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X-ray diffraction study of the charge distribution in niobium monocarbide

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Abstract. The structure factors F of niobium monocarbide have been determined from the integrated intensities of Bragg reflections. The intensities from nearly stoichiometric powder samples were measured with monochromatized Cu Kα radiation, and they were put on an absolute scale with respect to the absolute value F (111) of aluminium. The electron distributions of the atoms were analysed in terms of cubic harmonic expansions. It was found that, in comparison with the free-atom model, the charge density of the niobium atom has extended radially and the carbon atom has contracted. Traces of a non-spherical component of the lowest order, which would indicate covalent bond formation, were observed in the carbon atom but not in niobium. A charge transfer of $1{\cdot}0 \pm 0{\cdot}2$ electrons from the niobium Wigner–Seitz cell to that of carbon was found. This is in agreement with the results of recent spectroscopic measurements and band-structure calculations, which indicate that in refractory carbides the metal atoms act as electron donors.

1. Introduction

The addition of boron, carbon, nitrogen and oxygen to the transition metals of groups 4b, 5b and 6b forms series of substances which are noted for their hardness, brittleness and high melting point, properties usually associated with typical covalent compounds. On the other hand, their resistivities and first derivatives of resistivity with respect to temperature are quite characteristic of metals. In view of these unusual properties, interest in these substances, which are frequently referred to as refractory hard metals, has increased greatly in the last few years.

The binding in the hard metals is expected to arise from simultaneous contributions of metallic, covalent and ionic bonding to the cohesive energy. For a discussion of bonding only the outer orbitals of the constituent atoms are of interest; the energetical ordering and the degree of admixture of the 2s and 2p levels of the anion with the d and s transition-metal states play a decisive role in the bond character. Several models and theories of bonding have been proposed to explain the properties of these compounds.

The electronic properties and structure of the transition-metal borides, carbides, nitrides and oxides have been investigated by techniques such as magnetic susceptibility, electrical resistivity, optical reflectivity, thermoelectric power and Hall effect. Results of these experiments have been used to guide the choice of parameters required for the semi-empirical calculation of band structure (Lye and Logothetis 1966). Furthermore, theoretical band-structure calculations using linear combinations of atomic orbitals and augmented plane wave methods have been made for some of these compounds (Bilz 1958, Ern and Switendick 1965, Conklin and Silversmith 1968). Very recently, several measurements have been made on the x-ray emission and absorption and electron spectra (Holliday 1967, Fischer and Baun 1968, Ramqvist 1969). On the basis of these investigations it has been possible to obtain information on problems such as the degree of ionicity in the bond and the electron transfer and, thus, to correlate the experiments to models of the electronic structure.

Experimental studies with x-ray or electron diffraction methods have been made on interstitial compounds γ'-Fe_4N (Elliot 1963, Nagakura 1968), ϵ-Fe_2N and ζ-Fe_2N (Nagakura and Tanehashi 1968), Mn_4N (Kuriyama *et al.* 1963), VN (Hosoya *et al.* 1968) and β-Mo_2C (Nagakura *et al.* 1966). The results of these investigations have a common

attribute, that the non-metal atoms are in negatively ionized states. In spite of the fact that the scattering of x-rays from crystalline solids gives the Fourier coefficients of the charge density, and is thus able to give information on the electron distribution within atoms, this method has not so far been applied to transition-metal carbides. It therefore seemed desirable to carry out x-ray diffraction investigations on these materials. The face-centred cubic niobium monocarbide (NbC) was chosen as the object of the present work. Its availability in the form of fine-grained, nearly stoichiometric powder justified the use of the powder method in measurements.

2. The samples

Modern diffractometers and photon detection and counting systems have been improved to the point that it is possible to reach an accuracy of better than 1% in x-ray intensity measurements on ideal specimens of materials for which the Bragg peaks are intense and widely separated, provided that the details of the experimental arrangement have been studied thoroughly. To keep the accuracy at this level in powder measurements, the effects arising from sample porosity, surface roughness, preferred orientation and extinction require careful consideration.

