Unexpected Ferromagnetism in Alkaline-Earth Silicides

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Abstract

Ferromagnetism without transition metals has been the subject of intense debate. Here, we report measurements performed on high purity crystals of alkaline-earth silicides (ÆSi), where we found weak ferromagnetism at room temperature. The small saturation moment is not correlated to the number of electrons in d states. However, Æ d-states are part of a badly conducting network, as a result of charge transfer and mixing with the Si valence band. Polarization of a low density electron gas is the most likely explanation of the observed moment of ∼10⁻⁵μB per formula unit.

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Ferromagnetism has been always associated with transition metal content\[1, 2\]. As with any other type magnetic ordering, it is related to the exchange interaction involving electrons in partially filled \(d\) or \(f\) shells. Nevertheless, whether main group compounds can develop magnetic ordering under certain conditions remains an open subject. This question has received increasing attention with the advent of more precise experimental techniques, which make the reproducible synthesis and study of new materials possible. Intermetallics, for example, can be very reactive in the natural environment (they can be obtained and analysed now in highly controlled atmospheres) and they can have electronic configurations which differ from the conventional electronic arrangements\[3\].

Recently, theoretical calculations have predicted magnetically polarized ground states in some materials containing only main group elements\[4, 5, 6\]; some of them, being half-metals (conducting in only one spin direction), have drawn attention to themselves for possible applications in spintronics. As yet, not enough success has been achieved in experiments for this to be practical. Other interesting cases are those of La-doped alkaline-earth hexaborides\[7\], which seemed to be the first experimental realizations of the very controversial polarized electron gas, predicted theoretically by Bloch\[8\] and Capperley\[9, 10\]. This explanation of the weak ferromagnetism with high Curie temperature observed in \(\mathcal{A}B_6\), was supported by the fact that these compounds were considered bad metals, with a small overlap of the hexaboride derived valence band and metal valence band at the \(X\) point of the Brillouin zone, due to electron-hole coulomb effects and mixing. However, more recent calculations indicated that the scenario is different; the hexaborides are semiconductors and the magnetism seems to occur due to a Stoner instability, either in the La-impurity band at the metallic side of a metal insulator transition\[11, 12\] or in the peak of the density of states formed by gap states related to boron vacancies (or substitution by C and Si impurities) and lattice distortions\[13\].

The subject of the present letter is the evidence of weak ferromagnetism found in another family of main group compounds: the alkaline-earth silicides CaSi, SrSi and BaSi. \(\mathcal{A}\)Si (\(\mathcal{A}\)=Ca, Sr and Ba) crystallize in the CrB structure type\[14\]. One might be tempted to describe them according to the Zintl-Klemm-Busmann (ZKB) concept\[15\]. In short: there is a complete transfer of valence electrons from the most active metals to the most electronegative elements; the latter accommodate all the valence electrons and form polyanions if necessary, in order achieve a closed shell configuration. The anion sublattice is similar to
that formed by the isoelectronic atom and is responsible for the electronic structure. In these terms the silicon substructure fulfills the geometrical conditions for a six valence electron species, i.e. sulfur; Si$^{2-}$ anions form eclipsed zigzag chains, $1_{\infty}[\text{Si}^{2-}]$, and $\text{Æ}^{2+}$ cations are isolated. This would imply a diamagnetic semiconducting behavior which has long been taken for granted for Zintl phases. However, the planarity of the chains is surprising and hints to an additional interaction which is not considered in this simple model. Some time ago it has been shown that many Zintl compounds with planar silicon substructure exhibit metallic properties\cite{16}. Our recent experiments show a quite unexpected magnetic response.

By traditional methods of solid-state synthesis, high purity single crystals and powder of CaSi, SrSi and BaSi were obtained. Elemental analysis by several methods (LA-ICP-MS, EDX, XRD) have proved a negligible content of magnetic impurities; no Fe, Ni or Co was detected whilst the content of Mn amounts to less than 50 ppm.

