

Anisotropy and thermopower in Ti_3SiC_2 Laurent Chaput,^{1,*} Gilles Hug,² Pierre Pécheur,¹ and Hubert Scherrer¹¹Laboratoire de Physique des Matériaux, UMR 75560, ENSMN, Parc de Saurupt, 54042 Nancy, France²Laboratoire d'Etude des Microstructures, CNRS-ONERA, Boîte Postale 72,92322 Châtillon Cedex, France

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The Seebeck coefficient of the Ti_3SiC_2 compound has recently been measured and found to be constant and negligible over a wide range of temperature. Materials with essentially zero thermopower allow us to measure the *absolute* thermopower of another material and could therefore be considered as reference material in thermoelectric measurements. In this paper we analyze the origin of this unusual behavior. The thermopower is calculated from *ab initio* electronic structure in the framework of Boltzmann transport theory. Under the Mott approximation for the relaxation time, we found the thermopower negative along the z axis and positive in the basal plane. The very small value which is experimentally observed can be ascribed to a compensation between the nonequivalent crystallographic axes.

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Ti_3SiC_2 is a ternary carbide which has recently received attention since it exhibits intermediate properties between a metal and a ceramic. It has a high melting point, high Young's coefficient, and low Vickers hardness. The combination of a high melting point, large electrical and thermal conductivity, and good machinability makes it a candidate for numerous applications. It also has very unusual electronic properties. In particular, the thermopower S is almost zero over a wide range of temperature.¹⁻⁵ This compound could therefore be used as a reference material in thermoelectric measurements. The reasons for this vanishingly small thermopower are still unclear. In this paper the thermopower is calculated using a realistic electronic band structure according to Boltzmann transport theory. The results suggest that the small value observed for the thermopower is due to the anisotropy in the thermoelectric tensor or more precisely by a compensation between the crystallographic components of the thermoelectric tensor.

Ti_3SiC_2 crystallizes with a hexagonal structure with space group $P6_3/mmc$. The experimental lattice parameters are $a=b=5.793$ a.u. and $c=33.315$ a.u. There are two inequivalent Ti atoms, which we call Ti(1) and Ti(2), at position $2a$ and $4f(z=0.365)$, respectively. The C atoms are in $4f$ position with $z=0.572$ and Si atoms are in $2b$ positions. The structure is shown in Fig. 1 of Ref. 6.

The structure for Ti_3SiC_2 is calculated using the WIEN2K program,⁷ in the framework of density-functional theory. The exchange correlation potential is computed with the generalized gradient approximation (GGA) using the functional of Perdew *et al.*⁸ The structure has been optimized and the equilibrium lattice parameters are found around $a=5.785$ a.u. and $c=33.936$ a.u. The free z parameter for C and Ti(2) atoms are 0.572 03 and 0.370 83, respectively. The self-consistency cycle was achieved with 1000 k points in the first Brillouin zone and we use muffin tins with radii $R=1.85$ a.u. for C and Ti atoms and $R=2.4$ a.u. for Si. The electronic structure we obtain (see Fig. 1) is quite similar to those previously reported in the literature.^{6,9} The low-lying states comes from s and p states of C and Si. Higher in energy, we find a metallic network which arise from a (C p)-(Si p)-(Ti d) bonding. At

the Fermi level the states are predominantly d states from Ti(2) atoms (Fig. 7) with an important contribution from the interstitial region.

The electronic structure is used to calculate the thermopower. The usual formula of Boltzmann transport theory¹⁰ is used with 100 000 k points in the Brillouin zone and the relaxation time is evaluated according to the Mott approximation for transition metals¹¹: $\tau(E) \propto 1/g(E)$. In this approximation, we neglect the k - k' dependence of the scattering matrix elements. The only anisotropy that is taken into account comes from the distribution of velocities at the Fermi surface.

The resulting Seebeck coefficient as a function of temperature is presented in Fig. 2. For each temperature the

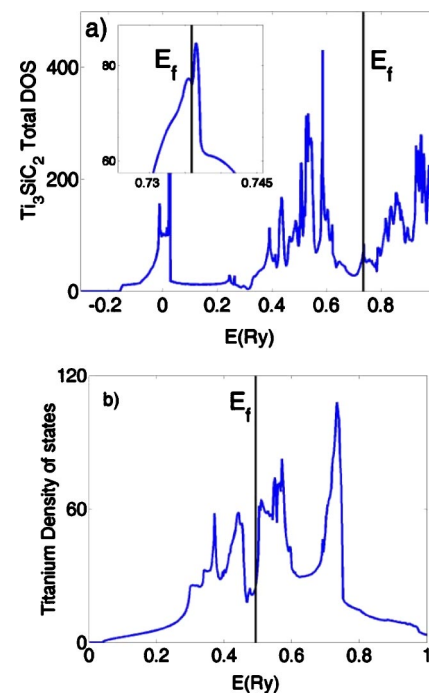


FIG. 1. (Color online) Total density of states for Ti_3SiC_2 compound and for pure Ti. The latter is used in the discussion.

