

Metallic Character of a Metal Hydride, V_2H^\dagger

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Both the residual and ideal electrical resistivities of V_2H approximate those of vanadium metal down to 4.2°K. The addition of hydrogen to the metal lowers the superconducting transition temperature. This is discussed from the standpoints of both lower crystal symmetry and higher electron-to-atom ratios.

In an earlier paper¹ the electrical resistivity of body-centered tetragonal (bct) V_2H was shown to approximate that of vanadium metal over the temperature range 140 to 300°K. The present results show that the compound retains its metallic character down to 4.2°K.

The material, hydrogen charging, and technique have been described.² A conventional cryostat was used. The specimen was surrounded by helium gas and a coil heater so that the temperature and thermal gradients were controlled by adjustment of pressure and current. The temperature of the specimen was measured by a calibrated platinum-resistance thermometer.

The residual resistivity of a V-32 at. % H sample was $1.53 \mu\Omega \text{ cm}$ compared with values ranging from 0.45 to $1.41 \mu\Omega \text{ cm}$ for dehydrogenated vanadium.² The ideal resistivity ρ_i of the compound is compared with that of the metal in Fig. 1. For the metal, a Debye characteristic temperature of $\theta = 320^\circ\text{K}$ was determined³ from the Block-Grüneisen relation. A similar analysis was not attempted for the hydride because of the following considerations: The plot of resistivity versus temperature had a monotonically increasing slope up to 440°K.² According to the Block-

Grüneisen relation, the slope should show a maximum at some temperature. While at the lower temperatures the monotonic increase is characteristic of metals, we attributed this behavior at higher temperatures to disordering of hydrogens in interstitial sites.² We cannot determine the temperature for the onset of disordering by measurement of the resistivity. Thus, we were unable to choose a temperature range for testing the fit of our experimental results to the Block-Grüneisen relation for completely ordered V_2H . A Debye characteristic temperature of $293 \pm 10^\circ\text{K}$ was determined from measurements of specific heat in V_2H between 1.7 and 4.2°K.⁴

Matthias⁵ has stressed the importance of cubic symmetry and the metallic character of metal carbides or nitrides if they are to exhibit high critical temperatures for superconductivity. While V_2H is metallic, it does not have cubic symmetry and one might suspect that the critical temperature would be considerably lower than that of vanadium metal ($>5^\circ\text{K}$). Indeed, our own experiments have shown that the hydride is not superconducting at 4.2°K and Rohy and Cotts⁴ find no evidence of superconductivity in V_2H down to 1.7°K. A high transition temperature ($>8^\circ\text{K}$) has been found for one metal hydride, Th_4H_{15} ,⁶ but it is body-centered cubic.^{7,8} The lower hydride, ThH_2 , is bct^{8,9} and does not exhibit superconductivity.^{6,10}

Hydrogen may play still another role in lowering the superconducting transition temperature of vanadium. It has been noted^{5,10} that alloying group-V metals with metals to the right of them in the periodic table lowers the transition temperature. Supposedly this results from the contribution of electrons to the band structure of the metal. Aronson, Reilly, and Wiswall¹¹ have shown that additions of hydrogen to vanadium and niobium have the same effect on their magnetic susceptibilities as increasing the electron-to-atom ratio by alloying with chromium and molybdenum, respectively. Thus, hydrogen is probably donating electrons to the band structure of

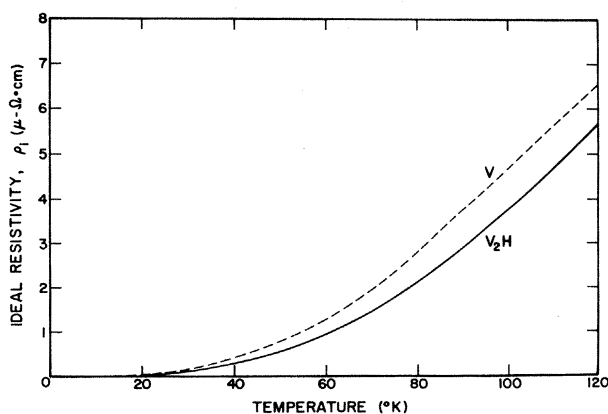


FIG. 1. The dependence on temperature of the ideal resistivities of vanadium metal (Ref. 3) and V_2H . The curve for V_2H represents 66 experimental points with a standard error of estimate equal to $0.02 \mu\Omega \text{ cm}$.

