PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

X-Ray Determination of the 3*d*-Orbital Population in Vanadium Metal

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(Received 29 March 1965; revised manuscript received 8 July 1965)

The ratio of the integrated intensities of the (330)-(411) and the (600)-(442) reflections was measured with Mo $K\alpha$ x rays on a [110] vanadium single-crystal plate 0.004 in. thick. From these ratios the population of the t_{2g}-orbital charge density was determined to be (81±6)% (remainder e_g) compared with 60% t_{2g} for a spherically symmetric charge density. The t_{2g}-orbital charge density points toward the eight nearest neighbors in bcc vanadium.

INTRODUCTION

In bcc vanadium metal there are pairs of x-ray reflections occurring at the same $(\sin\theta)/\lambda$. Two such pairs are the (330)-(411) and (600)-(442). If one obtains a single-crystal plane-parallel plate with the [110] direction normal to the surface, it is possible in transmission to obtain separately each of the Bragg peaks by merely rotating the crystal around this [110] direction. Since the absorption factors, Debye-Waller factors, geometrical factors, etc., are identical for both reflections of each pair, one would ordinarily expect the integrated intensities to be identical *providing that the charge density is spherically symmetric.* Deviations from spherical symmetry can give rise to differences in the atomic scattering factors, hence differences in the integrated intensity. In this way we have experimentally found the charge density to point toward the eight nearest neighbors in vanadium metal, and based on the oft-used model of triply (t_{2g}) and doubly (e_g) degenerate 3*d* orbitals we find the population of the 3d charge density to be (81±6)% t_{2g} (remainder e_g).

EXPERIMENTAL PROCEDURE

A zone refined vanadium crystal was prepared by Metals Research Ltd., Cambridge, England. The crystal was oriented and a 0.004-in. [110] platelet was prepared by spark machining. For the monochromatic Mo $K\alpha$ (LiF[200] monochromator) employed in the measurements the transmission of the vanadium was of order $1/e(\mu=149/\text{cm})$. In all other respects the experimental procedure was identical to that reported previously.[1] Since the observed differences in the integrated intensities of these pairs are only a few percent, it is necessary to investigate the following sources of error.

1. Extinction

Extinction was present in our vanadium crystal and this was particularly noticeable in the low-angle reflections (110), (200) when measured on an absolute basis. However, the reflections of interest (600)-(442) and (330)-(411) are sufficiently weak that extinction effects are quite small. A measurement of the (600) reflection on an absolute basis revealed it to be essentially free of extinction while the (330) peak exhibited approximately (2±2)% extinction. However, extinction is essentially a second-order effect when comparing the integrated intensity of each reflection in a pair. If the extinction is predominantly primary then one expects both reflections of a pair to be the same, while if it is secondary an estimate of the extinction for each reflection can be obtained from the rocking curves. In our crystal the (330) peak was narrower than the (411) peak and yet exhibited more intensity. (This intensity difference, of course, is the effect we are measuring.) Furthermore, a measurement of the transmitted beam as the crystal was rocked through the Bragg peak failed to reveal extinction in either the (330) or (411) peaks. If 2% secondary extinction were present in the (330) peak then one would have observed an average 2% diminution in the transmitted beam coinciding with the Bragg peak.

2. Debye-Waller Factor

Calculation of the absolute intensity of these high-angle diffraction peaks depends markedly on a knowledge of the Debye-Waller factor. The characteristic temperature deduced from specific-heat or elastic-constant measurements is not sufficiently accurate since these measurements reflect different averages over the frequency spectrum. Fortunately the phonon frequency spectrum has been determined with neutrons[2] and graphical integration gives the exponent in the Debye-Waller factor

$$2M=1.324(\sin\theta/\lambda)^2\,, \tag{1}$$

where λ is the wavelength in Å. The "effective" Debye characteristic temperature is 323°K compared to 338°K obtained from low-temperature specific heat[3] and 399°K from low-temperature elastic constants.[4]

3. Anharmonicity and Thermal-Diffuse-Scattering Corrections

Maradudin and Flinn[5] have shown that in a cubic crystal anharmonicity formally leads to different

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[1] J. J. DeMarco and R. J. Weiss, Phys. Rev. **137**, A1869 (1965).

[2] A. T. Stewart and B. N. Brockhouse, Rev. Mod. Phys. **30**, 236 (1958).

[3] W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and A. Wexler, Phys. Rev. **102**, 656 (1956).

