Gd Eu Tb Sm Dy Pm Ho RARVS Nd Er Pr Tm Ce Yb La Sc Y Lu ®

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Ames Laboratory
Institute for Physical Research and Technology
Iowa State University / Ames, Iowa 50011-3020 / U.S.A.

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S-U-P-E-R (continued)

In last month's issue of **RIC Insight** (July 1, 1995) we featured four articles on rare earth superconductivity, but because of space limitations we were unable to include the story on the discovery of the first rare earth fulleride superconductor. The first item below deals with this topic.

First Rare Earth Superconducting Fulleride

Superconducting fullerides have been known for about five years, and consist of intercalated alkali or alkaline earth metals occupying the interstitial sites of the face-centered cubic structure of the C_{60} buckeyballs. Scientists from AT&T Bell Laboratories, Murray Hill, New Jersey, and Yale University, New Haven, Connecticut, headed by E. Özdas, reported in the May 11, 1995 issue of **Nature, 375** 126-129, that they have prepared $Yb_{2.75}C_{60}$, determined its crystal structure and discovered that it is superconducting at 6K. Before this discovery, all of the known rare earth fullerenes were endohedral phases in which the rare earth atom(s) are contained inside of the C_{60} buckeyball [see **RIC Insight 5** [4] (April 1, 1992), **5** [10] (October 1, 1992) and **8** [3] (March 1, 1995)]. In this $Yb_{2.75}C_{60}$ phase, the C_{60} buckeyball solidifies in a distorted, superlattice face-centered cubic structure with the Yb atoms occupying the vacant spaces between the C_{60} molecules. A careful x-ray analysis showed that (1) the compound has an orthorhombic structure; (2) all of the octahedral (O) interstitial sites and seven of the eight tetrahedral (T) sites are occupied by Yb atoms; and (3) the T-site vacancies are ordered, which leads to a doubling of the pseudo cubic until cell. Near-edge extended x-ray absorption fine structure studies showed that the ytterbium is divalent. The $Yb_{2.75}C_{60}$ phase can only be formed over a narrow temperature range, 630 to 670°C. Below 630°C the diffusion rate of ytterbium is too slow for the reaction to take place in a reasonable amount of time. While above 670°C the structure decomposes into an amorphous phase. The authors state that all of the information obtained on this compound indicates that there is "a strong, short-range, directional interaction between Yb and C_{60} consistent with the description of predominantly covalent bonding between Yb and C".

RE Permanent Magnets in Large Electric Motors

Today, large electric motors (those which are rated larger than 15 kW) consume more than one-third of the electrical energy generated in the USA. These motors are quite efficient, with a maximum efficiency of about 96%. However, just a small increase in efficiency (i.e. 1%) would lead to a considerable reduction in the annual USA electrical consumption — 50 billion kWh, which amounts to an annual savings of $2.5 billion. A study by Daedalus Associates indicated that rare earth-transition metal permanent magnet materials hold considerable promise for attaining this goal. However, to achieve this improvement, the designs of large PM (permanent magnets) electric motors need to be optimized. Since PM motors do not need bulky excitation windings, the size and weight are about one-half that of conventional motors, which helps to make

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Telephone: (515) 294-2272
Facsimile: (515) 294-3709

Telex: 269266
Internet: RIC@AMESLAB.GOV

them cost effective. There are, however, some problems which need to be solved: these include motor fabrication, servicing, and pulsating torque during acceleration. This last problem makes them unsuitable for line-start operations.

Glassy Oxide Coatings

Plasma spraying is used to coat metal and ceramic materials as a means of protecting the substrate against a corrosive and/or oxidizing atmosphere. Crystalline coatings generally are quite porous (as high as 10%), and thus not too effective. R_2O_3 and Al_2O_3 materials (alone or as ternary oxide compounds) are quite stable in many corrosive and oxidizing environments, but suffer from the porosity problem. Gourlaouen *et al.* [**European J. Solid State Inorg. Chem 32,** 57-70 (1995)] reasoned that if a glassy coating could be deposited on substrates, they might eliminate the porosity problem. Since the Al_2O_3-R_2O_3 system has a deep eutectic at ~20 mol% R_2O_3, it would be ideally suited to form glassy alloys. Their work shows that glassy alloys containing between 20 and 50 mol% Y_2O_3 could be plasma sprayed onto substrate surfaces. At higher Y_2O_3 contents crystalline phases were found in the coatings. Devitrification occurs at ~900°C, leading to crystalline phases. Thus, these coatings are limited to uses in which the service temperature remains below 900°C. They have also studied the formation of glassy Al_2O_3 coatings by plasma spraying Al_2O_3-Dy_2O_3 and Al_2O_3-Er_2O_3 mixtures. These results could lead to some small but important rare earth markets.

Super GMR Single Crystals

A little over a year ago (June 1, 1994 issue of **RIC Insight 7**, [6]) we noted the discovery of the super GMR (Giant Magnetoresistance) effect in La-Ca-Mn-O thin films, and pointed out that several possible applications utilizing the GMR effect could be important rare earth markets, if the oxide materials could be reproducibly processed to give optimum GMR properties at room temperature. Recently X. T. Zeng and H. K. Wong (from The Chinese University of Hong Kong) reported on their development of a process for growing single crystal La-Ca-Mn-O thin films [**Appl. Phys. Lett. 66** 3371-3 (12 June 1995)]. The GMR properties of these oxide films can vary considerably, depending upon the sample composition and the preparation process. In particular, special post annealing techniques are required to achieve the large GMR effect. Most of the earlier work used samples prepared by the pulse laser deposition (PLD) method, but it is difficult to prepare uniform samples using PLD. Zeng and Wong used instead the facing-target sputtering (FTS) technique which overcomes the weakness of the PLD method, and also eliminates the post annealing step. The La-Ca-Mn-O films were deposited on a single crystal of $NdGaO_3$ with the <110> orientation using a sputtering target of the nominal $La_{0.67}Ca_{0.33}MnO_3$ composition in an $Ar{:}O_2$ atmosphere at 60 mTorr. The most critical factor was the substrate temperature. At temperatures much different than 680°C, either higher or lower, the La-Ca-Mn-O film was textured or even polycrystalline. After deposition the chamber was filled with 1 atmosphere of O_2 and the sample was then cooled to room temperature by turning off the power to the substrate heater. The resultant c-axis epitaxial single crystal thin films of $(La,Ca)MnO_3$ had a very smooth surface. The rocking curves, which had a full-width at half maximum of about 0.01°, indicated that the single crystals thin films were of an excellent quality. Resistivity and magnetoresistance values were comparable to those reported by the AT&T Bell Laboratories scientists {**RIC Insight 7**, [6] (June 1, 1994)}, but smaller than those given by the University of Maryland personnel {**RIC Insight 8**, [4] (April 1, 1995)}.

Karl A. Gschneidner, Jr.

K. A. Gschneidner, Jr.
Director, RIC