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The specific Debye–Waller factor and a search for antiferromagnetism in vanadium

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Abstract. X-ray energy-dispersive and neutron diffraction measurements on a vanadium single-crystal over a temperature range 25 to 165 K have been analysed for the Specific Debye–Waller factor (DWT) and for any antiferromagnetic behaviour. The DWT measurements are consistent with the density of vibrational states in V determined from neutron inelastic scattering experiments. They can also be fitted with a Debye frequency distribution corresponding to a Debye temperature of 370 K. An anomaly at 100 K remains unexplained. The neutron scattering measurements place an upper limit of $0.02 \mu_B$ per atom on any antiferromagnetic moment in vanadium.

1. Introduction

The Debye–Waller factor $\exp(-2M)$ which reduces the intensity of Bragg reflections is related to the phonon frequency spectrum through the expectation value of the thermal mean square displacement $\langle U^2 \rangle$ of the atoms in a crystalline solid (Willis and Pryor 1975).

For a monatomic cubic material

$$I = I_0 \exp(-2M) = I_0 \exp[-(4\pi \sin \theta/\lambda)^2 \langle U^2 \rangle] \quad (1)$$

where

$$\langle u^2 \rangle = \frac{1}{(12\pi^2 mN)} \int_0^\infty E(\nu)/\nu^2 d\nu$$

and

$$E(\nu) = h\nu/[\exp(h\nu/kT) - 1] + \frac{1}{2}h\nu$$

giving

$$\langle u^2 \rangle = \frac{h}{12\pi^2 mN} \left(\int_0^\infty q(\nu) d\nu / (\nu[\exp(h\nu/kT) - 1]) + \frac{1}{2} \int_0^\infty (q(\nu)/\nu) d\nu \right) \quad (2)$$

where m is the atomic mass and $q(\nu)$ is the phonon frequency spectrum normalised to $3N$ normal modes:

$$\int q(\nu) d\nu = 3N. \quad (3)$$

The rate of change of $2M$ with temperature is known as the specific Debye–Waller factor (DWT) and is

$$\text{DWT} = \frac{d(2M)}{dT} = -\frac{1}{I} \frac{dI}{dT} = \frac{4}{3} \left(\frac{\sin \theta}{\lambda} \right)^2 \frac{h^2}{mNkT^2} \int_0^\infty \frac{q(\nu) \exp(h\nu/kT)}{[\exp(h\nu/kT) - 1]^2} d\nu \quad (4)$$

while the heat capacity of a crystal is given by

$$C_v = \frac{h}{kT^2} \int_0^\infty \frac{\nu^2 q(\nu) \exp(h\nu/kT)}{[\exp(h\nu/kT) - 1]^2} d\nu \quad (5)$$

differing in the integrand from DWT by a factor ν^2 .

(In the Debye approximation $q(\nu) = 9N\nu^2/\nu_D^3$ and DWT may be written as

$$\text{DWT} = 12(\sin \theta/\lambda)^2 (h^2 T/mk\theta_D^3) \int_0^{\theta_D/T} \{x^2 \exp(x)/[\exp(x) - 1]^2\} dx \quad (6)$$

where ν_D is the Debye frequency, θ_D is the Debye temperature and $x = h\nu/kT$. At high temperature ($T \gg \theta_D$), DWT tends to a constant value of $12(\sin \theta/\lambda)^2 h^2/mk\theta_D^2$ and at low temperature ($T \ll \theta_D$) is approximately linear in T with a gradient of $4\pi^2(\sin \theta/\lambda)^2 h^2/mk\theta_D^3$.)

In the present paper we report on the measurement as a function of temperature of the DWT of vanadium by energy-dispersive x-ray diffraction and a comparison of the result with that calculated from phonon frequency spectra. Vanadium was chosen since its frequency spectrum has been measured directly by neutron inelastic scattering (see, e.g., Stewart and Brockhouse 1958, Page 1967), and its elastic constants (Alers 1960) and heat capacity (de Launay 1956, Bendick and Pepperhoff 1982) are well known.

Energy-dispersive x-ray diffraction offers many advantages: since one measures all orders of a reflection simultaneously and in a fixed diffraction geometry, the particular values of structure factor, Debye–Waller factor, absorption and geometric corrections do not influence the ratio $\Delta I/I$ which is used in calculating DWT. In addition, long-term stability of the generator is not important.

