Rare-earth Information Center NEWS

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

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InP and $Gd_3Ga_5O_{12}$ Bonding

The bonding of various semiconductor materials to one another is an important consideration when constructing circuits requiring photonic functions such as light emission and optical amplification. Some semiconductor compounds are suitable, and hence, present little problem when developing integrated circuits. However, when nonreciprocal devices such as optical isolators, which are essential in stabilizing laser diode oscillations, are constructed of magneto-optic crystals instead of III-V semiconductors, a method for effective bonding is required.

A recent paper reports on the experimental results of the direct bonding of two substances, InP and Inp/GaInSb with gadolinium gallium garnet, ($Gd_3Ga_5O_{12}$, GGG) {M. Totoki *et al., Jpn. J. Appl. Phys.*, **34**, 510-14 (1995)} without the use of a glue. The experiment was carried out using commercially-available mirror-polished InP and optical mirror-polished GGG 5 mm x 5 mm wafers. The GaInSb layer that was grown on the GGG substrate by metallorganic chemical vapor deposition (MOCVD) was also used for direct bonding to InP. The GaInSb layer was 0.1-1.0 µm. After cleaning each sample, chemical etching of InP was conducted with an H_2SO_4:H_2O_2:H_2O mixture and GaInSb with NH_4OH:H_2O_2:H_2O, and then dipped into a buffered HF solution. GGG was slightly etched with H_3PO_4 at a temperature of 150°C.

An annealing furnace with an ambient H_2 atmosphere at 450°C to 750°C was used to heat treat the samples while under a pressure of 380 torr. After bonding, each sample was subjected to typical semiconductor/magneto-optic device fabrication processes to test the durability of the bond. These processes included: baking at a temperature of 200°C for 30 min; wet etching in a solution of HCl and H_3PO_4; Ar sputter etching

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(the process used in the production of magneto-optic waveguides); and finally, thermal annealing at 600°C in H_2 for 30 min.

The samples with the GaInSb intermediate layer showed the highest durability, primarily because the flatness, crystalline quality, and layer thickness of the sample all affect bonding strength. The stronger bonded samples had GaInSb layers more than 0.5 µm in thickness. The authors conclude that the bonding mechanism of InP/GaInSb on GGG must be due to interdiffusion between P and Sb. However, in the bonding of InP/GGG, no interdiffusion was observed. This promising new technology may be applied to integrating semiconductor and magneto-optic devices in the future. ▲

Rare Earths at Lviv State University

The Department of Inorganic Chemistry, Lviv State University, Lviv, Ukraine, is celebrating its 100th year of science. The first studies of rare earth binary and ternary rare earth systems were conducted here and the results published in 1959. The department has since studied more than 480 isothermal sections of phase diagrams of ternary systems and established the existence and described the structure of 2,500 intermetallic binary and ternary rare earth systems. Some of the systems turned out to be quite interesting, including the Ce-Ni-Si system which forms 21 compounds, and the 516 chemical species of the $CeGa_2Al_2$ structure type.

The department of Inorganic Chemistry now has 42 co-workers who are studying these materials. Among those in the group are, from left to right, first row: Drs. M. Konyk, L. Komaravska, O. Zarechnyk, G. Tyvanchuk, E. Gladyshevskii, Z. Shpyrka and Yu. Stadnyk, second row: B. Kotur, T. Yanson, I. Mokra, O. Bodak, L. Akselrud and O. Sologub, third row: E. Goreshnik, P. Starodub, M. Mys'kiv, V. Pavlyuk and P. Salamakha, fourth row: O. Oleksyn, A. Fedorchuk, V. Olijnyk, B. Mykhalichko, Ya. Kalychak, V. Kinzhibalo and M. Manyako. Not pictured are R. Skolozdra, V. Zaremba and O. Kharchenko. ▲

MORIS '96

The Magneto-Optical Recording International Symposium (MORIS '96) will be held April 29-May 2, 1996 in Noordwijkerhout, The Netherlands. The purpose of MORIS '96 is to provide a forum for information exchange on magneto-optical recording and related theories. A broad range of topics covering materials, physics, technology of recording, as well as fundamental studies will be addressed. Among the topics to be presented at the conference are: magneto-optical materials (rare earth-transition metal, oxides, multilayers and intermetallic compounds); magnetism (surface magnetism, micromagnetics, coercivity and anisotropy); magneto-optical effect; processing techniques (sputtering, evaporation and plasma processing, target materials and thin film structure); dielectric layers and substrates; reliability; high density recording including short wavelength technology and super resolution; direct overwrite; domain physics and dynamics; advances in head and related drive technology; and alternative recording technologies.

For more information on MORIS '96, contact: Mrs. J.A. Spierenburg, Oude Drienerlolaan 5, 7522 NB Enschede, P.O. Box 217, 7500 AE Enschede, The Netherlands; Tel: 31 53 332035; Fax: 31 53 356770 (after October 10, 1995: Tel: 31 53 4332035; Fax: 31 53 4356770); E-mail: j.a.spierenburg@basics.utwente.nl. ▲

ICSC-F'96

The International Conference on Substrate Crystals and HTSC Thin Films: Growth and Characterization, will be held in Szczyrk, Poland, September 16-20, 1996. The purpose of the conference is to provide an interdisciplinary forum for scientists and engineers to exchange information on the growth of substrate single crystals and thin films of High Temperature Superconductors (HTSC).