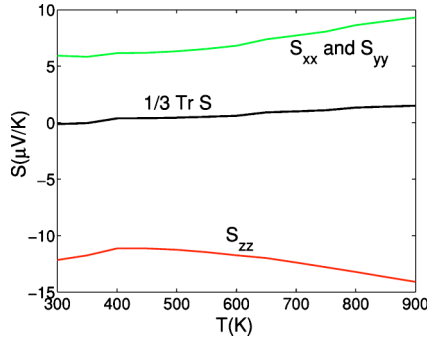


FIG. 2. (Color online) Calculated thermoelectric tensor for Ti_3SiC_2 . $S_{xx}=S_{yy}$ and S_{zz} are the components of the thermoelectric tensor in the basal plane and along the z axis.

chemical potential is calculated in such a way that the integral of the occupied density of states convoluted by the Fermi-Dirac distribution is equal to the total number of electrons. This leads to a varying position of the Fermi energy with temperature. In addition a small shift, constant with temperature, is introduced to best fit the experimental data (Fig. 3). This correction found to be lower than 2 mRy could originate from numerical instabilities in calculations or defects in the crystal as suggested by Barsoum *et al.*² The accurately determined position of the Fermi level is shown in the inset of Fig. 1. In Fig. 2, $S_{xx}=S_{yy}$ are the components of the thermoelectric tensor in the basal plane and S_{zz} is the component along the z axis. They are opposite in sign and S_{zz} is about twice as large as S_{xx} . Since the experimental measurements in Fig. 3 are performed on polycrystalline samples, the observed value S should be compared to the average value of the theoretical thermoelectric tensor \bar{S} ($S = \frac{1}{3} \text{Tr } \bar{S}$) reported in Fig. 2. Thus, in agreement with the experimentally observed behavior, our model predicts a vanishingly small value for the Seebeck coefficient which clearly originates from a compensation between the “in plane” and z components of the thermoelectric tensor. So far we have shown that the small value for the thermopower is due to a compensation between its components but the physical reasons for it are not yet clear.

In this respect we notice that within the metallic approximation, in the orthonormal frame where the thermoelectric tensor is diagonal its components can be rewritten as

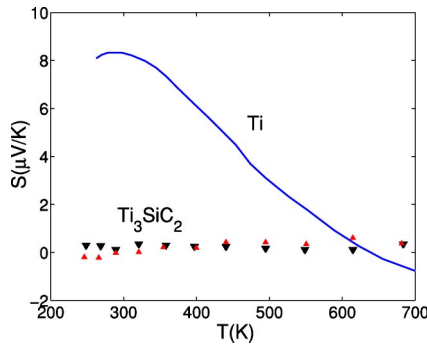


FIG. 3. (Color online) Experimental thermopower for Ti_3SiC_2 and pure Ti. The figure is reproduced from Ref. 1.

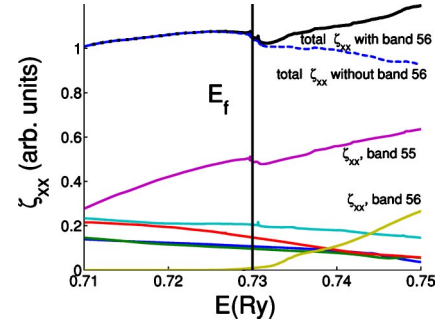


FIG. 4. (Color online) Bands decomposed ξ function: in plane components. The smallest ξ functions corresponding to bands 51 to 54 are not labeled in the figure.

$$S_{ii} \propto - \frac{\dot{\sigma}_{ii}(\mu)}{\sigma_{ii}(\mu)} = \frac{\dot{g}(\mu)}{g(\mu)} - \frac{\dot{\xi}_{ii}(\mu)}{\xi_{ii}(\mu)}, \quad (1)$$

where the dots indicate the derivative with respect to energy and i stands for x , y , and z . With \vec{v}_k^n being the velocities of the electrons, the tensor ξ is defined as

$$\xi = \sum_{nk} \vec{v}_k^n \vec{v}_k^n \delta(\varepsilon - \varepsilon_k^n).$$

In Fig. 1 we compare the density of states of Ti_3SiC_2 and pure titanium. In the case of Ti_3SiC_2 , the Fermi level falls in a minimum (see the inset in Fig. 1) and therefore in Eq. (1) the $\dot{\xi}/\xi$ term easily dominates. Even if most of the states around the Fermi level come from Ti in Ti_3SiC_2 , the picture is very different for pure titanium. In particular, the thermopower does not average to zero. The Fermi level falls in a region where the density of states is rapidly increasing and therefore the first term in Eq. (1) dominates. In our model, the anisotropy comes from the $\dot{\xi}/\xi$ term. It is therefore hidden for pure titanium whereas it dominates for Ti_3SiC_2 . This may explain why the compensation is apparent for Ti_3SiC_2 in Fig. 3 and not for titanium.

