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ELECTRONIC SPECIFIC HEAT OF VANADIUM

by

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RENORMALISATION EFFECT IN
THE ELECTRONIC SPECIFIC HEAT OF VANADIUM

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In the Sommerfeld-Bethe theory ¹⁾ the electronic part of the specific heat of a metal is given by the density of states at the Fermi surface. To first order in T/T_F the electronic specific heat varies linearly with temperature and may be written in the form

$$C_e = \frac{1}{3}\pi^2 k^2 N(E_F) T = \gamma_S T, \quad (1)$$

where $N(E_F)$ is the density of states at the Fermi surface. This result is valid only if one neglects the electron-phonon interaction. The latter leads to two renormalisation effects, firstly it modifies the normal mode frequencies of the crystal, and secondly it modifies the free energy of the electrons. The first correction is small and amounts to only a few percent ^{2,3)}. The second effect ^{4,5)} may be rather large and, depending on the strength of the electron-phonon interaction, may lead to an essential contribution to the electronic specific heat of the same order as the Sommerfeld value. This interaction part comes from electron transitions in the thermally excited region near the Fermi surface. The perturbation is strong if kT is small, i.e., this renormalisation effect is temperature dependent and reaches its maximum at low temperatures.

For completeness we may mention another effect, that is, the dependence of the free energy of the crystal on shear effects which involve changes

in the electron distribution ⁶⁾. The magnitude of this effect depends on the relation between the Fermi surface and the Brillouin zone boundary, being the stronger the closer the Fermi surface comes to the Brillouin zone. The corresponding contribution to the specific heat augments the Sommerfeld value and varies linearly with temperature in the liquid helium range. This effect is expected to be appreciable only when the electron energy differs considerably from the free electron case.

Even neglecting the last effect, we see that the experimental low-temperature value of γ is not always related to the density of states in a simple way, or in other words the effective γ -value becomes a function of temperature. Until now a direct experimental check on this has not been possible, since it involves the knowledge of the lattice specific heat, resp., of the lattice vibrational spectrum. The calculation of such spectra for metals is not yet reliable enough, since a lattice vibrational model which takes proper account of the electrons is still missing ⁷⁾. However, this unfavourable situation is changing with the possibility to determine such spectra experimentally by neutron techniques. As a first case we present here some results on vanadium.

Fig. 1 shows the lattice vibrational spectrum of vanadium, calculated from the differential inelastic scattering cross section for slow neutrons ^{8,9)}.

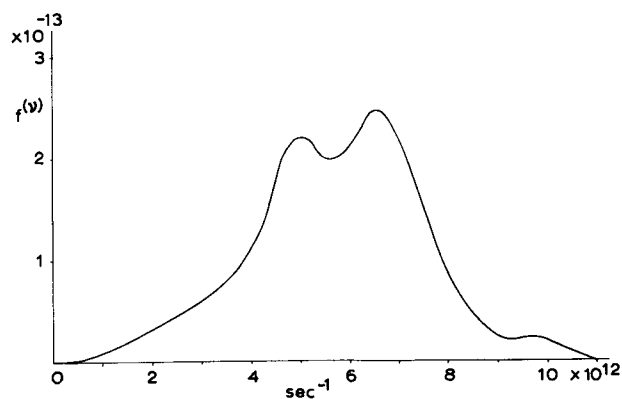


Fig. 1. Experimental lattice vibrational spectrum of vanadium at 300°K.

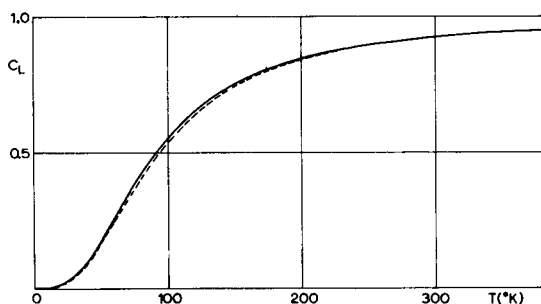


Fig. 2. Lattice specific heat of vanadium, calculated from the spectrum in fig. 1. The dashed curve takes account of the difference in the anharmonic contributions between room temperature and the corresponding temperatures.

