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High-temperature weak ferromagnetism in a low-density free-electron gas.

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Authors
Young, DP
Hall, D
Torelli, ME
et al.

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values have been obtained by surface-sensitive measurements, while \( \Delta_{\text{r}} \) values have been obtained from both surface (Andreev) and bulk measurements (\( \lambda(T) \) and Raman), and may therefore be more reliable. Yet the presence of \( \Delta_{\text{r}} \) above \( T_{\text{c}} \) in the underdoped regime is in good agreement with a decrease of the spin susceptibility below a temperature \( T' > T_{\text{c}} \), which is a bulk measurement\(^1\).

A related question is that of the mechanism leading to pair formation. A non-mean-field behaviour may just indicate the presence of strong phase fluctuations, and not necessarily the presence of preformed pairs in the Mott sense\(^1\). Both local pairs and the stripe model may explain the continuous increase of \( \Delta_{\text{r}} \) in the underdoped regime. But if the existence of two energy scales was simply due to fluctuation effects, one would expect \( \Delta_{\text{r}} \) to saturate in the underdoped regime\(^2\). It is also possible that \( \Delta_{\text{r}} \) might be unrelated to a pairing amplitude.

In any case, I consider that the existence of two energy scales is well established in the underdoped regime, with the scales converging in the overdoped regime. I have assigned the lower scale, obtained from Andreev reflection experiments, to coherence properties of the condensate; the higher scale reflects the properties of single-particle excitations.

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Note added in proof: I have learned of theoretical work on the superfluid density and the excitation gap in a BCS–Bose–Einstein crossover scenario\(^3\).
can be thought of as a simple cubic CaCl-type arrangement of B6-

octahedra and metal ions. The early electronic structure cluster
calculations of Longuet-Higgins and Roberts7 found that the linked
B6-network required 20 electrons for a ‘closed shell’ electronic config-

uration, indicating that the alkaline-earth hexaborides would be
semiconductors. A study of the low-temperature properties of single

crystals of SrB6, however, found a non-zero conductivity due to

approximately 0.001 electrons per SrB6, and indications of the impor-

tance of electron–hole Coulomb effects6. More recent band structure
calculations10 show that hexaborides with divalent cations should be
semimetals, with a small direct overlap of a primarily boron-derived
valence band with a primarily alkaline-earth-derived conduction band
at the X-point in the Brillouin zone.

Our experiments, including measurements of the electrical resistiv-

ity, the magnetic susceptibility and the magnetization, were

performed on single crystals of CaB6 doped with trivalent La;
these crystals were grown from stoichiometric amounts of the
hexaboride components in molten Al. On similarly prepared single

crystals of Sr1–xCexB6, we have verified that Ce is incorporated

stoichiometrically into the crystals by measuring the magnetic
susceptibility and fitting the data to a Curie–Weiss law with an

effective moment \( \mu_{\text{eff}} = 2.54 \mu_B \) per trivalent Ce ion. It is reasonable
to assume that the neighbour of Ce in the rare-earth sequence, La, is
also incorporated stoichiometrically in SrB6 and CaB6. X-ray dif-

craction has confirmed the cubic hexaboride structure in all cases.

Figure 1 shows the electrical resistivity data obtained between 5 K

and 300 K from single crystals of Ca1–xLaxB6. Already for \( x = 0.005 \),
we find a change to a metallic-like temperature dependence and a

drop in resistivity by a factor of \( \sim 50 \) at low temperature, relative to
the pure host \( (x = 0) \). A single band interpretation of the Hall
constant obtained using the van der Pauw geometry for the

\( x = 0.005 \) sample indicates electron-like carriers, with a density of

0.005 electrons per formula unit, as one naively expects for the

trivalent La substitution. Our preliminary de Haas-van Alphen
experiment on \( x = 0.005 \) La-doped CaB6 along (100) reveals two

orbits. Interpreting these as orthogonal extremal orbits of an

ellipsoid gives an occupied volume (taking account of the ellipsoids
at the equivalent X-points in the Brillouin zone) enclosing \( \sim 0.01 \)
electrons for unpolarized electrons. This value is within experi-
mental error of 0.005 electrons, given the small number of oscilla-
tions observed; the observation of two rather than four extremal
orbits is consistent with the small hole pocket being filled, leaving
only a small filling of the conduction band.

The unusual aspect of these La-doped borides is seen in Fig. 2,
where we plot magnetization versus field at 5 K for a range of values
of \( x \), measured on single crystals of Ca1–xLaxB6. A weak ferromag-
netic moment is evident, its magnitude peaking near \( x = 0.005 \)

0.07 \( \mu_B \) per La, with no moment found in crystals with composition

Ca0.95La0.05B6 (Fig. 3); hysteresis loops for the \( x = 0.005 \) material are

shown in Fig. 3 inset. We find nearly identical magnetic effects with

La-doping of CaB6, SrB6 and BaB6. In all cases, the maximum
moment is found at \( x = 0.005 \). That this moment is a function of

temperature is supported by data for Ca0.95La0.05B6 and Ca0.95Th0.05B6

(Fig. 2 inset): here the moment is maximum at \( x = 0.0025 \). Because Th is incorporated in a tetravalent con-

figuration, it will contribute one more electron than trivalent La, and

hence if the moment is a function of carrier count, compounds with

Th0.0025 and La0.005 should have the same moment. In Fig. 4, we show
the temperature dependence of the magnetic moment of Ca0.95La0.05B6
in a fixed field of 0.1 T as a function of temperature: the data show loss of magnetization near the Curie temperature, \( T_C \),
of approximately 600 K.