2. Energy-dispersive x-ray measurements

A large vanadium single crystal cut and polished parallel to a (110) plane was mounted in an x-ray cryostat cooled by a helium DISPLEX system. A white x-ray beam from a tungsten target impinged on the crystal in symmetrical reflection and the scattering was measured with a Ge solid-state detector at a fixed scattering angle of $2\theta = 100^\circ$. The generator was operated at 55 kV and 10 mA and the incident beam defined by slits with an angular divergence of 0.5° . All orders $hh0$ were collected simultaneously and the vanadium fluorescence line was used to monitor the strength of the x-ray beam. Data were collected at small temperature intervals of 2 or 5 K from 20 to 165 K. Data analysis was limited to the range of orders from (660) to (10100) ($\sin \theta/\lambda = 1.40$ to 2.33 \AA^{-1}) to ensure that at least 10^4 counts were measured at each temperature. A significant thermal diffuse scattering correction is necessary, and has been calculated using the elastic

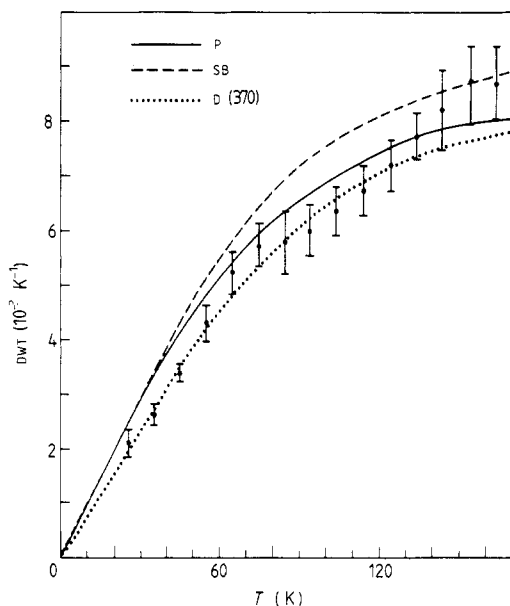


Figure 1. The measured specific Debye–Waller factor for V (full circles). The data were averaged over two runs each for the (660) to (10100) reflections and have been corrected for TDS and normalised via $(\sin \theta/\lambda)^2$ to (770). The uncertainties indicated represent the scatter about the mean of the values for different orders. The full curve (P) has been calculated from the inelastic neutron scattering frequency spectrum measured by Page (shown in figure 2). The broken curve (SB) has been generated from a spectrum of Stewart and Brockhouse, and the dotted curve from a Debye frequency spectrum with $\theta_D = 370$ K.

constants for V given by Alers (1960). The correction for DWT is independent of temperature, but its effect is to raise the experimentally observed values of $(1/I) dI/dT$ by $\approx 1.4 \times 10^{-3} \text{ K}^{-1}$. The DWT factors for all orders have been normalised to that of (770) by multiplying by the appropriate $(\sin \theta/\lambda)^2$ ratio and an average value taken. The variation of this average with temperature is illustrated in figure 1. The error bars represent the scatter of values about the mean.

Extinction effects were expected to be small since the reflections observed corresponded to wavelengths less than 0.5 \AA . All orders of diffraction were found to be internally consistent in their dependence on $(\sin \theta/\lambda)^2$; no systematic trends were observed with wavelength and therefore no extinction correction was thought to be necessary.

The effects of multiple scattering were not expected to change with temperature (there was no change in the diffraction geometry) and any that were present are contained within the scatter shown on the diagram.

3. Discussion of DWT x-ray results

3.1. Predictions of DWT from neutron inelastic scattering spectra

The most recent and most accurate frequency spectrum $q(\nu)$ for vanadium observed by neutron inelastic scattering is that of Page (P of figure 2). The earliest and perhaps