The following topics will be discussed concerning substrate single crystals: oxide crystals of perovskite and pseudoperovskite type structures, crystal growth techniques, automatically controlled growth, and properties of crystals (structure, physical properties, morphology, impurities, defects, spectroscopy, and dielectric and electrical properties). The topics for HTSC thin films will include misfit film-substrate (lattice constant and distances of ions, orientation, defects ordering, and surface reconstruction) and physical properties of films related to the substrate crystal.

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For more information contact: Dr. M. Berkowski, Secretary, ICSC-F'96, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland; Fax:(48-22) 430926; e-mail:berko@ifpan.edu.pl. ▲

Conference Calendar

*** A NEWS STORY THIS ISSUE**

September '95

European Magnetic Materials and Applications Conference (EMMA 95)
Wein, Austria
September 4-8, 1995
RIC News, XXIX, [1] 3 (1994)

Rare Earth Metals: Raw Material Processing, Technology of Compounds and Related Products
Krasnoyarsk, Russia
September 11-15, 1995
RIC News XXX, [2] 2 (1995)

International Conference on Strongly Correlated Electron Systems (SCES '95)
Goa, India
September 27-30, 1995
RIC News, XXIX, [3] 2 (1994)

October '95

13th Technology Short Course
Detroit, Michigan, USA
October 23-25, 1995
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November '95

III Latin-American Workshop on Magnetism, Magnetic Materials and their Applications
Mérida, Venezuela
November 20-24, 1995
RIC News, XXX, [2] 2 (1995)

April '96

MORIS '96
Noordwijkerhout, The Netherlands
April 29 - May 2, 1996
*This issue

September '96

Fourteenth International Workshop on Rare-Earth Magnets and Their Applications and Ninth International Symposium on Magnetic Anisotropy and Coercivity in Rare-Earth Transition Metal Alloys
São Paulo, SP, Brazil
September 1-5, 1996
RIC News, XXX, [1] 2 (1995)

International Conference on Substrate Crystals and HTSC Thin Films (ICSC-F '96)
Szczyrk, Poland
September 16-20, 1996
*This issue

October '96

Solidification and Powder Processing of Rare Earth-Based Materials
Cincinnati, OH, USA
October 6-10, 1996
*This issue

Goodbye, BITNET!

As of July 1, 1995, all electronic mail, file transfers, and other wide-area network operations with RIC are now supported exclusively by Internet. Our Internet address is: ric@ameslab.gov. Refer to the publisher information at the bottom of column 1 on page 7 which contains our complete address and contact numbers. ▲

Solidification and Powder Processing of RE Materials

The symposium "Solidification and Powder Processing of Rare Earth-Based Materials" will be held as part of TMS/ASM Materials Week '96, October 6-10, 1996 in Cincinnati, OH. Topics presented in the symposium will focus on the science and technology of the production, processing, and application of rare earth materials involving solidification and/or powder technologies.

For more information contact: T.W. Ellis, 242 Spedding Hall, Ames Laboratory, Ames, IA 50011-3020; Tel:515 294 1366; Fax:515 294 3709; or I.E. Anderson, 122 Metals Development, Ames Laboratory, Ames, IA 50011-3020; Tel:515 294 8252; Fax:515 294 8727. Abstracts will be due January 15, 1996. ▲

Early Summer in Genova and Zürich

The editor had the opportunity to visit two of Western Europe's rare earth research groups in late June. In addition to the excititing scientific agenda, the weather cooperated during most of the trip, especially the day when driving through the Italian and Swiss Alps from Northern Italy to Zürich.

Instituto di Chimica Generale

My first stop was to visit Prof. Ricarrdo Ferro, who is the head of the Istituto di Chimica Generale, Universita di Genova, and his co-workers. The main emphasis of their research activities is the measurement of thermochemical properties of rare earth intermetallic compounds and alloys. They also (1) determine rare earth binary and ternary phase diagrams as necessary in relation to the thermochemical studies, (2) calculate phase diagrams using the thermodynamic data and the known phases of binary and ternary systems, and (3) evaluate the known thermochemical data published on rare earth alloys.

Workshop on Rare Earth Chemistry and Metallurgy

Prof. R. Ferro organized a one and a half day symposium on rare earth chemistry and metallurgy. Most of the speakers were persons from Europe who have cooperative research programs funded by various European Union organizations to support joint research projects. These include Prof. Peter Vogl, University of Vienna, who talked on ternary rare earth borides; Henri Noel, Rennes University, who described his current activities on uranium germanium intermetallic compounds; and Dr. Günther Effenberg, Materials Sciences International Services, who described the European Networks on Metal Sciences and the activities he is funding. Prof. Ferro also presented an overview of the work going on in his group, while Prof. G. Bruzzone of the Institute of Physical Chemistry, University of Genova, described the research activities going on in his institute which compliments the work going on in Prof. Ferro's group. While at the workshop the editor presented two invited papers on "Effect of Impurities on the Formation of Rare Earth Intermetallic Compounds" and "Systematics are Important in Understanding Rare Earth Science".