the metal, and could, therefore, be expected to lower the superconducting transition temperature of group-V metals. Matthias⁵ indicates that the transition temperature has maxima for electron-to-atom ratios slightly less than 5 and 7 and a minimum for e/a slightly less than 6. At hydrogen concentrations greater than VH and NbH, hydrogen seems to contribute less than one electron per atom¹¹ to the band structure. Thus, the superconducting transition temperature of the rather unstable hydrides VH₂ and NbH₂, which should have effective $[e/a]$ (ratio of the number of valence electrons to the number of metal atoms) values <7 , may be fairly high, especially since these compounds have fcc crystal structures.^{12,13}

With regard to the effect of e/a on the superconducting transition temperature, it is interesting to reflect on the aforementioned superconducting metal hydride. Th₄H₁₅ would have an apparent $[e/a] > 7$, but it has a high transition temperature equal to that of technetium with $e/a = 7$. If this is an indication that hydrogen contributes less than one electron per atom to the band structure of thorium, then ThH₂ would have $[e/a]$

slightly less than 6 and its transition temperature would be expected to be very low.⁵ Indeed, it is.^{6,10}

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¹D. G. Westlake, S. T. Ockers, and W. R. Gray, *Met. Trans.* **1**, 1361 (1970).

²D. G. Westlake, *Trans. AIME* **239**, 1341 (1967).

³D. G. Westlake and L. C. R. Alfred, *J. Phys. Chem. Solids* **29**, 1931 (1968).

⁴D. Rohy and R. M. Cotts, *Phys. Rev. B* **1**, 2484 (1970).

⁵B. T. Matthias, *Amer. Sci.* **58**, 80 (1970).

⁶C. B. Satterthwaite and I. L. Toepke, *Phys. Rev. Lett.* **25**, 741 (1970).

⁷W. H. Zachariasen, *Acta Crystallogr.* **6**, 393 (1953).

⁸W. L. Korst, *Acta Crystallogr.* **15**, 287 (1962).

⁹R. E. Rundle, C. G. Shull, and E. O. Wollan, *Acta Crystallogr.* **5**, 22 (1952).

¹⁰B. T. Matthias, T. H. Geballe, and V. B. Compton, *Rev. Mod. Phys.* **35**, 1 (1963).

¹¹S. Aronson, J. J. Reilly, and R. H. Wiswall, Jr., *J. Less-Common Metals* **21**, 439 (1970).

¹²A. J. Maeland, T. R. P. Gibb, Jr., and D. P. Schumacher, *J. Amer. Chem. Soc.* **83**, 3728 (1961).

¹³G. Brauer and H. Müller, *J. Inorg. Nucl. Chem.* **17**, 102 (1961).

Exciton-LO-Phonon Interaction and the Anti-Stokes Emission Line in CdS

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Phonon interaction with the I_1 (4888-Å) emission line in CdS (exciton bound to a neutral acceptor site) has often been observed. For the first time the optical frequency anti-Stokes transition, involving the collapse of a bound exciton, has been observed in the emission from selected platelets at 1.2°K. Since the thermally excited phonon field at this temperature is negligible, the observation of anti-Stokes emission directly supports the conclusion that LO phonons are generated to a nonthermal level of distribution as the excitons decay.

Phonon sidebands on the I_1 emission line in CdS have been reported by Scott, Leite, and Damen.¹ The phonon interaction was through the $LO_{(\Gamma)}$ phonon and it was the Stokes lines that were observed. In the current experiment, emission from CdS platelet-type crystals was studied under uv excitation at low temperatures (~1.2°K). In selected crystals both the Stokes lines and an anti-Stokes line are observed. A diagram showing the general features of the emission from CdS is shown in Fig. 1. The I_1 line shows the strongest coupling to the LO phonon of any of the sharp emission lines in CdS. It is this transition

that gives rise to the anti-Stokes line. The I_1 line can be removed from the crystal by appropriate heat treatment.² Such treatment quite naturally removes both Stokes and anti-Stokes lines.

A densitometer trace showing both the Stokes and anti-Stokes transitions is shown in Fig. 2. It has previously been shown that the Stokes transition is very sharp, in fact, so sharp that both the Γ_1 and Γ_5 LO phonons are observed. The anti-Stokes transition is somewhat broadened and this structure cannot be resolved. However, the energy of the LO phonon calculated from the anti-Stokes line is the same as the average energy