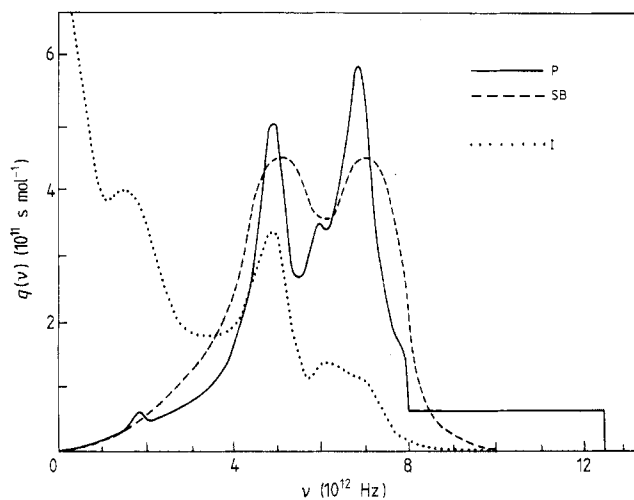


Figure 2. Frequency distributions in V measured by neutron inelastic scattering by Page (P) and by Stewart and Brockhouse (SB). Both distributions have been normalised to one mole of vanadium. The dotted curve I shows the contribution to DWT at 100 K from the integrand of equation (4) as a function of frequency, using the curve labelled P for $q(\nu)$. It can be seen that the DWT is particularly sensitive to the low-frequency spectra.

the best known determination was by Stewart and Brockhouse (SB of figure 2). Both distributions have been normalised for one mole of material. When inserted into equation (4) these distributions give the calculated curves shown in figure 1, in agreement with the observed DWT values.

An examination of the contribution from different frequency ranges to the curves shows that the calculation is extremely sensitive to the mean density of vibrational states at small ν . This is illustrated by the dotted curve (I) in figure 2, which is the contribution from the integrand at 100 K obtained using the density-of-states function of Page. The effect of the small peak at ≈ 2 THz can be seen to be greatly enhanced compared with those of the major peaks at 5 and 7 THz.

3.2. Predictions with $q(\nu)$ derived from a Debye model

Debye theory predicts a quadratic variation of $q(\nu)$ with ν and it is instructive to see how well this fits the DWT data. (Stewart and Brockhouse noted that their low-frequency data were well fitted by a Debye spectrum with a θ_D of 338 K.) Of course, this is not to say that $q(\nu)$ is Debye-like throughout, but that this offers a convenient description of the behaviour of the spectrum at low frequencies, to which DWT is particularly sensitive. The best fit to the experimental DWT curve is with a Debye spectrum having a θ_D of 370 K. The fit is sensitive to the level of correction made for thermal diffuse scattering, and we judge it to be uncertain by about 10 K.

3.3. The intensity ratio method

Linkoaho (1974) has described an intensity ratio method for the evaluation of Debye-Waller factors and obtained a value of $\theta_D = 372$ K for the Debye temperature of

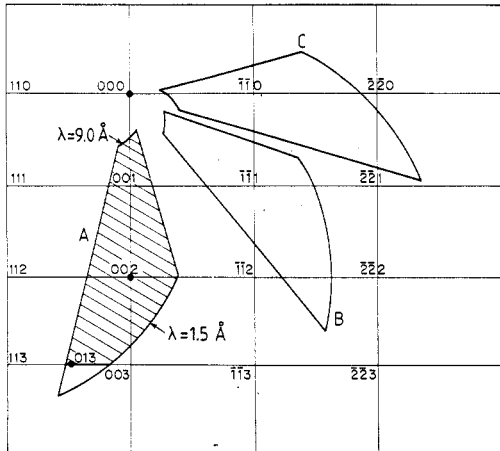


Figure 3. A plan on (110) of the volumes of reciprocal space measured by neutron diffraction with the SCD diffractometer at Argonne National Laboratory. The detector subtends equal angles in the horizontal and vertical directions.

vanadium. Following his method, taking the ratio of the intensity of the (880) reflection at 295 K to that at 35 K, we obtain a value of $\theta_D = 400$ K.

4. Anomalous variation in the DWT curve

Koumelis (1971) has measured the Debye temperature of chromium above and below its antiferromagnetic transition temperature of 310 K and found a discontinuity of some 8 K.

There is a noticeable flattening in our observed DWT curve at 100 K, which can only be produced by a frequency spectrum that varies with temperature. A change of $q(\nu)$ such as occurs in a phase transformation could be the cause of this behaviour and a search for a phase change in vanadium was therefore undertaken by elastic neutron diffraction, which is sensitive to changes in the crystallographic or magnetic structure of a material.