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Eidgenössische Technische Hochschule Zürich

After a weekend touring Northern Italy the next stop was to visit Prof. Peter Wachter's solid state physics group at Eidgenössische Technische Hochschule Zürich (ETH). Prof. Wachter leads the largest solid state physics group at the ETH, and his research efforts cover a variety of topics. The major focus is on the optical properties of semiconductors and semimetals covering a wide range of wavelengths (up to five orders of magnitudes in frequencies from ~10 to 10^5 cm^{-1}). Some of the materials they are studying are rare earth pnictides and chalcogenides, high temperature superconductors (including $YBa_2Cu_3O_{7-x}$), the superconducting fullerenes (such as K_3C_{60} and Rb_3C_{60}), and the magneto-optical properties of rare earth monochalcogenides. Some recently prepared single crystal samples of CeSb have Kerr rotations of 80 to 90° at 1.5K in a 5.0T field, breaking their previous record Kerr rotation found on this material. At room temperature this material still has an unheard of Kerr rotation of ~ 3°, almost an order of magnitude better than any other material at room temperature. They also found that LaSe also has a large Kerr rotation, which is surprising for a material which has no magnetic *4f* or *3d* electron. This behavior is consistent with an empty *4f* level near, but still above the Fermi energy. Prof. Wachter believes that the position of the empty *4f* level is important in explaining the observed physical properties of a number of *4f* materials. Indeed, he has been able to show by optical techniques that the empty $4f^{14}$ state in YbN is only 0.2eV above the Fermi level, while the occupied $4f^{13}$ level is 6eV below the Fermi level, and that YbN is not a heavy fermion material, but probably a Kondo system.

It was a great , but brief, trip and it was wonderful to meet old acquaintances and to make new friends. ▲

Stanford Materials Co.

Stanford Materials Co. is a supplier of various rare earth oxides, metals, and compounds. Recently, Dr. James Chen who has recently joined Stanford Materials Co. to give the company an added dimension in customer service. For more information, contact: Dr. James Chen, Stanford Materials Co., 120 W. 3rd Ave. Suite 1110, San Mateo, CA 94402-1502 USA; Tel:415 348 3482; Fax: 415 348 4263. ▲

Passive Q Switching of Er-Doped YAG

Q-switched, eyesafe lasers have important applications in various laser uses, such as remote sensing, lidar, and eyesafe rangefinding. Saturable absorbers offer a simple, low cost solution for Q-switching, but recently, significant advances in passive Q-switch technology have been made for the 1.64 µm wavelength region. A Q-switched erbium-doped $Y_3AL_5O_{12}$ (YAG) laser operating at 1.64 µm using U^{2+}:SrF_2 and U^{2+}:CaF_2 was recently demonstrated by M.B. Camargo *et al.* {*Appl. Phys. Lett.*, 66, [22] 2940-2 (1995)}.

Although Er:glass has been reported to be a good saturable absorber Q-switch, Er:YAG may be advantageous for several reasons. The 1.64 µm Er^{3+}:YAG laser is a quasi-four-level laser because of the large splitting of the ground-state ($^4I_{15/2}$) manifold, whereas Er:glass is a three-level laser. Another consideration is that Er:YAG has a thermal diffusivity of more than an order of magnitude greater than that of glass.

The experiment involved an Er:YAG laser which was longitudinally pumped with a free-running 1.534 µm Er:glass laser. The authors employed this procedure to directly populate the upper energy level manifold ($^4I_{13/2}$) of the 1.64 µm laser transition which minimized the amount of heat deposited in the YAG crystal. The Er:YAG crystal (0.3% Er) was doped with 15% ytterbium and was fabricated into a 0.635 mm x 7.62 cm rod. It was reported that the ytterbium ions did not affect the 1.64 µm laser, since only the erbium upper laser level was pumped.

The room-temperature $^5I_5$ fluorescence (~2.6µm) lifetimes of 25 and 5µs for U^{2+}:SrF_2 and U^{2+}:CaF_2 were measured. The authors assumed that since all of the U^{2+} ions pumped by the 1.64 µm Er:YAG laser decay back to the $^5I_5$ metastable level, then the absorption relaxation lifetime is at least as long as the fluorescence lifetime, which is an application of the slowly relaxing absorber theory. The results of the experiment show that efficient passive Q switching can be obtained for the 1.64 µm Er:YAG laser using U^{2+}:SrF_2 and U^{2+}:CaF_2 saturable absorbers. ▲

ERBIUM, atomic number 68, was discovered by C.G. Mosander in 1843, who originally called it terbium. Because later workers by accident called "Mosander's terbium" erbium, element 68 is now known as erbium. The name erbium is also derived from the village of Ytterby.

