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Ferromagnetism of the chimney-ladder compound $Cr_{11}Ge_{19}$

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Abstract

Using a non-self-consistent tight-binding-LMTO method, we have obtained the densities of states for $Cr_{11}Ge_{19}$ and $Mn_{11}Si_{19}$. The calculations show a deep minimum in the density of states at an energy corresponding to a valence electron concentration of 14 per Cr (Mn) atom. For $Cr_{11}Ge_{19}$, the Fermi level lies in a high density of states region, suggesting magnetism. Experimentally we have found that this compound is indeed ferromagnetic below 100 K. © 1997 Elsevier Science S.A.

Keywords: Intermetallic compounds; Band structure; Magnetism

1. Introduction

$Cr_{11}Ge_{19}$ and $Mn_{11}Si_{19}$ have the same crystallographic structure; their tetragonal unit cell includes 120 atoms with a large c parameter (48 Å and 52 Å). They belong to a large family of transition metal compounds, the so-called 'chimney-ladder' [1]. The stability of these compounds is controlled by the valence electron concentration (VEC), defined as the total number of valence electrons divided by the number of transition metal atoms. This VEC practically never exceeds the 'magic' number of 14. Moreover, a VEC of 14 appears to be a good criterion for the occurrence of a band gap in these materials (Ru_2Si_3, $RuAl_2$, $Mn_{11}Si_{19}$) which suggests an energy stabilisation of the structure due to the lowering of filled bonding states and the rise of empty antibonding states.

Nothing much is known of the physical properties of these compounds, except that $Mn_{11}Si_{19}$ is a naturally p-doped semiconductor, which has been used in thermoelectric devices. We have performed band structure calculations and magnetic measurements on both $Cr_{11}Ge_{19}$ and $Mn_{11}Si_{19}$.

2. Computational method and results

The calculations have been performed using the tight binding LMTO method and the LMTO parameters tabulated by Andersen [2]. The recursion procedure in real space was used to obtain the densities of states [3]. This procedure avoids the diagonalization of large matrices. The atomic sphere radius for Mn (Cr) and Ge (Si) have been chosen so as to obtain the local neutrality. The calculations are not self-consistent, however, the method gives reasonable results for $TiSi_2$ and $RuAl_2$ where a comparison with other calculations is possible. There are no adjusted parameters.

The calculations show a deep minimum in the density of states at an energy corresponding to a VEC of 14 (Figs. 1 and 2). This minimum, between bonding and antibonding states is related to the hybridization

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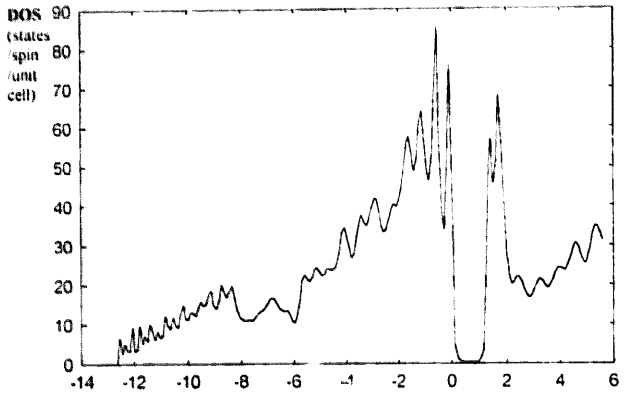

Fig. 1. Density of states of $Mn_{11}Si_{19}$. The Fermi level is at $E = 0$.

between the s and p orbitals of Si (Ge) and the d orbitals of the transition element. The minimum appears within the partial density of d states. It is also found in all 'chimney-ladder' compounds for which we have performed similar calculations and is indeed related to the stability of these peculiar structures.

For $Mn_{11}Si_{19}$, the Fermi level (VEC = 13.9) is in a low density of states region, slightly below the minimum. Although the method we use, which is in fact a reconstruction of the densities of states from their moments, cannot distinguish between a deep minimum (quasi gap) and a real band gap, the calculation strongly suggests that this minimum corresponds to the experimental gap of $Mn_{11}Si_{19}$. For $Cr_{11}Ge_{19}$, the Fermi level (VEC = 12.9) is at a lower energy, in a region of high density of states. The Stoner criterion is just satisfied (using a value of 0.76 eV for the Stoner constant), which suggests itinerant magnetism (with a low moment).

3. Sample preparation and magnetic measurements

$Cr_{11}Ge_{19}$ and $Mn_{11}Si_{19}$ were prepared from commercially available high purity elements: Mn, Cr and Si (powder, 99.9%). Pellets of a stoichiometric mixture were compacted using a steel die and then introduced into silica tubes sealed under argon (200 mm Hg). Preliminary homogenization were conducted at 1273 K. The samples were then annealed for 1 week at 1373 K and 1173 K for $Mn_{11}Si_{19}$ and $Cr_{11}Ge_{19}$, respectively. The purity of the final product was checked by a powder X-ray diffraction technique (Guinier, Cu Kα). Refinement using silicon as an internal standard gives the following parameters (S.G. P – 42 n):

$Cr_{11}Ge_{19}$: $a = 5.803$ (1) Å; $c = 52.31$ (1) Å,

$Mn_{11}Si_{19}$: $a = 5.508$ (4) Å; $c = 47.85$ (6) Å,

which are in good accordance with the previous values of Kolenda et al. [4] and Schwomma et al. [5].

The magnetic measurements were carried out between 4.2 and 300 K using a MANICS magnetosusceptometer in a field up to 1.7 T.

3.1. $Mn_{11}Si_{19}$

At the studied temperature, the $Mn_{11}Si_{19}$ compound exhibits Pauli paramagnetic behaviour (Fig. 3).