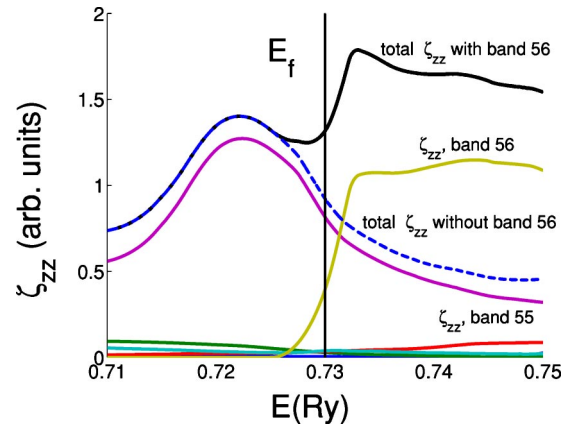


FIG. 5. (Color online) Bands decomposed ξ function: z component. The smallest ξ functions corresponding to bands 51 to 54 are not labeled in the figure.

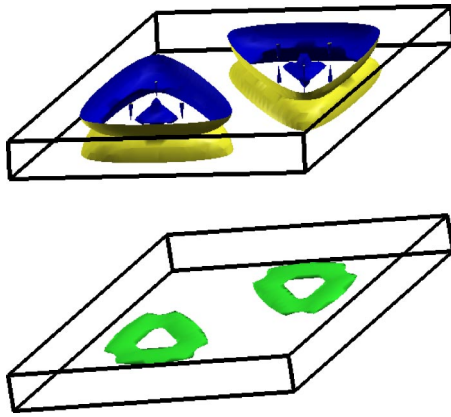


FIG. 6. (Color online) Fermi surfaces for bands 55 and 56.

From the above comment it appears, from a qualitative point of view, that we can restrict the discussion of the thermopower to the ξ/ξ term in the Ti_3SiC_2 compound. In Fig. 4, we show the band decomposition of the tensor ξ in the plane xy and in Fig. 5 along the z axis. The bands are numbered according to Fig. 7 which also show their atomic character. Along the z axis band 56 gives the negative sign and band 55 dominates the contributions in the xy plane. At the Fermi level, other bands contribute (51,52,53,54) but their role is not fundamental as shown in Figs. 4 and 5. The particular role of band 55 and 56 is also seen on their Fermi surface. They are represented on Fig. 6 separately. The Fermi surface of the band 56 is very flat and is located around the $z=c/2$ plane. Since the velocities are normal to the Fermi surface they are mainly along the z direction. It explains the predominant role of this band along the z component of the function ξ and its relatively minor role in the basal plane. On the other hand, the normals to Fermi surface of band 55 have large components in the xy plane and therefore contribute to the component of the ξ function in the basal plane.

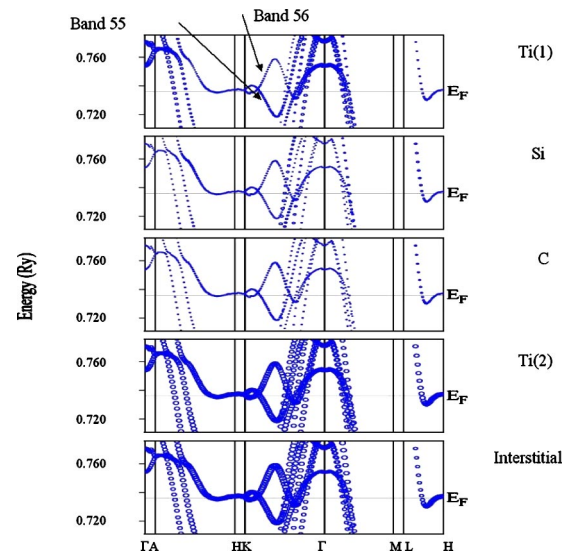


FIG. 7. (Color online) Characters energy bands in Ti_3SiC_2 . The different plots show, respectively, the projection on Ti(1), Si, C, Ti(2) and for the interstitial part. Darker symbols indicate a larger contribution to the bands. The bands 55 and 56 are indicated. The other bands which cross the Fermi level correspond to bands from 51 to 54.

To summarize we have shown that the small value for the thermopower comes from a compensation between the crystallographic components of the thermoelectric tensor. This compensation can be attributed to the particular behavior of band 55 and 56. Band 55 is holelike at the Fermi level and contributes mostly along the xy axes while band 56 is electronlike and contributes mostly along the z axis. Such behavior may also exist in other $M_{n+1}AX_n$ nanolaminates (MAX), but the near perfect compensation found in Ti_3SiC_2 polycrystals is probably quite unique. Further studies are being pursued.

*Email address: chaput@mines.inpl-nancy.fr

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