The essential point is to determine that the observed weak
ferromagnetism is an intrinsic effect and not of some extrinsic
origin. The magnitude of the ordered moment is \( \sim 1 \) e.m.u. per mol
hexaboride for \( x = 0.005 \) in CaB6, and is \( \sim 2 \) e.m.u. per mol for

Sr0.95La0.05B6. We find consistently that the moment per mole is at

a maximum near \( x = 0.005 \) in both SrB6 and CaB6. The same

systematic study has not yet been made for BaB6. We find similarly
that Ce- and Sm-doped SrB6 samples have an ordered moment

which peaks at \( x = 0.005 \). In addition, however, we recognize the

expected paramagnetic background due to the local magnetic

moment due to the f-electrons of these atoms, which is absent for

La-doped material. These data indicate that the doping does not
produce the moment through trace rare-earth impurities carried by
the high-purity La used for the doping. For the pure alkaline-earth
hexaborides, we find that a moment is present sometimes, and that
this varies from crystal to crystal. This moment is generally

distinctly smaller than that found at \( x = 0.005 \), usually by at least
an order of magnitude. We also find a variation in the temperature
dependence of the electrical resistivity of pure SrB6 and CaB6 from
crystal to crystal; crystals showing weak ferromagnetism have a
more metallic temperature dependence of the electrical resistivity.
Doping divalent hexaborides with other alkaline earths also
produces weak ferromagnetism, for instance in Ca0.95Ba0.05B6. We

can understand this variable behaviour of the crystals with no
carrier doping on the basis of the band structure of the alkaline-earth hexaborides. Calculations\(^1\) show that the details of the overlap of valence and conduction bands at the X-point of the Brillouin zone depend sensitively on the crystallographic parameter fixing the location of the borons in the unit cell; this parameter determines the relative length of the inter- and intra-octahedral boron–boron bonds. Even small changes in this parameter can in the calculations alter the behaviour from insulating to metallic. So we might expect vacancies and foreign-atom additions to alter significantly the properties of the divalent hexaborides for very small dopings, such as seen in materials with similar band structure features (for example, grey tin and bismuth).

Two suggestions for the origin of the weak ferromagnetism which we have observed are (1) ordered defect moments and (2) ferromagnetic polarization of the low-density electron gas. Because no obvious source for a strong coupling giving rise to a Curie temperature as high as \(T_C = 600 \text{ K}\) presents itself, the coupling of magnetic moments localized on the La or other unspecified impurities on this scale seems rather implausible. A more likely candidate for the origin of the magnetic polarization emerges from studies of electronic correlations in the low-density electron gas, such as those of Ceperley and Alder\(^1\). This is a topic of theoretical speculation with a long history, going back to Block and Wigner\(^2\). The study of Ceperley and Alder is a \(T = 0 \text{ K}\) computation, comparing unpolarized and completely polarized states of the electron gas, with ferromagnetism showing up for values of \(\alpha_S\) of the order 80 \(a_B\). (Here \(a_B\) is the radius of the sphere containing one conduction electron; \(a_B\) the Bohr radius.) Later calculations have lowered this value to \(\sim 20 \alpha_B\) (ref. 12). For \(x = 0.005\), we compute \(r_S = 15.0 \text{ Å} = 28.4 \alpha_B\), using the Bohr radius for the free electron. A recent calculation by Ortiz, Harris and Ballone\(^1\) treating partially spin-polarized states of the low-density electron gas has, in fact, found evidence that near \(r_S = 30 \alpha_B\) the stable state is one with ferromagnetic polarization of the order of 10%; this essentially our experimental finding of an ordered moment of \(\sim 0.07 \mu_B\) per carrier at \(x = 0.005\). The natural energy scale here is the Fermi energy, \(E_F\); for free electrons we have \(E_F = 0.062 \text{ eV} = 720 \text{ K}\) for \(x = 0.005\) in CaB\(_6\), of the order of the observed Curie temperature.

The ferromagnetic ground state of a dilute, three-dimensional electron gas has not previously been reported experimentally. But such a ground state seems to provide a possible description of the weak ferromagnetism reported here, although the temperature scale of the phenomenon is unexpected. Detailed calculations appropriate to the lattice case at finite temperature are clearly needed, as is much further experimental elaboration of the details of this ferromagnetism.

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**Improved quantum efficiency for electroluminescence in semiconducting polymers**

Yong Cao, Ian D. Parker, Gang Yu, Chi Zhang & Alan J. Heeger

UNIAX Corporation, 6780 Cortona Drive, Santa Barbara, California 93117-3022, USA

Some conjugated polymers have luminescence properties that are potentially useful for applications such as light-emitting diodes, whose performance is ultimately limited by the maximum quantum efficiency theoretically attainable for electroluminescence\(^1\). If the lowest-energy excited states are strongly bound excitons (electron–hole pairs in singlet or triplet spin states), this theoretical upper limit is only 25% of the corresponding quantum