RE Overlayers on Si

The use of rare earth silicides in modern semiconductor circuit design can be traced back to pioneering research work conducted at IBM laboratories. The peculiar physical and chemical properties of rare earth metal overlayers on silicon enable these thin metal films to react with Si to form silicides.

F.P. Netzer {*J. Phys.: Condens. Matter*, 7, 991-1022 (1995)} wrote a paper entitled "Rare Earth Overlayers on Silicon" which reviews the physiochemical properties of thin layers of rare earth metals and rare earth silicides on silicon substrate surfaces. The formation of reactive interfaces at room temperature, the evolution of ordered surface structures at elevated temperatures, and the oxidation of rare earth interfaces and silicides are discussed. Special emphasis is placed on the discussion of geometrical and electronic structure of ordered overlayer phases.

The author reviews the photoemission spectra of the valence band region of Gd, Gd_5Si_3, GdSi, and Gd_3Si_5, and includes relative binding energies of other rare earths such as Er and Yb silicides. A three-dimensional phase diagram of the experimental results of the Yb-Si (111) interface is included and proves to be a handy tool for understanding the behavior and structure of these silicide materials.

Rare earth-Si ordered superstructures are discussed, and low energy electron diffraction (LEED) structures of Sm, Eu, and Yb overlayers at submonolayer to monolayer coverages are included. Present-day research on the formation of epitaxial rare earth silicide overlayers on Si is receiving much attention and the author sheds some light on this area, as well.

The oxidation properties of rare earth-Si interfaces have been studied for a number of reasons, and some of these outcomes will determine if these materials can be utilized in commercial applications. The growth if insulating layers on top of Si is important in the technology of Si devices, and the search for new dielectric thin-film phases is necessary to develop improved Si-based charge coupled devices. Also, the oxidation of Si to SiO_2 requires severe temperature conditioning and methods to oxidize Si at lower temperatures by means of reactions catalyzed by metal overlayers have been investigated extensively. Finally, the stability of rare

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***RE Overlayers on Si**/Continued* ⇨

earth-silicide overlayers that are exposed to the corrosive effects of O_2 and H_2O must be established before these materials can be used in everyday applications.

This review paper includes 3 tables, 20 figures, and 114 references. ▲

Scintillator and Phosphor Materials

Interest in improved scintillator materials has been steadily increasing in recent years. Scintillator materials are used in detectors that are used in high-energy physics experiments, medical imaging, astrophysics, geophysics exploration and industrial applications. Because crystal scintillators provide unique physics measurements capabilities, a number of large detectors employing thousands of crystals have been proposed for future high-luminosity colliders. One of the key material requirements for this application is radiation hardness - the survivability of the scintillator material itself. *Scintillator and Phosphor Materials* is a collection of 72 papers presented by researchers of scintillator materials from 15 countries. The book is Volume **348** of the Materials Research Society Symposium Proceedings series.

The proceedings is divided into nine parts, eight of which are made up of papers (about one-third of the total) that contain information on rare earths. These parts are entitled: scintillator materials and applications-overview; scintillator materials-crystals; scintillator materials-plastics and glasses; scintillation processes-experiment; scintillation processes-theory; radiation damage; phosphor materials; and materials preparation and fabrication. The alternatives to crystals in high energy physics calorimetry include Ce-doped fluoride glasses, and these are explored as well. Radiation damage to $Ce:YAlO_3$, $Ce_xLa_{1-x}F_3$, and rare earth-doped BaF_2 and cerium fluoride crystals are discussed. Eu-doped phosphor materials, their cathodoluminescent properties and electronic trap defects are covered, as well as recent work on enhanced luminescence from rare earth-doped thin films.

A review on the recent progress made in scintillator research indicates that CeF_3 scintillator crystals are used in nuclear physics, gamma ray astronomy, medical imaging, safety systems, and non-destructive industrial applications. Crystal growth and scintillation properties of cerium fluoride

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***Scintillator and Phosphor**/Continued* ⇨

scintillator crystals are described, as well as cerium-doped orthophosphate, yttrium-aluminum perovskite (YAP) and lanthanum beryllate materials.

Scintillator and Phosphor Materials was published in 1994, contains 565 pages, and is edited by M.J. Weber, P. Lecoq, R.C. Ruchti, C. Woody, W.M. Yen and R-Y. Zhu. The publication is available in either hardcover or microfiche and can be purchased for $55.00 US (MRS members), $63.00 US (U.S. list) and $72.00 US (others). For further information contact the Materials Research Society, Publications Department, 9800 McKnight Road, Pittsburgh, PA 15237; Tel:412 367 3012; Fax:412 367 4373. ▲

Y-Ba-Cu-Se High T_c Superconductor?

