# Contribution to the Low-Temperature Specific Heat of Vanadium-Doped $Ti_2O_3$ by a One-Dimensional Electron Gas*

M. E. Sjöstrand and P. H. Keesom
*Physics Department, Purdue University, Lafayette, Indiana 47907*

(Received 30 September 1971)

The low-temperature specific heat of $Ti_2O_3$ doped with 3.9% $V_2O_3$ is compared with a theoretical model of a one-dimensional Fermi-Dirac gas proposed by Labbé and Friedel. Quantitative agreement is found between the model and the experimental results for a Fermi temperature of 5.3 K. The system under study furnishes an unusual example of an electron gas obeying a one-dimensional density-of-states function both for the extreme degenerate case and in the transition to the classical region.

We have measured the specific heat of two single crystals of $Ti_2O_3$, one pure and one doped with 3.9% $V_2O_3$, between 0.4 and 20 K employing a heat pulse technique. The accuracy is about 1%, except in the high- and very low-temperature regions where it is somewhat less. In Fig. 1 is shown the extra specific heat, defined as the difference between the specific heat of the vanadium-doped sample and that of the pure sample, as a function of temperature. The full curve in Fig. 1 is calculated from a model proposed by Labbé and Friedel.[1] The essential feature of this model is a one-dimensional density-of-states function $g(\epsilon)$ proportional to $\epsilon^{-1/2}$ ($\epsilon$ is the electron energy).[2] From Fig. 1 it is seen that the calculated result agrees with the experimental data. The parameters that characterize the extra specific heat include the Fermi temperature $T_F$ and the number of carriers per mole, $n$. From these two parameters the density-of-states effective mass is calculated to be $2.2m_0$, where $m_0$ is the free-electron mass.

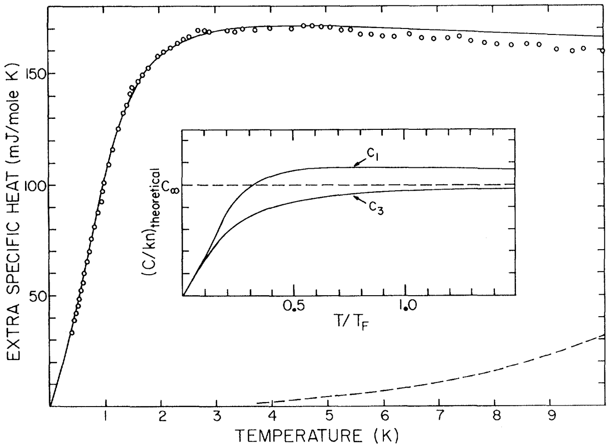

FIG. 1. The extra specific heat of $Ti_2O_3$ doped with 3.9% $V_2O_3$ as a function of temperature. The circles represent experimental data, and the full curve is calculated for a one-dimensional electron gas with $T_F = 5.3$ K and $n = 2.1 \times 10^{22}$ carriers per mole. For comparison the specific heat of pure $Ti_2O_3$ is also displayed as the dashed line. The insert shows the calculated reduced specific heat $C/nk$ for both a one- and a three-dimensional gas as a function of reduced temperature $T/T_F$.

Pure $Ti_2O_3$ at low temperatures is an insulator, and only the phonons contribute to the specific heat $C_L$. Below 15 K, $C_L = 31.7\ T^3$ $\mu$J/mole K which corresponds to a Debye temperature $\Theta_D = 674$ K for fifteen degrees of freedom in the $Ti_2O_3$ molecule. For comparison the specific heat of pure $Ti_2O_3$ is also displayed in Fig. 1; its magnitude for $T \lesssim 5$ K is small compared to that of the extra specific heat. Hence any variation in $C_L$ due to the change in the phonon spectrum when vanadium is incorporated in the lattice will be negligible in the extra specific heat below 5 K.

The insert in Fig. 1 shows the theoretical reduced specific heat $C/nk$ as a function of the reduced temperature $T/T_F$ for a one-dimensional and a three-dimensional electron gas. A method developed by Stoner[3] was employed to derive an explicit expression for the reduced specific heat which for the one-dimensional gas can be written as

$$C/nk = 1.5F_{1/2}(\eta)/F_{-1/2}(\eta) - 0.25F_{-1/2}(\eta)(dF_{-1/2}(\eta)/d\eta)^{-1}, \qquad (1)$$