5. Neutron diffraction measurements

From the absence of any measurable intensity at the (100) Bragg position in a neutron diffraction powder pattern of V at 20 K (Shull and Wilkinson 1953) it was deduced that any ordered vanadium atom magnetic moments must be smaller than $0.1\mu_B$. With the advent of energy-dispersive (time-resolved) neutron diffraction from pulsed sources using area multidetectors, a better resolved and more detailed search of reciprocal space than that obtainable from a powder diagram is possible.

The vanadium single crystal was mounted about a $\langle 110 \rangle$ axis in a helium DISPLEX on the SCD diffractometer (Schultz and Leung 1986) at the IPNS source at the Argonne National Laboratory. Spectra were observed at 30 K and at 80 K for three crystal

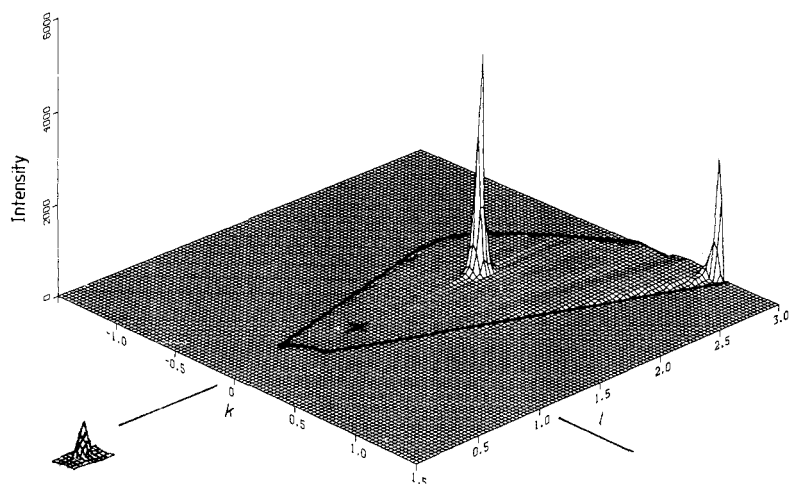


Figure 4. A $0kl$ section through reciprocal space around (002) in a V single crystal at 80 K measured by the neutron time-of-flight technique on the sCD at the IPNS. The section surveyed is outlined and is shown in projection in figure 4 as the shaded area A.

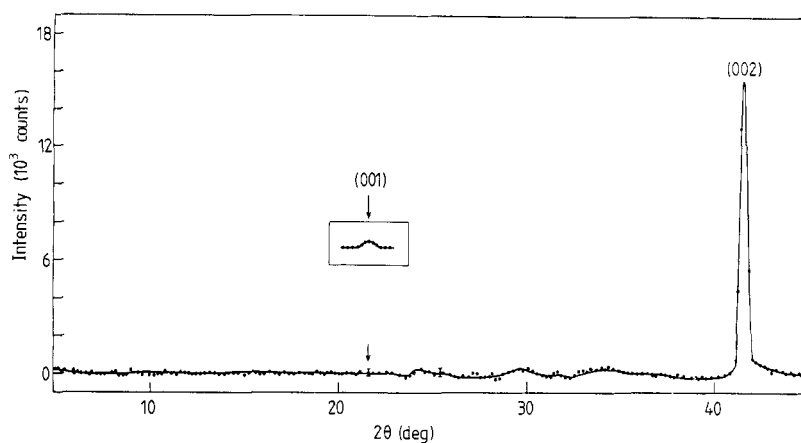


Figure 5. A neutron diffraction (00 h) scan of the V single crystal at 68 K measured on a conventional diffractometer at a wavelength of 1.09 Å. The cryostat background and incoherent scattering from the V crystal have been subtracted.

orientations over a wavelength range 1.5 to 9.0 Å. Figure 3 shows a projection down [110] of the reciprocal-space volumes A, B, C surveyed. The Anger camera detector subtends equal angles (of 40°) at the specimen in both the vertical and horizontal directions, and the orientations chosen sample the volume of one asymmetric unit of the reciprocal lattice out to $\sin \theta/\lambda = 0.66 \text{ \AA}^{-1}$, well beyond the range where the magnetic form factor is significant. While the expected nuclear reflections with $h + k + l$ even were clearly visible, no additional reflections were observed above the incoherent background scattering. Figure 4 shows an $0kl$ section (inclined to the projection axis of figure 3) through reciprocal space in the vicinity of the (002) Bragg position. The area

surveyed by the detector is outlined and the projection of this section is shown as the hatched area A in figure 3.