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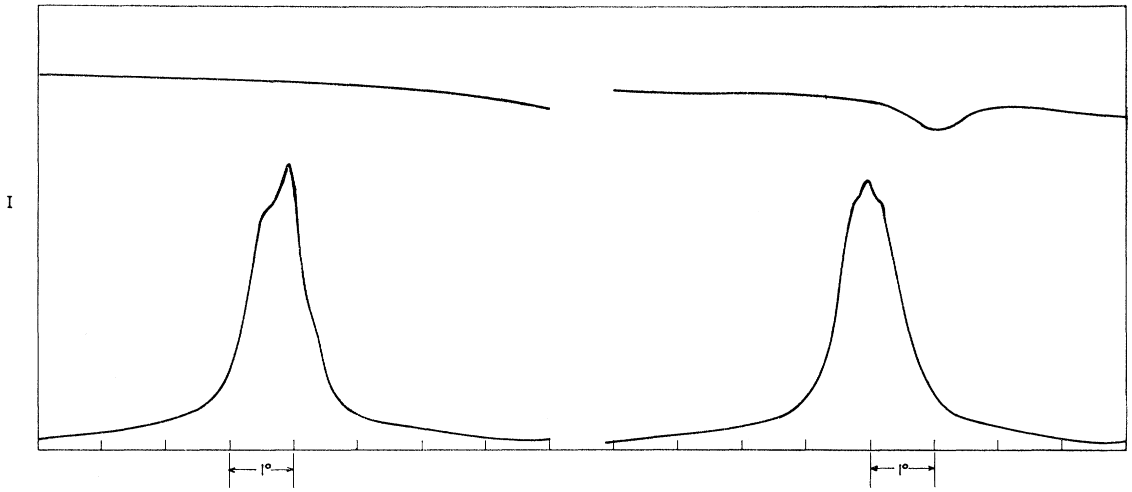

FIG. 1. Chart recordings of two of the 411 peaks together with the intensity of the transmitted beams (upper curves). The peak at the right evidences the presence of a second peak from the dip in the transmitted beam.

Debye-Waller factors for paired reflections. In a general way, for cubic elemental crystals they write the Debye-Waller factor as a product of two terms which for $(T/\Theta)\cong 1$ is

$$\exp[-2M]\exp[-D(h^2+k^2+l^2)^2 \times\{1-(h^4+k^4+l^4)/3(h^2+k^2+l^2)^2\}], \quad (2)$$

where $\exp[-2M]$ is the harmonic Debye-Waller factor and the second term is a correction due to anharmonicity. The value of D depends on the particular element and the h,k,l are the Miller indices. For lead they give D a value $\sim 10^{-9}$ and since it is not expected that D will vary by more than two orders of magnitude the correction term in Eq. (2) is negligible for V at room temperature. Furthermore the *ratio* of the correction terms for the (600)-(442) pair is 1.29 and for the (330)-(411) pair 1.14, which further reduces the relative effect of anharmonicity on pairs of reflections.

Anharmonicity also introduces a correction term in Eq. (1) of the form $(1+AT)$ where A is of order 10^{-4}. For room-temperature measurements of V this correction is negligible.

We have used the nondispersive treatment of Nillson[6] for the TDS (thermal-diffuse-scattering) correction. This is valid if the integration over the Bragg peak is carried out over a sufficiently small angular range so that dispersive effects are not important. Our integration covered a total angular range of $\sim 6°$ (2θ scale) for a Bragg angle of 45° (θ scale) (600) peak. When the Nilsson formula is valid, the TDS correction is identical for each peak of a paired reflection except, of course, for any variation in the atomic scattering factor due to lack of spherical symmetry.

The ratio of TDS to Bragg scattering for V at room temperature is given by

$$0.04\,\sin 2\theta(\sin^2\theta)\Delta\,, \quad (3)$$

where θ is the Bragg angle and Δ is the angular range of integration in degrees (2θ scale). The coefficient in Eq. 3 was determined from the elastic constants of Alers.[4] A TDS correction of $\sim 12\%$ for the (600)-(442) pair and $\sim 5\%$ for the (330)-(411) pair was made in placing them on an absolute basis but for the ratio of the integrated intensities the TDS was combined with the coherent intensity since both vary in the same way owing to lack of spherical symmetry.

4. Absorption Effects

Even though the crystal thickness was uniform to about 5% this still gives rise to appreciable variations in absorption. However, the integrated intensity of the Bragg peaks in transmission depends on the product of the absorption coefficient and crystal thickness (μt) through the function $ute^{-\mu t}$, since the intensity increases linearly with thickness and the absorption increases exponentially. The two effects thus tend to compensate each other, particularly the case $\mu t=1$ for which the function $\mu te^{-\mu t}$ is stationary. Since our crystal thickness corresponds to $\mu t\sim 1.4$, variations of 5% in μt only give rise to variations of $\sim 1.5\%$ in $\mu te^{-\mu t}$. Furthermore by averaging opposite pairs of reflections [i.e., (330) and $(\bar{3}\bar{3}0)$] the variations in $\mu te^{-\mu t}$ required a correction of only a few tenths of a percent.

