Rare-earth Information Center Insight

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### *La Doping Produces Magnetic Moment*

For the physicist, one attractive aspect of studying rare earth compounds is that you can pretty much count on the magnetic behavior of the materials being well-behaved because of the relative isolation of the 4-*f* shell. La, Lu or Y compounds, where the RE has no magnetic moment, are used to separate lattice contributions from magnetic effects. Thus, recent results for lanthanum-doped calcium hexaboride are rather surprising. D. P. Young et al. {*Nature*, **394**, 412-14 (1999)} report that the addition of a small amount of La results in the formation of weak ferromagnetism in $CeB_6$. The magnetic ordering temperature of the ferromagnet is 600 K. When La is doped into $Ca_{1-x}La_xB_6$, the magnetic moment per La atom rapidly rises from zero to a maximum of 0.07 $\mu_B$ for x = 0.005 and then decreases almost as rapidly dropping below .01 $\mu_B$ /La for x = .015. Clearly, this is not associated with a magnetic moment on the La, or a small amount of magnetic rare earth impurity in the La. The explanation is even more unusual; and, as a result, the paper has been extensively reported in editorial comments in *Nature*, the *Journal of Metals* and *Advance Materials & Processes*. The *Nature* editorial comments that are approximately half as long as the paper itself are the most extensive and informative. What makes the $Ca_{1-x}La_xB_6$ results so interesting is that they have been predicted for seventy years. In 1929, Block suggested that the electron gas was susceptible to magnetic ordering at low density. In 1934, Wigner showed that in most metals, the electrons form a normal Fermi liquid with equal populations of spin up and spin down. However, if the density of conduction electrons is sufficiently low, the potential energy dominates the kinetic energy, and the gas forms an ordered state. Over the years, there has been some controversy over whether this state could ever be achieved. The energy differences involved are extremely low, meaning that very accurate calculations are required in order to correctly calculate the ground state. The new experimental results start with semimetallic $CaB_6$ and then add conduction electrons by replacing the $Ca^{4+}$ with $La^{3+}$. In this case it is the conduction electron contribution of the La and not the 4-*f* rare earth contribution, which is important. The low level doping allows the realization of a very low density electron gas, which as predicted by Wigner, forms a ferromagnetically ordered system. The electron density for the ferromagnetic material is found to be .005 electrons per formula unit. Young et al. demonstrated that the conduction electrons can come from La or Th, and the matrix can be $CaB_6$, $SrB_6$ or $BaB_6$.

### *90° Kerr Rotation?*

In 1996, R. Pittini et al. {*Phys. Rev. Lett.*, **77**, 944 (1996)} reported a 90° Kerr rotation in CeSb at low temperature (1.5 K) and in a 5 T field. Recently, F. Salghetti-Drioli et al. {*Solid State Commun.*, **109**, 687-91 (1999)} set out to confirm this report and to investigate if increasing the field to 10 T had any effect on the observed Kerr rotation. The current work measured the original sample of Pittini, both with original surface and a clean polished surface. In addition, new single crystals were produced.

Measurements on the original surface of the Pittini sample were in reasonable agreement with the original data, despite the fact that the air sensitive sample had been stored for two years. The surprising result was that the new samples did not reproduce the 90° Kerr rotation, but exhibited a maximum value of the Kerr rotation of -17°. Furthermore, polishing the original sample resulted in a surface that produced results in essential agreement with the new sample, i.e., no 90° Kerr rotation. As a result, the explanation of the unusual Kerr rotation from the original surface of the Pittini sample is unexplained.

***Ceria Electrolytes in Solid Oxide Fuel Cells Electric Power Generation***

Solid oxide fuel cells (SOFCs) are capable of providing up to 65% electrical efficiency in converting fossil fuel into electricity; and, hence, have drawn considerable attention as a alternative energy conversion technology. In state-of-the-art SOFCs yttria-stabilized zirconia is used as the electrolyte. Unfortunately, the cells must be operated at 800-1000°C in order to achieve sufficient ionic conductivity. Sm doped $CeO_2$ has superior conductivity at 600-800°C; however, under reducing conditions, there is a tendency for the $Ce^{4+}$ reduced to $Ce^{3+}$. Under these conditions the ceria becomes a mixed conductor with both electron and hole conductivity. This tends to short out the fuel cell. In an effort to evaluate this problem in stacks of fuel cells, C. Milliken et al. {*J. Electrochem. Soc.*, **146**, [3], 872-82 (1999)} have developed a model for stack behavior and experimentally validated the model. The analysis indicates that electrical efficiency as high as 42% can be obtained in power plant operation. The obtainable efficiencies are considerably higher than expected, and challenge the assumption that mixed conductors are not suitable for such operations.

***Trivalent Ytterbium Metal***

Of the rare earth elemental metals, only Eu and Yb are divalent because of the tendency for half-filled or fully-filled $4f$ shells, respectively. Thus, chemically Eu and Yb resemble Ca, Se and Ba more than the other trivalent rare earth metals. The atomic volume of Yb in the elemental metal is 41% larger than its trivalent neighbor Lu. This suggests that if the atomic volume could be reduced, the Yb would become trivalent. Indeed, high-pressure measurements demonstrated that a gradual valence transition from $4f^{14}(spd)^2$ to $4f^{13}(spd)^3$ occurs as the pressure is increased to 30 GPa. Experiments to 90 GPa suggested that the structural changes of Yb, under pressure above 30 GPa, did not follow the regular hcp-Sm-type – double hcp – fcc-distorted fcc sequence that other trivalent rare earths follow under pressure. Now, G. N. Chesnut and Y. K. Vohra {*Phys Rev Lett.*, **82**, [8], 1712-15 (1999)} have shown that in the above 100 GPa, the gradual divalent to trivalent transition is completed, and the Yb is isostructural with Sm and Nd under high pressure. The experimental studies are technically interesting in that the pressures are performed in a diamond anvil cell with the 25-μm-diameter sample space. Structural determination is by synchrotron x-ray diffraction; however, since the diamond anvil offers limited x-ray beam access, the diffraction measurement turns Brag's law around from the way we usually use it. Normally, in diffraction, we fix the wavelength and vary the angle in order to find the spacing of the atomic planes. The diamond cell geometry requires that the angle be fixed. If the sample is then exposed to a white x-ray beam, only those wavelengths that satisfy the Brag condition are diffracted through the fixed angle; and, thus, energy analysis of the diffracted beam gives the diffraction pattern.

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