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Hall Effect in VO_2 near the Semiconductor-to-Metal Transition*

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Hall-effect measurements as a function of temperature have been made on single-crystal samples of VO_2 at temperatures both above and below the semiconductor-to-metal transition temperature; the Hall mobility in the semiconducting phase was approximately 0.5 cm^2/V sec and in the metallic phase approximately 0.35 cm^2/V sec.

INTRODUCTION

A number of transition-metal–oxide compounds exhibit large, nearly discontinuous decreases in their resistance at a specific temperature as their temperature is increased; the mechanism causing these semiconductor-to-metal transitions and its relationship to the unusual properties of both the semiconducting and metallic phases of these materials are not well understood at this time. Vanadium dioxide is a good example of such a material; good single-crystal samples of VO_2 have shown a semiconductor-to-metal transition at 67 °C at which their resistance decreased by as much as a factor of 10^5 in less than 0.1 °C with a hysteresis on cooling of about 1 °C.[1] This resistivity transition is accompanied by a structural transformation in which the tetragonal (rutile) high-temperature phase is converted into a related monoclinic low-temperature structure in which the vanadium atoms form alternate staggered pairs along the c_r axis.[2] Discontinuous changes in the magnetic susceptibility and optical properties and a latent heat of about 1020 cal/mole have also been observed at the semiconductor-to-metal transition.[3] Various theories which describe the semiconductor-to-metal transition make more or less specific statements concerning the change in electrical carrier density at the transition or the processes by which the electrical conduction occurs in the high- or low-temperature phase. The low mobility of the carriers in VO_2 makes measurement of their properties difficult. In spite of the difficulty of interpreting Hall-effect measurements in terms of carrier densities and carrier mobilities, it was felt that such measurements would be of some use in discussing the application of certain theories to VO_2.

EXPERIMENTAL DETAILS

Our samples were high-quality VO_2 single crystals grown by the slow cooling of VO_2 dissolved in a flux of V_2O_5 in a sealed fused-silica ampoule, in a manner similar to that of Ladd.[1] The best crystals were grown at a cooling rate of 3.6 °C/h, cooling from 1070 to 720 °C with about a 2.5 °C/cm temperature gradient, and starting from an initial mixture of VO_2 and V_2O_5 with a composition corresponding to $VO_{2.41}$.[4] The samples were approximately 5 mm long and 0.5×0.5 mm in cross section with their long axes in the c_r direction; all electrical measurements reported here were made parallel to this direction.

Hall-effect measurements were complicated by the unusually large amount of noise observed between the Hall contacts in the semiconducting phase which seems to be associated with strain in the sample arising from the discontinuous change of the lattice dimensions at the semiconductor-to-metal transition. For this reason, our Hall-effect measurements were made with a specially constructed Hall-effect apparatus which employs a dc electric current and an ac magnetic field.[4] An ac magnetic field at 35 Hz with an amplitude of 11 kG peak-to-peak was furnished by a small magnet with a 0.32-cm air gap driven through a resonant circuit by a modified 40-W ac power amplifier. In order to minimize inductive pickup from the magnetic field, all leads to the sample were formed as twisted

pairs except the Hall lead, which was a miniature (0.008-cm-o.d.) coaxial cable. The inductive-pickup signal which remained in the Hall-voltage circuit was nulled against an inductive-pickup signal from a wire loop mounted near the Hall sample. This apparatus was capable of detecting Hall voltages as small as 10 nV in semiconducting VO_2 samples with resistance of roughly 3 KΩ and as small as 0.5 nV in metallic phase samples with resistance of roughly 1 Ω.

RESULTS

Hall-effect data are presented most conveniently in terms of the parameters of a one-band nearly-free-electron model in which the number of Hall carriers n_H is related to the measured Hall coefficient R_H by $n_H = -1/R_H e$ and the Hall mobility μ_H is defined by $\mu_H = R_H/\rho$. In the semiconducting phase, the Hall coefficient has the sign corresponding to electrons as the majority carrier for conduction, and the number of Hall carriers is very nearly an exponential function of the reciprocal temperature over the temperature range which could be reached by our apparatus; see Fig. 1.[4] This behavior is very similar to the behavior which would be expected from a conventional semiconductor in which the conduction was by electrons moving in a conduction band with an activation energy of 0.45 eV. The Hall mobility in the semiconducting state has a value of 0.53 ± 0.05 cm^2/V sec at room temperature which decreases slowly with increasing temperature at a rate of about 0.5% per °C. This mobility agrees well with measurements made on a single crystal at a fixed temperature by Barker *et al.*,[5] but is approximately four times larger than the values reported on pressed powder samples.[6] Thin films of VO_2 have yielded room-temperature mobilities ranging from 0.07 to 0.4 cm^2/V sec.[7,8]