where the Fermi integral $F_k(\eta)$ is defined by

$$F_k(\eta) = \int_0^\infty [x^k/(1+e^{x-\eta})]dx,$$

and $\eta = \mu/kT$ with $\mu$ the Fermi energy. $\eta$ is obtained from the reduced temperature through the relation $T/T_F = 4/[F_{-1/2}(\eta)]^2$. Tabulated values[4] of $F_k(\eta)$ were used in the evaluation of Eq. (1). The full curve in Fig. 1 was then obtained by adjusting the two parameters $T_F$ and $n$. The best fit to the experimental data was found for $T_F = 5.3$ K and $n = 2.1 \times 10^{22}$ carriers per mole. The agreement with the experimental observations is very satisfactory. Above 6 K this agreement diminishes, partly because of experimental difficulties and partly because of the subtracted phonon part which in this temperature region is increasing rapidly. However, up to 20 K the deviation between experimental and calculated values does not exceed 5%. The vanadium-doped sample was also measured in magnetic fields of 5 and 9 kOe but no magnetic contribution to the specific heat could be seen.

The significant feature of the extra specific heat is a steep rise up to $T \simeq 1.2$ K indicating a very high electron density of states at the Fermi energy. Thereafter the curve bends over and the electrons (holes) become nondegenerate. The specific heat calculated for an isotropic three-dimensional electron gas with a density-of-states function $g(\epsilon)$ proportional to $\epsilon^{1/2}$ could not be fitted to the experimental data. The insert in Fig. 1 shows that the specific heat of a one-dimensional gas, $c_1$, and that of a three-dimensional gas, $c_3$, differ in several respects. As a function of temperature $c_3$ monotonically increases to its high-temperature classical limit, while $c_1$ first goes through a very broad maximum ($c_{1\,\mathrm{max}} = 0.58k$) and then decreases monotonically to its classical limit. In the low-temperature expansion of $c_3$ the two leading terms are of opposite sign, while for $c_1$ they are both positive. This last feature of $c_1$ is indeed found for $T \lesssim 0.8$ K in the experimental data as well as the broad maximum at about 5 K. The specific heat of a two-dimensional gas [$g(\epsilon)$ is constant] was also compared with the experimental data. However, this case showed strong qualitative resemblance with $c_3$ and was ruled out.

Below room temperature pure $Ti_2O_3$ is an intrinsic semiconductor but the addition of $V_2O_3$ in concentrations of 1–5% renders the material metallic.[5,6] Vanadium-doped samples are $p$-type conductors and this has been explained on the basis of the indirect role of vanadium in introducing holes in the otherwise filled valence band of the host material.[6] The crystal structure of $Ti_2O_3$ is that of corundum with the $Ti^{3+}$ cations located on the $c$ axis. In a band model for $Ti_2O_3$ due to Goodenough *et al.*,[5] the bands formed by the $d$ orbitals directed between nearest-neighbor cations along the $c$ axis are split and the band lowest in energy is identified as the intrinsic valence band (or the conduction band for the hole carriers when vanadium is added). In the Labbé-Friedel picture each linear chain of transition metal ions is treated independently leading to a one-dimensional density-of-states distribution for the band defined above. The density-of-states effective mass $m^*$ for the carriers in this band can be calculated from

$$m^* = 3d^4n^2h^2/32kT_FV^2,$$

where $V$ is the molar volume of $Ti_2O_3$ and $d$ is the distance between two adjacent chains. With $d = 2.98$ Å,[7] we found $m^* = 2.2m_0$. It should be emphasized that the above expression for the effective mass is quite different from that of a three-dimensional gas.

A full discussion of this work is planned to be published later when current investigation of $Ti_2O_3$ doped with different concentrations of vanadium is completed.

We wish to acknowledge an informative discussion with Professor S. Rodriguez. We are also grateful to Professor J. M. Honig for supplying the crystals and his stimulating interest in this work.

---

*Work supported by the Advanced Research Projects Agency.

[1] J. Labbé and J. Friedel, J. Phys. (Paris) 27, 153 (1966).

[2] It should be pointed out that the singularity at $\epsilon = 0$ violates the continuity condition of the density-of-states function. This is not serious when the energy region of interest is limited to a narrow range around the Fermi energy.

[3] E. C. Stoner, Phil. Mag. 21, 145 (1936).

[4] A. C. Beer, M. N. Chase, and P. F. Choquard, Helv. Phys. Acta 28, 529 (1955).

[5] L. L. van Zandt, J. M. Honig, and J. B. Goodenough, J. Appl. Phys. 39, 594 (1968).

[6] J. M. Honig, L. L. van Zandt, T. B. Reed, and J. Sohn, Phys. Rev. 182, 863 (1969).

[7] C. N. R. Rao, R. E. Loehman, and J. M. Honig, Phys. Lett. 27A, 271 (1968).