The same crystal was examined at various temperatures between 30 K and room temperature with neutrons of wavelength 1.09 \AA from a steady-state reactor at AERE Harwell. Scans are recorded in high-symmetry directions through (001) and (111) positions, where magnetic scattering might be expected. However, scans at temperatures below 100 K showed no significant diffraction peaks additional to those above 100 K. Figure 5 shows a scan along (00 h) at 68 K. The cryostat background and incoherent scattering from the vanadium crystal measured in a general direction in reciprocal space have been subtracted. There are small oscillations at points in the remaining 'background', but these showed no temperature variation and are thought to be due to Bragg reflections from small crystallites in the outer aluminium tail of the cryostat.

6. Discussion of neutron measurements

No change in the background level is detectable in either the pulsed or steady-state source neutron measurements anywhere near (001), where magnetic scattering might be expected in the event of an antiferromagnetic transition.

Using the calculated structure factor for the (002) reflection ($=0.0892 \times 10^{-12} \text{ cm}$) as a scale, the size of a reflection in the (001) Bragg position corresponding to an ordered magnetic moment of $0.02\mu_B$ per V atom has been added to figures 4 and 5. It is clear that an even smaller peak could be detected at the (001) position of figure 4. This sensitivity is due to an enhancement of the scattering by sixteen times from the (002) to the (001) reflection (the incident beam flux at the two wavelengths is almost the same), due to the fourth-power law for the variation of the scattered intensity with wavelength. The advantage would be lost if the reflection were near to (002), but that in its turn would involve the appearance of a strong, Lorentz-enhanced reflection at a low angle in figure 5. We therefore feel that we have improved by a factor of at least five on the lower limit of $0.1\mu_B$ set by Shull and Wilkinson.

7. Conclusions

The effective Debye temperature of 370 K, which fits our DWT data, is derived from low-frequency vibrational states of the vanadium lattice and is in agreement with values obtained from specific heat, Debye–Waller and elastic constant measurements (table 1), and is only slightly higher than that fitted from neutron inelastic scattering measurements.

The change in slope of the DWT observed at $\approx 100 \text{ K}$ remains unexplained. As mentioned above, due to the form of the integrand of equation (4), no density-of-states function that is the same at all temperatures can account for this. The flattening of the DWT curve does not apparently correspond to an antiferromagnetic phase transition, which would be expected to reveal itself in the form of additional low-angle Bragg reflections in the neutron diffraction pattern. Our neutron diffraction measurements are not, however, sensitive to small distortions of the nuclear structure, which would give rise to changes in the width and intensity only of high-angle reflections.

Table 1. The effective Debye temperatures for V as determined from various measurements.

θ_D (K)	Experiment	Temperature of experiment (K)
338	Neutron inelastic scattering (Stewart and Brockhouse 1958)	300
383	X-ray TDS (Colella and Batterman 1970)	300
372	X-ray Debye-Waller Factor (Linkoaho 1974)	4-300
400	(This measurement)	35-295
390	Specific heat (de Launay 1956)	100
399	Elastic constants (Alers 1960)	4
370	DWT (This measurement)	20-165

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References

- Alers G A 1960 *Phys. Rev.* **119** 1532
 Bendick W and Pepperhoff W 1982 *J. Phys. F: Met. Phys.* **12** 1085
 Colella R and Batterman B W 1970 *Phys. Rev. B* **1** 3913
 de Launay J 1956 *Solid State Phys.* **2** 219 (New York: Academic)
 Koumelis C N 1971 *Acta Crystallogr. A* **27** 246
 Linkoaho M V 1974 *Phil. Mag.* **23** 191
 Page D I 1967 *Proc. Phys. Soc.* **91** 76
 Schultz A J and Leung P C W 1986 *J. Physique Coll.* **47** C5 137
 Shull C G and Wilkinson M K 1953 *Rev. Mod. Phys.* **25** 100
 Stewart A T and Brockhouse B N 1958 *Rev. Mod. Phys.* **30** 250
 Willis B T M and Pryor A W 1975 *Thermal Vibrations in Crystallography* (London: CUP) ch 4