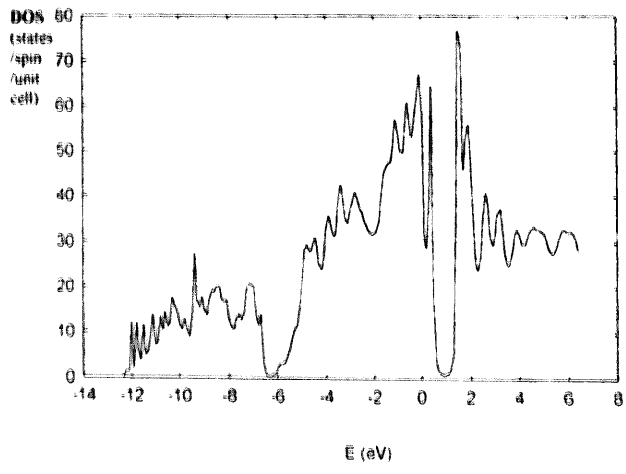

Fig. 2. Density of states of $Cr_{11}Ge_{19}$. The Fermi level is at $E = 0$. The Stoner criterion is satisfied.

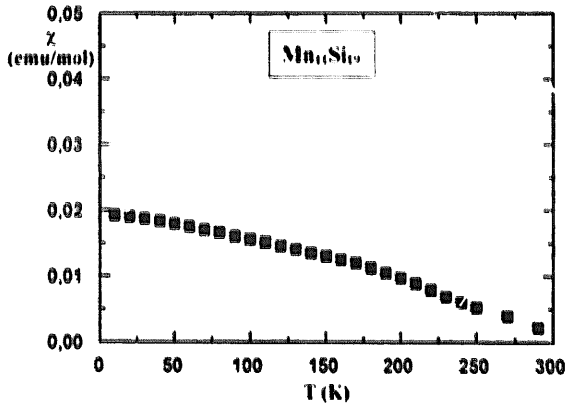

Fig. 3. Magnetic susceptibility of $Mn_{11}Si_{19}$.

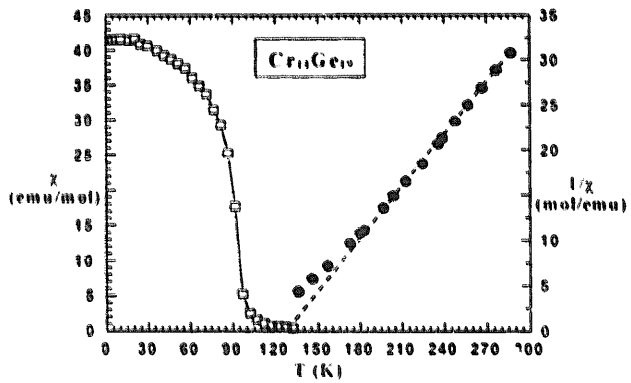

Fig. 4. Magnetic susceptibility of $Cr_{11}Ge_{19}$ above and below T_c.

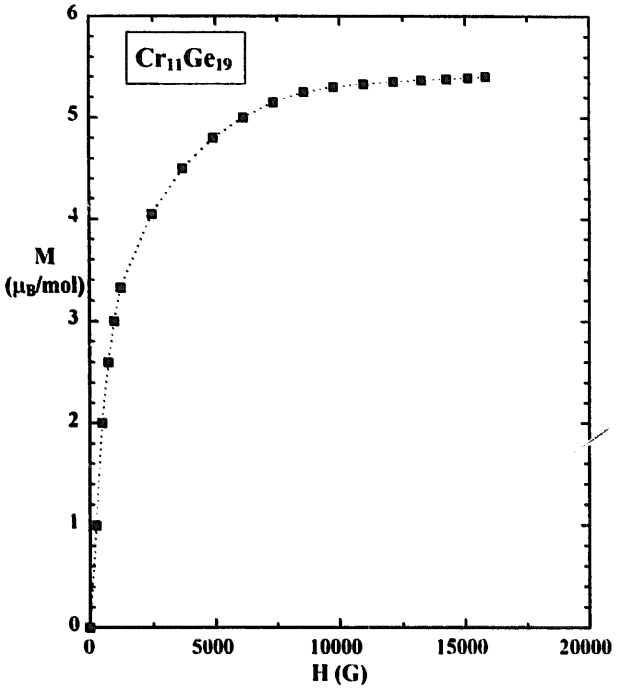

Fig. 5. Magnetization of $Cr_{11}Ge_{19}$ vs. H at 5 K.

The magnetic susceptibility values are about 4.10^{-6} emu g^{-1} and 10^{-5} emu g^{-1} at 285 K and 5 K, respectively.

3.2. $Cr_{11}Ge_{19}$

The $Cr_{11}Ge_{19}$ compound is characterized by a ferromagnetic transition at 97 (3) K (Fig. 4). At 5 K, the maximum magnetization value is 5.4 μ_B/mol (Fig. 5), yielding 0.5 μ_B/Cr. The coercitive field is found to be very small, approximately 100 G. Above the Curie point, the temperature dependence of the inverse susceptibility obeys a Curie–Weiss law: The corresponding data is given below:

$\mu_{eff} = 6.6\ \mu_B$/mol; μ_{eff}/Cr = 1.99μ_B/mol; θp = 130 (5) K

4. Conclusions

The expectations of the band-structure calculation have been confirmed experimentally: $Mn_{11}Si_{19}$ is paramagnetic, while $Cr_{11}Ge_{19}$ is *ferromagnetic* below 100 K with a moment of 0.5 μ_B per atom of Cr. $Cr_{11}Ge_{19}$ appears as an example of an electronic phase [1], whose structure is stabilized by a hybridization giving a low density of states above the Fermi level, but with a high density of states at the Fermi level itself, which leads to magnetism.

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