A new high temperature superconducting compound, $YBa_2Cu_3Se_7$, has been prepared and reported to have T_c=371 K {V.D. Shabetnik *et al.*, *Tech. Phys. Lett.*, 21, [5] 382-4 (1995)}. The superconducting transition temperature of the new compound was increased by starting out with a perovskite material based on the famous $YBa_2Cu_3O_7$ compound, but replacing the oxygen with selenium. The chemical formula of the compound is reported to be $YBa_2Cu_3Se_{7-x}$, where *x*, the deviation from stoichiometry for Se, varied from 0 to 0.5.

The authors designed and built a device of their own to demonstrate the superconducting properties of the new material. The device measures T_c by the change in sign of the magnetic susceptibility and the jump of the resistance of the material under study. The variation of these properties in $YBa_2Cu_3Se_7$ around 370 K was essentially the same as that observed in $YBaCu_2O_7$ at ~90 K, suggesting that the former becomes superconducting below 371 K. This increase in T_c is reported to be due to the presence of the selenide ion Se_2^{-2} in the crystal lattice. The sample volume of the material that is in the superconducting phase was determined to be 12%. The authors believe that their new compound, $YBa_2Cu_3Se_7$, can be classified among those superconductors which exhibit superconducting properties "all the way up to the boiling point of water." If this discovery turns out to be true, it will be a bigger advance in superconductivity than the initial discovery by Bednorz and Müller of superconductivity in the ceramic oxides in 1986. ▲

Magnetic Correlations in High-T_c Superconductivity

As research continues on the rare earth-cuprate family of high temperature superconductors, the understanding of the properties and behavior of these materials increases. Recent experiments in this area indicate electronic properties that include strong local Coulomb correlations. Characteristic normal state properties appear to be beyond the conventional framework of Landau's Fermi liquid theory.

"Magnetic Correlations in High Temperature Superconductivity", by A.P. Kampf {*Phys. Repts.*, **249**, 219-351 (1994)} has a twofold purpose. The first part of the paper reviews the results of basic experiments which probe the magnetic correlations in the CuO_2 planes of superconductors. The second part of the paper reviews the current phenomenological and microscopic approaches in the context of purely electronic Hubbard type models which focus on the role of antiferromagnetic spin fluctuations.

The paper covers materials and structure of $YBa_2Cu_3O_6$ antiferromagnetic superconducting compounds, including La_2CuO_4 insulating parent compounds and phase diagrams of $La_{2-x}Sr_xCuO_4$, $Nd_{2-x}Ce_xCuO_4$ and $YBa_2Cu_3O_{6+x}$. Experimental results of static magnetic susceptibility, magnetic neutron scattering, nuclear magnetic resonance, Raman scattering, transport and impurity effects, and gap anisotropy are included. Phenomenologies of the normal state and microscopic models are reported as well. In addition, theoretical results for the magnetically-ordered and metallic states are reported. These include: magnetic order in insulators, spin correlations in the doped metallic state, dynamic spin susceptibility, and single particle properties. The final section of the paper reviews pairing from antiferromagnetic spin fluctuations, including the spin-fluctuation-exchange mechanism, pairing correlations from small cluster studies, and phenomenologies for d-wave pairing.

It is obvious that the author has done his best to provide as much information as possible about magnetic correlations in high-T_c superconductors. The 4 tables and 73 figures are nice additions to include in a paper such as this, as well as the numerous equations which guide the reader through the sometimes complicated labyrinth of this fascinating and important subject. It would be difficult to argue the points, subjects and topics presented in the paper as the work is backed up by 478 references. ▲

Electron Correlations in Cuprate Superconductors

A review of the concepts and effects of electron correlations in copper-oxide superconductors was written by W. Brenig and appeared in *Phys. Repts*, **251**, 153-266 (1995). The paper, "Aspects of Electron Correlations in the Cuprate Superconductors", has a twofold purpose. The author first provides an overview of results of various electron spectroscopies, Raman scattering and optical conductivity studies with particular emphasis on experimental results which identify the charge and spin correlations relevant to the cuprates. He then focuses on microscopic theories of the single-particle excitations, and the charge and spin dynamics of the normal state of cuprates whose models incorporate strong electron correlations.

The parent materials and electronic structure of rare earth high temperature superconductors (in particular, the cuprate perovskites, including La_2CuO_4 and $YBa_2Cu_3O_{6-x}$) are described using diagrams of their crystal structures. Phase diagrams of $YBa_2Cu_3O_{7-\delta}$, $La_{2-x}Sr_xCuO_4$, and $Nd_{2-x}Ce_xCuO_4$ are presented showing insulating, antiferromagnet, superconductor, and spin glass phases. Electron spectroscopy is necessary in understanding the electronic structure of the cuprates, and so angular integrated spectroscopy and angular resolved spectroscopy are covered, including the multi-band model parameters of these materials. Electronic Raman scattering and optical conductivity measurements of these materials are explained including the experimental results of these methods.

