GMR oxide.

The record for the super GMR effect has been increased by more than another order of magnitude, which is now up to 2.5 x 10^7%. B. Raveau *et al.* from the University of Caen, France [**J. Solid State Chem. 117**, 424-426 (1995)] prepared polycrystalline $Pr_{0.7}Sr_{0.05}Ca_{0.25}Mn_{3-\delta}$ by heating a mixture of $SrCO_3$, CaO, Pr_6O_{11} and MnO_2 at 900°C for 12 hours to decarbonate the reaction product. This material was then compacted by a pressure of 1 ton/cm^2, sintered at 1500°C for 12 hours and finally slow cooled to room temperature. Resistance measurements indicate a resistivity change of 2.5 x 10^7% at 85K in a magnetic field of 5T. Interestingly, this new record was obtained on a bulk polycrystalline material and not on thin films. They also studied the variation of the Ca to Sr ratio, and found that the GMR is strongly dependent on this ratio, the smaller the Sr concentration, relative to the Ca concentration, the greater the GMR effect. This strongly suggests that the size of interpolated cations plays a very important role, in addition to the mixed valence behavior of the manganese [i.e. Mn(III)-Mn(IV)].

In these manganese perovskite compounds the Mn-O_2 layers (in the *ab* plane) order ferromagnetically, and are separated by the nonmagnetic La-(Ca, Sr)-O layers . The magnetic ordering of the Mn-O_2 layers is antiferromagnetic (i.e. along the *c*-axis). The presence of the mixed Mn(III)-Mn(IV) valence state is thought to be responsible for the occurrence of both ferromagnetism and metallic conductivity.

In a second paper, S. S. Manoharan *et al.* (from the Indian Institute of Science, Bangalore) prepared highly textured $La_{1-x}MnO_{3-\delta}$ films on <100> orientated $LaAlO_3$ substrates. This material is unique since it does not contain a divalent element such as Ca, Sr or Pb to achieve the optimum electron valence concentration. The critical concentration was attained by limiting the La concentration to less than one per Mn atom. This self-doped material had a metal to insulator transition at 220K, and had respectable GMR values, $\Delta R/R_H > 550\%$ for a field of 6T at 210K and $\Delta R/R_0 = 85\%$, where R_0 is the zero field resistance).

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The defect concentration of lanthanum was 0.24 and that of oxygen was 0.27. These results were published in **J. Solid State Chem. 117**, 420-423 (1995).

Progress on obtaining a respectable GMR effect at room temperature was reported by J. Z. Liu *et al.* (University of California at Davis, and Argonne National Laboratory, Argonne, Illinois) in **Appl. Phys. Lett. 66**, 3218-3220 (1995). Although large GMR values have been reported by a number of researchers studying a variety of materials, all have been obtained between 75 and 230K. Unfortunately, as the temperature approaches room temperature the GMR values drop from greater than 10^5% to less than 100%. Since most devices operate near room temperature, it is important that materials with large super GMR values at room temperature are developed. To date, the best $\Delta R/R_0$ values were reported by Liu *et al.* on a single crystal of $La_{0.65}(PbCa)_{0.35}MnO_3$, i.e. $\Delta R/R_0 = 74\%$ at 300K for a field of 5.5T. The single crystals were grown from a liquid flux of PbF_2 and PbO in a platinum crucible by holding at the starting materials (La_2O_3, CaO, MnO_2, PbO and PbF_2) at 1280°C for 8 hours, slowly cooling to 1000°C at a rate of 0.5 to 1°C/hour, and then cooling to room temperature at 200°C/hour.

For prior information on the GMR effect see **RIC Insight 7** [6] (June 1, 1994); **8** [4] (April 1, 1995); and **8** [8] (August 1, 1995).

Magnequench Sale Completed

General Motors Corporation has agreed to sell its Magnequench product line and production facilities to Magnequench International, Inc. (MQI) subject to the approval by the U.S. government. MQI is owned by two Chinese state-owned companies: San Huan New Materials and Hightech, Inc.; and China National Nonferrous Metals Import and Export Corporation; and a U.S.-based investment firm, the Sexant Group, Inc., which has a significant minority interest in MQI. The Sexant Group is a New York City firm representing institutional investors. As reported in the April 1, 1995 issue of **RIC Insight 8** [4], the sale price was about $70 million: $56 million in cash and $14 million as a note. Magnequench sells about 85% of its products to non-automotive customers, with a majority of its sales in overseas markets. The 1994 sales have been reported to be $75 million. MQI facility will be managed, in large, by its current management team. MQI has also agreed to leave the Magnequench plant in Anderson, Indiana for at least 10 years.

Erbium-Three-Nickel Leads the Way

Toshiba Corp. has developed a cryocooler to cool a low temperature superconducting magnet down to 4.2K and attain a magnetic field of 10T (100 kOe) without the use of liquid helium. This surpasses their earlier record of 6T. The superconducting magnet, which uses a combination Nb-Ti and Nb_3Sn superconducting materials, was cooled by using a Gifford-McMahon cryocooler utilizing an Er_3Ni-based material for the lowest temperature stage. The leads for the electrical power are constructed out of a bismuth-based ceramic high temperature ceramic oxide superconductor. The system can be cooled to 4.2K in about 15 minutes. Toshiba claims that this was the first time a magnetic field of 10T had been attained by cooling of the superconducting magnet without the use of liquid helium.

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