Of more serious concern was the effect of multiple reflections. Their effect can be seen in Fig. 1 in which both the transmitted and diffracted beams are shown as the crystal is rocked through the Bragg peak. The dips in the transmitted beam indicate the presence of a strong second reflection with noticeable secondary extinction. One must account for this additional decre-

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[6] N. Nilsson, Arkiv Fysik **12**, 247 (1957).

ment of the beam since it decreases the power of the beam available for the reflection we are studying. When secondary extinction is not too large, a measurement of the transmitted beam provides a point to point correction to the scattered beam. The power in the diffracted beam P_H and in the transmitted beam P_T is given by

$$(P_H/P_0)=\sigma_i t\exp[-\mu t+\textstyle\sum_j\sigma_j t]=\sigma_i t(P_T/P_0)\,, \quad (4)$$

$$(P_T/P_0)=\exp[-\mu t+\textstyle\sum_j\sigma_j t]\,, \quad (5)$$

where σ_i is the reflectivity per unit layer of the ith Bragg reflection and the sum over j is taken over all reflections which are simultaneously set for Bragg diffraction. Thus a measure of P_T/P_0 directly yields the attenuation correction to the Bragg peak. The transmitted beam was point-counted with good statistics (error $<0.1\%$) but since the multiple Bragg reflections never occurred too near the maximum of our paired reflections the correction never exceeded 1%. It is believed that this correction can be made to an accuracy of $\sim 20\%$ so that the resulting uncertainty in our paired reflections did not exceed a few tenths of a percent. Furthermore the correction in the *ratio* was only $\sim\frac{3}{4}\%$ for the (330)-(411) pair and less than $\frac{3}{4}\%$ for the (600)-(442) pair.

A search was also made for double Bragg scattering (Renninger effect) by rotating the crystal slightly about an axis normal to the diffracting plane and measuring the integrated diffracted intensity and peak shape. To within an error $<1\%$ no Renninger scattering was observed.

RESULTS

The observed ratios of the two pairs of reflections are given in Table I. Corrected for absorption, they are

$$f^2(442)/f^2(600)=1.048\pm0.01\,,$$

$$f^2(330)/f^2(411)=1.025\pm0.01\,.$$

These ratios can be analyzed in terms of the relative population of the doubly and triply degenerate orbitals through the expressions of Weiss and Freeman.[7]

$$\begin{aligned}f&=\langle j_0\rangle+(A/2)\langle j_4\rangle \text{ per } e_g \text{ electron}\,,\\ f&=\langle j_0\rangle-(A/3)\langle j_4\rangle \text{ per } t_{2g} \text{ electron}\,, \qquad (6)\\ A&=[3(h^4+k^4+l^4)-9(h^2k^2+h^2l^2+k^2l^2)]/(h^2+k^2+l^2)^2\,.\end{aligned}$$

TABLE I. The observed integrated intensities of the paired reflections (600)-(442) and (330)-(411) in vanadium [110] taken in transmission. Each of the integrated intensities (minus background) is the average of four runs, one for each of the reflections $(4\bar{4}2)$, $(\bar{4}42)$, $(\bar{4}4\bar{2})$, $(\bar{4}4\bar{2})$, $(4\bar{1}1)$, $(41\bar{1})$, $(\bar{4}\bar{1}1)$, $(\bar{4}1\bar{1})$, and two for each of the reflections $(\bar{6}00)$, (600), $(\bar{3}30)$, $(3\bar{3}0)$.

Run number	Peak	Average integrated counts	Ratio[a]
1	442	22 184	1.043
	600	21 772	
2	442	21 656	1.033
	600	20 968	
3	442	21 680	1.053
	600	20 592	
4	442	21 936	1.043
	600	21 024	
5	442	22 368	1.037
	600	21 576	
6	330	69 552	1.021
	411	68 096	
7	330	69 864	1.014
	411	68 896	
8	330	70 224	1.016
	411	69 096	

[a] Average ratio for runs 1-5, 1.042 ±0.005; correction for absorption, 1.006 ±0.002; corrected average is 1.048 ±0.01. Average for runs 6–8, 1.017 ±0.005; correction for absorption, 1.008 ±0.003; corrected average is 1.025 ±0.03.

Values of $\langle j_0\rangle$ and $\langle j_4\rangle$ were calculated from the Watson *3d* wave functions.[8] Since $\langle j_0\rangle$ is identical for each reflection of a pair, the observed ratios are fairly insensitive to the choice of $\langle j_0\rangle$. Furthermore $\langle j_4\rangle$ is a fairly insensitive function of $\sin\theta/\lambda$ in the range 0.25 to 1.0 Å^{-1} and is fairly insensitive to the radial extent of the *3d* charge density. For a $3d^4\,4s$ configuration with a slightly expanded *3d* charge density due to solid-state effects we have employed values of $\langle j_4\rangle$ of 0.085 and 0.04 for the (330)-(411) and (600)-(442) pairs respectively. We believe these values to be uncertain by approximately $\pm 10\%$. This leads to the t_{2g} population of $80\pm7\%$ for the (330)-(411) pair and $83\pm5\%$ for the (600)-(442) pair.

A photograph of a model of the t_{2g} and e_g orbital charge density is given by Weiss.[9]

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[7] R. J. Weiss and A. J. Freeman, J. Phys. Chem. Solids **10**, 147 (1959).

[8] R. E. Watson, Massachusetts Institute of Technology Technical Report No. 12, 1959 (unpublished).

[9] R. J. Weiss, *Solid State Physics for Metallurgists* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1963), p. 52.