Single-particle excitations of the three-band Hubbard model of CuO_2 planes are analyzed and a description of the projection techniques, numerical results, and the implications for spectroscopy are explored. Since calculations that probe scales below the copper exchange energy are very involved, the author devotes a separate section to the aspects of electronic correlations which *assumes* that both one-band Hubbard, as well as the *t-J* Hamiltonian, are relevant effective low-energy models. Magnetic correlations, spin dynamics, and single particle excitations at both half filling and finite doping levels are explained, as are optical response functions of these superconductors. The phenomenology of the nearly antiferromagnetic and the marginal Fermi liquid is briefly presented. The paper includes 61 figures, 3 tables, and 551 references. ▲

Plasma-Sprayed REO

To protect substrates against corrosive elements and high temperatures, oxide coatings are deposited by plasma spraying techniques. However, porosity of conventional oxide coatings approaches 10%, which may not protect substrates exposed to aggressive environments. A new technique of plasma-sprayed deposits of alumina/rare earth oxide (REO) resulted with essentially no porosity ceramic coatings {V. Gourlaouen *et al.*, *Eur. J. Solid State Inorg. Chem.*, **32**, 57-70 (1995)}. The thermal behavior of these deposits and the consequences of devitrivication on their mechanical properties are also reported.

The deposited rare earth oxides were Ln_2O_3/Al_2O_3 (Ln=Dy, Y, Er) powders and were composed of 20 mol% Ln_2O_3 and 80 mol% Al_2O_3. Other compositions were tried as well: 45 and 76 mol% Y_2O_3/Al_2O_3 which corresponded to 2 other eutectic compositions in the Y_2O_3/Al_2O_3 phase diagram. To prepare the sprayed powders, two methods were employed. The first relied on coprecipitation in the amorphous state from precursors: this yields 50 g quantities which lead to thin coatings that are used to show the formation of glassy phases and was used in all of the compositions listed above. The second method involved spray drying a yttria/alumina mixture which provided 600 g of powder that was thick enough (2.3 mm) to determine the mechanical properties. This spray drying process consisted of transforming a water-based slurry into a dry powder by spraying it into a hot medium. The mixture was pumped into an atomizer located in a drying chamber, the droplets quickly dried and were annealed at 1400°C.

The resulting powders were plasma sprayed onto a graphite substrate to test the protective properties of the ceramic coatings. It was found that thermal treatment of the amorphous materials induces devitrivication at a temperature of about 900°C which then lead to progressively stable crystallized phases. Hence, these glassy deposits could be used for the protection of surfaces against corrosive atmospheres, but at temperatures <900°C. The microstructure of as-sprayed coatings determined that the "glassy deposits are made of a juxtaposition large grains with very low intergranular porosity." Deposits that were annealed at 1100°C formed a glass-ceramic that had both small and large grains, but had better

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LETTER TO THE EDITOR

22 May 1995

Dear Dr. Gschneidner,

Harold Gwyn Jeffreys Moseley, b. November 3 1887, d. August 10 1915 (Gallipoli), made his X-ray measurements in the Electrical Laboratory, Oxford. His original diagram is on display there, countersigned by the Professor, J.S. Townsend. The plot shows the square roots of the X-ray frequencies from Al to Au against the atomic number. There are some missing elements: Z=31 to 38, for example, but most of the lanthanides are there, apart from Z=69 to 72, and of course, 61.

Yours Faithfully,

Professor B. Bleaney,
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1995 Mineral Commodity Summaries

Mineral Commodity Summaries 1995 is a U.S. Bureau of Mines Report that provides nonfuel mineral industry data covering most of 1994. The report contains two pages of data for each commodity including: domestic production and use, salient statistics for the previous five-year period, and a discussion of significant events, trends, and issues. World mine production, reserves, and reserve base data are also presented. Rare earthers may find the two pages on rare earths interesting and useful, as well as the two pages each on scandium and yttrium.

The entire report is 202 pages in length and can be ordered by contacting: Superintendent of Documents, P.O. Box 371954, Pittsburgh, PA 15250-7954 USA; Fax:202 512 2250. Please include the stock number: 024-004-02394-5, cost is $13.00 for U.S. customers, $16.25 US elsewhere. Payment can be made by MasterCard or VISA. ▲

Plasma-Sprayed/*Continued from page 5* ➩

mechanical properties. Coatings that were treated at 1650°C were completely crystallized and composed of small grains, which had the best mechanical properties. These glass-ceramics, with inherent superior mechanical properties than as-sprayed oxide coatings, could find important uses in the ceramic and optical industries. ▲

1995 U.S.B.M. Annual Report

The 1993 United States Bureau of Mines Annual Report, published in 1995, *Rare Earths The Lanthanides, Yttrium, and Scandium*, written by J.B. Hedrick, is now available. This annual report is a useful guide to the world-wide rare earth industry that provides insight on the industry for the newcomer, and reviews and updates information to the seasoned rare earther. The softcover booklet covers the industry from mineral deposits, mining and processing, to the consumption of the final product. This thumbnail sketch packs a tremendous amount of information on the rare earths in a surprisingly small package (27 pages).