The results presented here were obtained from measurements performed on single crystals, using a Superconducting QUantum Interference Device (SQUID) from Quantum Design. FIG. 1 (a) shows the temperature scan of the magnetic susceptibility under a field of 0.1 T. The splitting of the zero-field-cooled and the field-cooling measurements indicates the presence of spin coupling with magnetic moment formation, which persist at least up to room temperature. Nevertheless, there is a jump at 75 K which might be due to the interplay of another exchange coupling. FIG. 1 (b) depicts the field loop at room temperature. In addition to a paramagnetic background with room temperature susceptibility of approximately $10^{-5}$ cm$^3 \cdot$ mol$^{-1}$, the hysteresis shows a remanent magnetization and saturation moment ($M_s$) of $5 \times 10^{-5}$ $\mu_B$ and $2.7 \times 10^{-5}$ $\mu_B$ per formula unit, respectively.

Irreversibility is also observed in BaSi and SrSi, with the difference that the background in these cases is diamagnetic. For the analysed samples, $M_s(\text{Sr})<M_s(\text{Ca})<M_s(\text{Ba})$. The moment observed in BaSi was $\sim 0.8$ emu per mol silicide, which is a small value but well above the margin of possible contributions from magnetic impurities.

Resistivity measurements were done on pellets made from powder, over the temperature range from 2 K to 300 K. The resistivity values at room temperature were 0.618 for CaSi, 127.6 for SrSi and 68.2 for BaSi, in units of $10^{-4} \Omega \cdot$ cm. These values are large for a normal metal but the temperature dependence is clearly metallic. According to our band structure calculations, to be presented in detail elsewhere, $\text{ÆSi}$ are metallic; the Fermi level crosses the anion valence band and the cation $\text{Æ}$-$s$ and $\text{Æ}$-$d$ states (FIG. 2 (a)). This charge transfer...
should not be much of a surprise since the Si$^{2-}$ configuration can be destabilized by the coulomb repulsion at silicon sites. In this way, instead of the typical “Zintl” closed shell semiconductor, these systems form conducting networks. First-principles spin-polarized calculations with the precision required ($10^{-5}\mu_B$) are still pending, since the currently available codes are not sensitive to so small a polarization\cite{21}. So far, theoretical polarizations obtained are in the range of the experimental values but are not robust.

An important question is whether or not the observed ferromagnetism is related to the
number of electrons in $d$ states coming either from the $\beta$E atoms or from possible non-magnetic impurities with $d$-valence states. ESi (E=Sc, Y) have the same structure type of the $\beta$ESi but have one extra electron coming from the $d$-valence state of the earth element. In the case of LaSi, there is no phase with the CrB structure type but one which crystalizes in the related FeB structure-type. It consists of a different arrangement of the same trigonal prismatic building blocks as the CrB structure type, therefore changing the effective overlap between silicon and metal orbitals. As such, ESi and LaSi are expected to (and they do) have

![Graph](image)

FIG. 2: Partial density of states: (a) CaSi, (b) ScSi. Dotted line: $s$-states, dashed line: $p$-states, solid line: $d$-states
a larger occupation of $d$ states (FIG. 2). The measurement on these materials show no systematic enhancement of the ferromagnetism with respect to the divalent-metal compounds (TABLE II). FIG. 3 shows the temperature scan and the field loop for ScSi, done under the same conditions as shown for CaSi in FIG. 1. Neither the remanent magnetization nor the saturation moment is larger in comparison with CaSi. Nevertheless, the paramagnetic background is stronger in ESi, which is related to the larger DOS at the Fermi level. A subcolumn has been added to TABLE II (numbers in square brackets) with the susceptibilities.
of the elemental metals to show the systematic reduction of the paramagnetic component, as it is expected due to the partial electron localization occurring with the transfer towards silicon valence states.