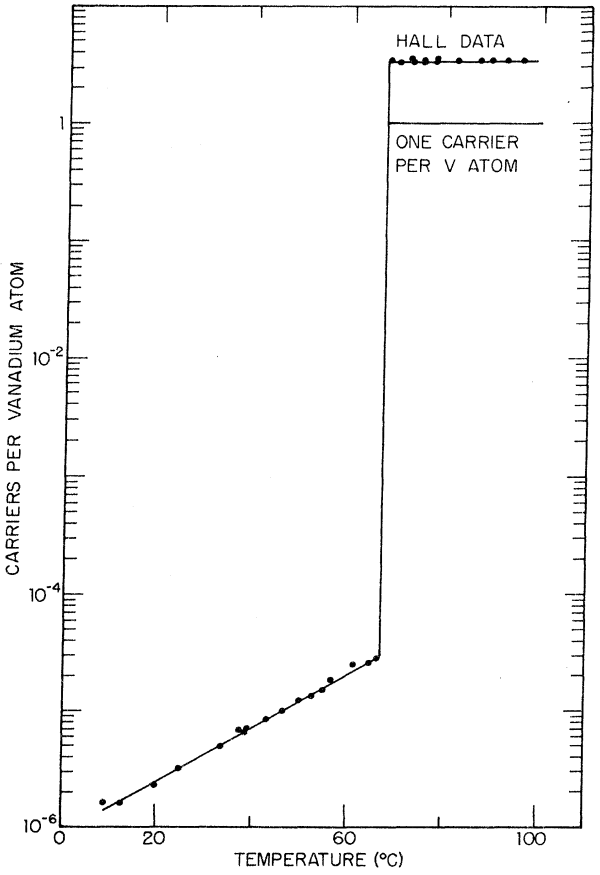

FIG. 1. Number of Hall carriers as a function of temperature in the semiconducting and metallic phases of VO_2.

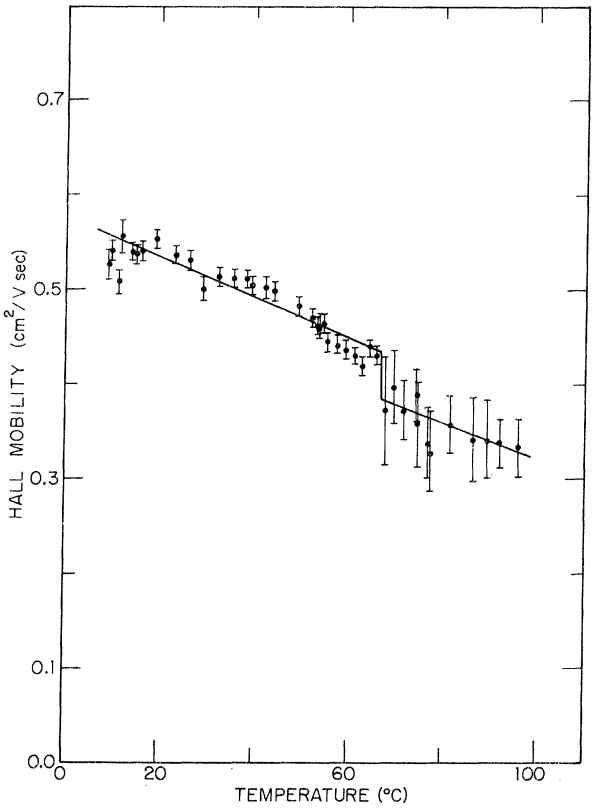

FIG. 2. Hall mobility as a function of temperature in the semiconducting and metallic phases of VO_2.

Our observations of the temperature dependence of the Hall mobility, Fig. 2, show that it decreases approximately as $T^{-3/2}$, as would be expected from scattering of band electrons from acoustic phonons. However, the temperature range was too limited to rule out other similar temperature dependences, which might be expected if there were also a significant contribution from impurity scattering. The Hall mobility was not temperature activated, as would be expected on the basis of many theories for the thermally activated hopping motion of small

polarons, although our data do not rule out the possibility of hopping by adiabatic small polarons which may give a nearly-temperature-independent Hall mobility over a limited temperature interval.[9]

The Hall mobility which we have observed is roughly 10^3 times smaller than the mobilities for most of the conventional semiconductors; if we assume an effective mass for the conduction electrons of $3.5m_0$, consistent with the optical data for the metallic phase,[10] the mobility corresponds to a mean free path for the electrons of only 0.7 Å, shorter than allowed by the nearly-free-electron approximation. Although it is quite possible that the semiconducting-phase effective mass is considerably larger than the metallic-phase effective mass, it is also quite possible that the transport effective mass is made considerably larger than the optical effective mass by dressing effects such as polaron formation, or that the Hall mobility may not be simply related to the drift mobility.

In the metallic phase, our measurements of the Hall coefficient correspond to approximately 3.3 electrons per vanadium atom when interpreted in terms of a one-band spherical-Fermi-surface model.[4] Although most pictures of the energy-level structure of VO_2 lead us to expect at most one conduction electron per vanadium atom, our experimental result can be explained in terms of conduction by carriers of opposite signs in two overlapping bands which could yield a number of Hall carriers larger than the actual number of carriers. Our measurements correspond to a Hall mobility of 0.35 ± 0.10 cm^2/V sec at 80 °C which decreases with increasing temperature at a rate of 0.6% per ° C.

Our experimental observations of the Hall effect in semiconducting and metallic VO_2 are consistent with the band structures for VO_2 proposed by Goodenough[11] and Hearn[12] in which the conduction in the metallic phase is in two overlapping vanadium d bands. The crystalline distortion accompanying the transition to the semiconducting phase splits one of these bands so that half of it, which is completely filled, lies below all of the remaining d bands. In the semiconducting phase, the majority carriers are apparently electrons thermally activated into the lowest unfilled d band. At the semiconductor-to-metal transition, the carrier concentration estimated from the Hall-effect measurements increases by roughly a factor of 5×10^4; this is considerably larger than the factor of 50 estimated from the narrow-band Adler–Brooks theory for a crystalline-distortion semiconductor-to-metal transition.[13]

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