The report provides basic information on the grades and specifications of rare earth minerals, concentrates, and raw materials used in the production of consumer products. The forms and purities of rare earths for use in the world-wide rare earth industry are reviewed. Rare earth mineral exploration, mineral reserves, mining and ore beneficiation provide the reader with insight on the primary industry of rare earths. Economic and operating factors related to the industry, as well as toxicity, employment figures, and productivity trends are covered as well. A brief discussion on legislation, government programs and other issues provide a brief look into 1993 public laws and earnings of selected primary producers.

As a review for old timers, or to introduce the rare earths to the neophyte, the consumption, applications, stocks and prices of rare earths give the reader an overview of our field. The outlook for the rare earth industry is reported to be strong, with perhaps a shift towards higher purity mixed and separated products.

RIC always looks forward to receiving the latest annual report from the U.S.B.M. and the 1995 edition is no exception. The report is well supplied with tables (9) and figures (8) that give the reader valuable rare earth market information at a glance. To receive the 1995 annual report *Rare Earths The Lanthanides, Yttrium, and Scandium*, contact: U.S. Government Printing Office, Superintendent of Documents, P.O. Box 371954, Pittsburgh, PA 15250-7954 USA; Tel: 202 512 2250; Fax: 202 512 1800. The publication is easy to spot with its distinctive graphics cover, which shows a Magnetic Resonance Image (MRI) of a human brain. The cost for each copy is $2.25 US. ▲

Permanent Magnet Short Course

Princeton Electro-Technology, Inc. will hold its 13th Technology Short Course, with accompanying exhibition, on Permanent Magnet Design on October 23-25, 1995 at the Holiday Inn Crowne Plaza, Detroit Metro Airport. This course is designed to apprise the permanent magnet designer, engineer or technical manager of the latest developments in material properties and processes, magnet behavior under increasingly demanding environmental conditions, modern methods for magnetic circuit design and analysis, with a number of design studies from today's most important commercial applications. These applications include motors, actuators and sensors. There will be special emphasis on neodymium-iron-boron and other advanced rare earth magnet types.

The lectures in the short course will be presented by four experts on permanent magnet materials, design and applications: Dr. Fred G. Jones on magnet properties, production methods and costs; Dr. Peter Campbell on magnet stability, circuit design and field analysis; Reinhold Strnat on magnetization and testing, techniques and equipment; and Professor David Howe on motion applications and design studies.

The course is based on the 1994 Cambridge University Press Text *Permanent Magnet Materials and Their Application* by Dr. Peter Campbell which was reviewed on page 5 of the March 1, 1995 issue of *RIC News*. Further information can be obtained from Princeton Electro-Technology, 5874 NW 32nd Way, Boca Raton, FL 33496 USA; Tel: 407 998 4249; Fax: 407 998 3286. ▲

Matchen Consulting

A Russian producer of rare earth metals, in varying degrees of purity ranging from 99.9 to 99.9999%, wishes to offer these for sale to customers in the U.S.A. and Canada. These metals include neodymium, samarium, and most of the heavy lanthanides plus yttrium. Interested parties should contact Matchen Consulting, 942 Alenmede Cres., Ottawa, Ontario K2B 8K5, Canada; Tel/Fax: 613 820 9415 or Alltec Consulting, 26 Woodstone Rd., Northboro, MA 01532 USA; Tel/Fax: 508 393 6998. ▲

Raudenbush International, Inc.

Raudenbush International, Inc., a Russian-Western company, claims a capability to supply rare earth metals, oxides, fluorides, phosphors, permanent magnet materials, and alloys, and will assist in the import to the United States, rare earth materials and ultra-pure metals that are produced in Russia. Various forms of each material, quantities, and purities can be specified by the customer in order to meet particular needs.

For more information, contact: Peter V. Raudenbush, Raudenbush International, Inc., 2079 Hopewood Drive, Falls Church, VA 22043 USA; Tel:703 237 8306; Fax:703 237 6815. ▲

Mineral Claims

Fifteen rare earth mining claims that are strategically placed throughout Music Valley, located in Riverside County, California, are being offered for transfer. The mining claims contain the rare earth minerals xenotime and monazite. Exploration on most of the claims has been conducted by Draco Mining Co., of Tucson, Arizona. The mineralized zones are reported to have a combined REO equivalent tonnage of 2.5 million tons every 100 feet of mining. The structure is reported to be 950 feet deep to the base of the synclinal trough.

For more information on these claims, contact Byron M. Walls, 19732 Lancewood Plaza, Yorba Linda, CA 92686 USA; Tel:714 970 2504. ▲

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Argentine RE Deposit

A rare earth-uranium-thorium deposit located in San Luis Province, Argentina is being developed for commercialization. The project, known as "Rodeo de los Molles", is located about 300 km southwest of Cordoba and 200 km northeast of San Luis, Argentina. Minerals of economic significance include bastnasite (rare earth fluorocarbonate), britholite (rare earth silicon phosphate), and allanite (rare earth silicate) with 2.0 to 2.5% rare earth content. Pilot plant mining has been conducted by open-pit methods and utilizing conventional rare earth processing techniques.