TABLE I: Some data of magnetic susceptibility. $\chi_{bg}$ is the susceptibility at room temperature under a field of 5 T. The numbers in square brackets are the susceptibilities of the corresponding metals (Ca, Sr, ... La). The saturation moments $M_S$ were obtained from the hystereses at room temperature after subtracting the paramagnetic (or diamagnetic) background. “?”: values obtained from measurements at the (recommended) confidence limits of the instrument. $\chi$ of Si is approximately $-0.357 \times 10^{-5}$ cm$^3$·mol$^{-1}$.

| MSi  | $10^4 \chi_{bg}$ (cm$^3$·mol$^{-1}$) | $M_{Rem}$ per f.u. ($10^{-5}\mu_B$) | $M_S$ per f.u. ($10^{-5}\mu_B$) |
|------|-----------------------------------|---------------------------------|---------------------------------|
| CaSi | 0.1 [0.4]                         | 0.6                             | 2.15                             |
| SrSi | -0.6 [-0.2]                       | <0.09 ?                         | <0.08 ?                         |
| BaSi | -0.25 [1.2]                       | 1.2                             | 15.22                           |
| ScSi | 0.2 [3.1]                         | ~0.1 ?                          | ~1.61                           |
| YSi  | 0.5 [4.7]                         | 0.6                             | 2.41                            |
| LaSi | 0.8 [1.2]                         | ~0.1 ?                          | ~0.17 ?                         |

The fit of the paramagnetic background (from 100 K to 300 K) to Curie+Pauli contributions gives, for ScSi, an effective local moment (per metal atom) of 0.118$\mu_B$ (zero for CaSi). The content of Mn is far too low to produce such a value of the localized moments. Our theoretical calculations predict a charge transfer from the metal atom to the silicon of only 0.37 e (0.82 e for CaSi). So, the small values of the localized moments are not caused by a transfer of the electrons to the silicon valence band but rather by a sharing or delocalization of electrons through the mixing between silicon and metal valence states.

Amongst possible explanations, the most likely origin of the observed ferromagnetism is, in our opinion, the polarization of the electron gas. The existence of this state has been controversial; it requires electron gas with densities lower than $10^{20}$ cm$^{-3}$ for the gain of exchange energy to overcome the loss of kinetic energy$^{17,18}$. At densities of similar order, the Wigner-crystal phase$^{17,19,20}$ competes and the system can undergo an electron
localization. The only experimental realization of polarized electron gas has been argued by Z. Fisk, H. -R. Ott et al[7] in the La-doped CaB\textsubscript{6} and similar compounds, where they have proved the polarization to appear in a specific range of doping related with the on-set of conductivity with low carrier density. Although this hypothesis has received much criticism and other possible origins of the magnetism have been proposed, this topic is by no means closed. We can not fully discard the role of vacancies in the origin of the magnetism in ÆSi; however, we do think it is not essential due the intrinsic metallicity of these compounds. For the hexaborides, the saturation moment peaked at a doping of 0.005 La per formula unit reaching a value of \( \sim 0.07\mu_B \) per added La. This value of the magnetic moment is similar to those observed in our case, as are the orders of magnitude of the electric resistivity. Variations of the total moment from sample to sample occur here as well. However, in our case it is believed to happen as a result of the sensitivity of the electron gas to the orbital overlap which is changed by the presence of defects and because of substitution of metal atoms by chemical equivalents with different atomic radii (for example, the presence of Sr and Ba in CaSi). As always, the hypothesis that this magnetism is due to the polarization of the electron gas is based on the intrinsic metallic character of the material. Theoretical studies with a better treatment of electron correlations may be also relevant for this case.

From the current understanding of the electronic structure of ÆSi, one can not discard the exchange between the electron gas and localized electrons, which could contribute to the net polarization. Still, the susceptibility curves of most alkaline-earth- and earth-silicides (shown here just for ScSi) have other features like a jump around 75 K and a kink around 35 K which have not been discussed in this report and, we think, deserve a place in further studies. The quantitative study of the effect of doping on ÆSi will also be considered in future work.

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[21] In band structure calculations, the spilling parameter is an indication of how good an atomic orbital basis set and a band set are in accounting for the charge distribution. Values of 0.1% are considered excellent and smaller numbers are rarely achieved. In order to get stable results for polarizations of \(10^{-5}\mu_B\) per unit cell, the accuracy has to be improved in at least two orders of magnitude.