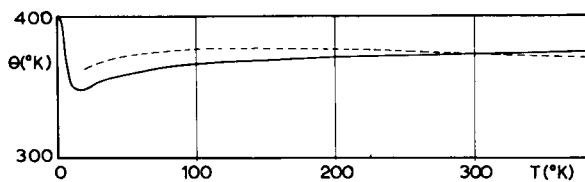


Fig. 3. Apparent Debye temperatures. (For the dashed curve see text in fig. 2.)

The lattice specific heat derived from this spectrum is given in fig. 2 *, the corresponding apparent Debye temperatures are shown in fig. 3. The θ versus T curve has the usual low temperature minimum, which is due to the deviation of the true lattice spectrum from the spectrum of a Debye solid. Since the neutron data were taken at room temperature, the specific heat calculated from the lattice vibrational spectrum is strictly valid only at this temperature. For other temperatures the anharmonic contribution to the specific heat will be different. We may roughly estimate this modification using Grüneisen's law for the relation between Debye temperature and volume change. We find

* For the lowest frequencies of the spectrum we have used the Debye approximation with $\theta = 399^\circ\text{K}$ (10).

$$\theta(T) = \theta(T_R) \{1 - 3\alpha \Delta T\}^K$$

(where T_R is the reference temperature, α is the coefficient of linear expansion, K is the Grüneisen constant), and calculate the new lattice specific heat from the corrected apparent Debye temperature, using the room temperature value as a reference. The result of this calculation is shown in figs. 2 and 3 by the dashed curves. Due to the uncertainty of this correction we will restrict our following discussion to temperatures, say, above 150°K.

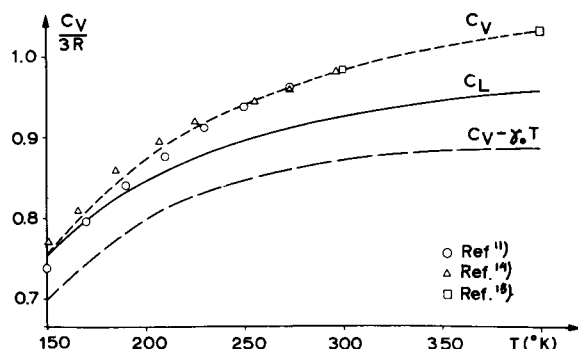


Fig. 4. Lattice specific heat of vanadium above 150°K. — neutron data, ---- calorimetric values of $C_V/3R$, -.-.- values of $(C_V - \gamma_0 T)/3R$ using the experimental low-temperature value for $\gamma_0 = 2.21 \times 10^{-3}$ cal mol⁻¹ deg⁻².

In fig. 4 we compare the lattice specific heat above 150°K derived from the neutron data with calorimetric measurements (11,14,15). If we subtract from the calorimetric data the electronic contribution using the low-temperature value (12), $\gamma_0 = 2.21 \times 10^{-3}$ cal mol⁻¹ deg⁻², we find points which lie for all temperatures below the lattice specific heat curve derived from the neutron data. Therefore, we conclude from fig. 4 that the γ_0 -value, which was found at low temperature, is no longer valid at higher temperature. We propose that this effect might be attributed to the renormalisation of the free energy of the electrons, which is caused by the electron-phonon interaction.

In order to give at least a qualitative justification of this view, we have evaluated the expression for the free energy of the electrons, given by Buckingham and Schafroth (5). Their theory is valid for free electrons in a Debye solid and can thus serve only as an approximative check for a relatively complicated metal like vanadium.

The electronic free energy consists in this approximation of two terms, namely of the usual Sommerfeld value ϕ_S and of a perturbation contribution ϕ_2 :

$$\phi_{el} = \phi_S + \phi_2 = \phi_S \{1 + [1 + g(T/\theta)] (\frac{1}{2}n)^{\frac{1}{3}} F\},$$

$$\phi_S = -\frac{1}{6}\pi^2 N(E_F) (kT)^2;$$

is the number of free electrons per atom, F is the interaction constant of Fröhlich¹³⁾, which for superconductor like vanadium is presumably larger than $(4n)^{-\frac{1}{2}}$; $g(t)$ is a sum of two integrals $f_a(t)$ and $f_b(t)$ which cannot be evaluated in closed form:

$$f_a(t) = \frac{4}{\pi^2} \int_0^\infty \frac{dx}{1 + \exp x} \left\{ t^2 x^2 \log \frac{1 - t^2 x^2}{t^2 x^2} - 2x \frac{1}{t} \log \left| \frac{1 - tx}{1 + tx} \right| \right\},$$

$$f_b(t) = \frac{24}{\pi^2} t^2 \int_0^\infty dx_1 \int_0^\infty dx_2 \frac{1}{(1 + \exp x_1)(1 + \exp x_2)} \times \left\{ (x_1 + x_2)^2 \log \frac{(x_1 + x_2)^2 - t^{-2}}{(x_1 + x_2)^2} - (x_1 - x_2)^2 \log \left| \frac{(x_1 - x_2)^2 - t^{-2}}{(x_1 - x_2)^2} \right| \right\}. \quad (4)$$

Our numerical calculation of these two integrals leads to the curves in fig. 5.

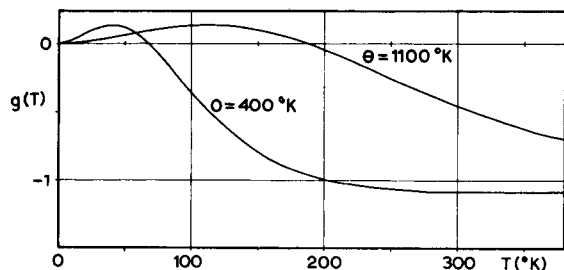


Fig. 5. The function $g(t)$, defined in eqs. (3) and (4), for two θ -values.

Using

$$C_e = -T(\partial^2 \varphi_e / \partial T^2) = \gamma_{\text{eff}} T, \quad (5)$$

we see from fig. 5 that the electronic specific heat depends on temperature. Only for temperatures of at least the order of the Debye temperature we obtain the usual Sommerfeld expression (1). For low temperatures the effective γ -value is higher depending on the interaction constant F .

We may estimate this constant from the difference between the lattice specific heat which was calculated from the neutron data and the values which were derived from caloric data^{*}, using the experimental low-temperature value $\gamma_0 = 2.21 \times 10^{-3} \text{ cal mol}^{-1} \text{ deg}^{-2}$. From

$$+ (\frac{1}{2}n)^{\frac{1}{3}} F = \frac{\gamma_0}{\gamma_s} = \frac{\gamma_0 T}{C_V^{\text{caloric}}(T) - C_L^{\text{neutron}}(T)} \quad (= 2.21/1.15),$$

For $T = 300 \text{ K}$.

assuming $n = 1$, we obtain $F = 1.16$. This value is larger than $(4n)^{-\frac{1}{3}} = 0.63$, as one expects for superconducting elements¹³⁾.

Besides the fact that we find at low temperatures an effective γ -value, which is remarkably higher than the high-temperature value γ_s , another interesting conclusion may be drawn from fig. 5. If we calculate the Debye temperature of vanadium from the elastic constants at low temperatures, as measured by Alers¹⁰⁾, we obtain $\theta_{\text{el}} = 3990 \text{ K}$, which is remarkably different from the caloric value obtained by Corak et al.¹²⁾, $\theta_{\text{cal}} = 3380 \text{ K}$. The caloric value was derived from the usual C/T versus T^2 plot. This experimental discrepancy may be caused also by the renormalisation effect discussed above.

From eqs. (3) and (4) follows for the γ -value at low temperatures, assuming that roughly $g = cT^2$ (see fig. 5):

$$\gamma = \gamma_s \left\{ 1 + (\frac{1}{2}n)^{\frac{1}{3}} F + 6(\frac{1}{2}n)^{\frac{1}{3}} F c T^2 \right\}. \quad (7)$$

In eq. (7) appears a T^2 -term, which generates an additional T^3 -term in the expression for the lattice specific heat. This term may account for the difference between elastic and caloric Debye temperatures. Estimating c from fig. 5, we find a new caloric Debye temperature, $\theta'_{\text{cal}} \approx 3700 \text{ K}$, which agrees better with the elastic value than the previous one. In view of the approximations made, this seems to be a further confirmation for the existence of an appreciable renormalisation effect in the electronic specific heat of vanadium.

It is a pleasure to thank Mr. Cocchi and Mr. De Bruyn from the Cetus Computational Centre for their help in the evaluation of the two integrals in eq. (4).

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