For additional information on this project, contact: Nicolas A. Viñas, Geologist, Michelotti e Hijos S.R.L., Sargento Cabral 916, (5151) La Calera, Cordoba, Argentina; Fax: 54 543 66335; E-mail: diego@isri.unlv.edu. ▲

Polished Diamond

As the use and preparation of deposited polycrystalline diamond films develops into a mature technology, the need to remedy surface roughness of the film remains an important concern. Traditional methods of polishing the surface of diamond films are time consuming and involve mechanical machining, high temperatures and special ambient atmospheres such as in a vacuum or non-oxygen environment.

A new and improved method of polishing diamond uses yttria-stabilized zirconia (YSZ) in the polishing process {J.E. Yahoda and J.J. Cuomo, *Appl. Phys. Lett.*, 66, [14] 1750-2 (1995)}. The reaction and polishing take place at the interface of an oxygen superionic conductor, YSZ, and the surface of the diamond. Oxygen anions are transported to the interface under the influence of an electric field and react with the diamond. The authors believe that a volatile product of CO or CO_2 is formed during the polishing process.

YSZ, Y_2O_3-ZrO_2, is one of a class of materials known as defect stabilized ceramic oxide superionic conductors. These materials are electric insulators, but at higher temperatures O^{2-} can be conducted through the material with conductivities approaching 10^{-1} $(\Omega cm)^{-1}$. The motion of anions is associated with the formation of oxygen vacancies due to ion substitutions in the material.

Continued in next column ⇨

ISO-9001

Treibacher Auermet Produktionsges m.b.H., Treibach-Althofen, Austria, has earned the Lloyd's Register Quality Assurance Ltd. standard ISO-9001. The quality management system is applicable to "Development and production of rare earth compounds and of rare earth alloys. Production of lighter flints and of rare earth metals." The company was awarded a certificate according to ÖNORM ISO 9001:94 and is valid until March 1998. ▲

ISO-9002

Johnson-Matthey Catalog Company has been awarded ISO-9002 certification following a full site audit conducted by the quality systems registrar, TÜV America. This strict quality standard is earned by companies that demonstrate not only defined and documented quality assurance procedures, but also prove that these procedures are consistently followed. TÜV America certified that Johnson-Matthey, a world-renowned supplier of a complete range of inorganics, organics, organometallics and pure elements (including many rare earth products) in both research and bulk quantities, has established comprehensive quality systems. RIC congratulates Johnson-Matthey Catalog Company on this most important achievement. ▲

***Polished Diamond**/Continued* ⇨

The scientists conducted the experiment by placing a polished piece of 20 mil (100) oriented YSZ wafer on top of a polycrystalline diamond film that had been grown by microwave chemical vapor deposition onto a crystalline (100) Si substrate. The sample was then heated which activated the O^{2-} to overcome the energy barrier that is present between the anion sites in the defect structure of the YSZ. A controlled etch was achieved by placing the sample under a potential of 50-80 V and a current of 1 mA. The sample was polished without mechanical motion, extreme temperatures, or controlled atmospheres. The authors report that other oxygen superionic conductors should work as well, and that the process may provide a method for shaping diamond and other hard materials such as CN_x. ▲

1994 Woody Award


G. Slade Cargill III

G. Slade Cargill III, a professor at Columbia University, received the 1994 Woody Award "in recognition of outstanding service and dedication on behalf of the Materials Research Society (MRS) as exemplified by Woody White, MRS President, 1984." During Cargill's tenure as MRS president, he was instrumental in receiving federal support for the Advanced Materials and Processing Program which improved the research in materials science and engineering. Cargill has been an advocate of interdisciplinary research, that is, the close cooperation between university, industry, and government. He has submitted a statement to the Special Commission on the Future of the National Science Foundation, asserting the key role that university research and graduate education in science and engineering plays in the U.S. economy and industrial competitiveness.

Rare earthers will undoubtedly recognize the contributions that Prof. Cargill has made to the understanding of rare earth magnetic amorphous alloys, thin films, and metals. Most of his work has been on rare earth binary compounds and the structure and magnetic properties of sputtered amorphous thin films. RIC congratulates Prof. Cargill for his achievements. ▲

Edward I. Onstott (1923-1995)

Edward I. Onstott, 72, died in February 1995 after a long fight with cancer. He joined the research staff at Los Alamos National Laboratory in 1950 as a chemist and retired in 1984. He then acted as a consultant for the Lab until his death. Old time rare earthers will remember him from his work on the separation and preparation of rare earth metals in the 1950's. His latest research dealt with the thermochemical properties of rare earth compounds. He was affiliated with the American Institute of Chemists, the American Chemical Society, and was a fellow of the American Association for the Advancement of Science. We extend our deepest sympathies to the family and friends of Edward I. Onstott. ▲

Supporters 1996

★★★★★★★★★★★★★★★★★★★★★★★★★

We start the new fiscal year with 43 organizations and individuals who have come to the financial assistance of RIC. This includes new support from 2 individuals and 6 institutions, and renewed support from 35 organizations and 1 individual. The supporters who wish to be listed, grouped according to their appropriate categories and with the number of years that they have supported RIC in parenthesis, are identified below.

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