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A Fourth Rare Earth Permanent Magnet Family?

Prof. J.M.D. Coey and his co-workers at Trinity College, Dublin, Ireland have just reported on their exciting new discovery of a rare earth-iron-nitride series of compounds with fairly high magnetic Curie temperatures which range from 400 to 500°C. These magnetic ordering temperatures lie between those of the SmCo_5 - $\text{Sm}_2\text{Co}_{17}$ (~725°C for SmCo_5 and ~925°C for $\text{Sm}_2\text{Co}_{17}$) and the Nd-Fe-B (~310°C) permanent magnetic materials. The compounds have the composition of $\text{R}_2\text{Fe}_{17}\text{N}_x$ with $x \approx 2.6$. The structures of the ternary nitride phases are closely related to the parent binary structures of the R_2Fe_{17} phases, which have either the hexagonal $\text{Th}_2\text{Ni}_{17}$ (R = heavies) or the rhombohedral $\text{Th}_2\text{Zn}_{17}$ (R = lights) type structures. The addition of nitrogen to the binary intermetallic R_2Fe_{17} compound expands the unit cell volume by about 7%, and approximately doubles the Curie temperatures (on the K scale). As a result of this lattice expansion the Fe-Fe exchange interactions are more than double, but the R-Fe exchange interactions are virtually unchanged. All of the $\text{R}_2\text{Fe}_{17}\text{N}_x$ phases exhibit easy-plane anisotropy, except $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ which is easy-axis. The intrinsic magnetic properties of the Sm compound are quite favorable for permanent magnet applications (Curie temperature 470°C, magnetization 1.54 T and anisotropy field ~15 T). The authors suggest that the uniaxial anisotropy of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ might be increased by substitution of some of the iron by cobalt or of the nitrogen by carbon.

The $\text{R}_2\text{Fe}_{17}\text{N}_x$ phases are prepared by reacting the binary R_2Fe_{17} compounds with N_2 or NH_3 at ~500°C. Further details may be found in the authors' publications: J. Magn. Mater. 87, L251 (1990) and J. Phys.: Condens. Matter 2, 6465 (1990).

Prof. Coey has also informed RIC that L. Schulz and his colleagues at Siemens Central Research Laboratory, Erlangen, Germany have produced a $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ alloy by mechanical alloying which has a coercivity of 3 T.

If scientists and engineers are successful in making good permanent magnets from $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ material, it could replace most of the SmCo_5 market, because its Curie temperature is sufficiently high for most SmCo_5 applications, and because of the lower price and political insensitivity of iron relative to cobalt. But because of the higher cost of samarium relative to neodymium, it is doubtful if this Sm-Fe-N compound will make great in-roads in the Nd-Fe-B permanent magnet market.

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Telephone: (515) 294-2272
Facsimile: (515) 294-3226

Telex: 269266
BITNET: RIC@ALISUVAX

Progress in Understanding High Temperature Superconductivity

Two inorganic chemists M.-N. Whangbo (North Carolina State University, Raleigh) and C. C. Torardi (Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington) have been able to correlate the superconducting critical temperature (T_c) of the cuprate superconductors with the bond valence sum (BVS), which is related to the electron hole density (n_H). The authors report [Science 249, 1143 (7 September 1990)] that for every class of the copper oxide superconductors a plot of T_c vs. either BVS or n_H showed a maximum, indicating there is an optimum hole density for superconductivity, which is ~ 0.19 holes per CuO_2 unit. When n_H drops to a value less than 0.04 or rises above 0.33, the compounds are no longer superconductors.

A hole is the absence of an electron in the valence band of these cuprate superconductors. They can be formed in the CuO_2 layers when cation substitutions, cation vacancies or excess oxygen atoms cause the Cu^{2+} ions to lose additional electrons. In order to see this correlation the authors divided the superconductors into various classes because nonelectronic effects also have a strong influence on T_c . Within each class the nonelectronic effect is constant, and thus the correlation becomes evident. The three classes are Ba-, Sr- and La-classes, which are distinguished by the size of the 9-coordinate site cation (i.e. Ba^{2+} , Sr^{2+} and La^{3+}). The Ba- and Sr-classes are further subdivided because of secondary nonelectronic factors, which are associated with the number of CuO_2 layers per unit cell or the cation substitution in the rock salt layers. The three subclasses are: $(\text{Tl}_{2-x}\text{Cd}_x)\text{Ba}_2\text{CuO}_6$, $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_8$ and $(\text{Tl}_{0.5}\text{Bi}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7$.

The authors also claim that the strength of the coupling constant for Cooper pairs, which is a measure of how strongly the paired electrons interact with each other, also correlates with the value of n_H . But this is to be expected if the BCS (Bardeen-Cooper-Schrieffer) theory of superconductivity holds for the cuprate superconductors. Hopefully this new knowledge will help theorists to better understand how these ceramic superconductors work.

A Magnetic Correction

For those who may have tried to find the article about our RIC Insight story in the last issue on "Who, What and Why in European Permanent Magnetism", the correct title of the journal should have been Materials Research Society Bulletin, or sometimes known as MRS Bulletin. The editor left out the word Society in the title -- sorry about that. I hope I did not inconvenience too many of our readers.

Karl A. Gschneidner, Jr.
Karl A. Gschneidner, Jr.
Director RIC