Preliminary measurements were made on a 325 mesh powder and on a submicrometre powder with the particle diameter of a few hundreths of μm. The relative integrated intensities of low-angle reflections measured with monochromatized Cu Kα radiation on the 325 mesh powder showed distinct reduction with respect to the submicrometre powder results. Presumably, this was due to the granularity and/or extinction effects. Therefore the submicrometre powder was used exclusively in proceeding with the work. By x-ray determination of the lattice parameter, $a = 4{\cdot}470$ Å, this powder (supplied by Koch–Light Laboratories Ltd, England; purity 99·9%) was found to be $NbC_{0{\cdot}98}$ or better in stoichiometry (Kempter *et al.* 1960).

Several samples were prepared by compressing an amount of powder into a cylindrical sample holder. The moulding pressures ranged from one just sufficient to hold the powder together to 700 kG cm^{-2}. The measurements made with Cu Kα radiation showed a slight increase of the integrated intensities with increasing moulding pressure which indicated an effect of porosity. Above 300 kG cm^{-2} the integrated intensities achieved a constant value, and it was accordingly concluded that effects of porosity were insignificant in these samples. This was an expected finding on the ground of the approximate expression given by DeMarco and Weiss (Weiss 1966, p. 94), which suggests that with reasonable sample densities the effect of porosity is negligible for the low value $\mu d \simeq 10^{-3}$, where μ is the linear absorption coefficient and d the particle diameter. On the above considerations, three samples which were moulded applying pressures 300, 500 and 700 kG cm^{-2} were qualified for further studies. The absence of surface roughness and extinction effects for these samples was established by consistent results being obtained on a change of wavelength from copper to molybdenum radiation. By measuring the diffracted intensities as a function of the sample polar angle, the effects of preferred orientation on the Bragg intensities were found to be less than 0·5%.

3. Measurements

For a Bragg reflection, the total energy diffracted from an ideal powder sample is given by

$$E = \text{constant}\,\frac{jF^2}{\mu V^2}\,\frac{1+K\cos^2 2\theta}{\sin\theta\sin 2\theta} \tag{1}$$

where j is the multiplicity, μ the linear absorption coefficient, K the polarization ratio of the monochromator placed behind the receiving slit, θ the Bragg angle, and F the structure factor of a cell of volume V. By comparing the diffracted energies measured under identical experimental conditions for NbC and for a material whose absolute structure

factors are known, one obtains from equation (1) the relation

$$F = F_s\left\{\frac{\mu V^2}{\mu_s V_s^2}\frac{p(\theta)}{p(\theta_s)}\frac{j_s E}{j E_s}\right\}^{1/2} \tag{2}$$

where $p(\theta) = \sin\theta \sin 2\theta/(1+K\cos^2 2\theta)$, and the subscript s refers to the standard material.

The intensity measurements on a relative basis were made with Cu Kα (35 kV, 20 mA) radiation. The recording apparatus comprised a NaI(Tl) scintillation counter, followed by a pulse-height analyser and a digital printout. The polarization ratio of the bent and ground quartz crystal monochromator of Johansson type has been found to be $K = 0{\cdot}803 \pm 0{\cdot}005$ (Suortti and Paakkari 1968). The monochromator was so adjusted that the intensity ratio of the $K\alpha_1$ and $K\alpha_2$ peaks was 2 : 1 (average wavelength $\lambda = 1{\cdot}5418$ Å), as determined with the aid of a single crystal in high order reflection. The accuracy of zero alignment for the x-ray line focus, the goniometer axis, the sample surface, and the receiving slit was better than 0·03° in 2θ. This will bring on insignificant corrections on the integrated intensities.

Initially, the background scattering was investigated by step scanning in order to establish the general behaviour of the background, and to determine the terminal points of the integration range of the Bragg peaks. Since the background was found to ensue mainly from the dark current of the detector, it was subtracted with the assumption of linear behaviour in the range of integration. The integrated intensities were measured in the region $\sin\theta/\lambda < 0{\cdot}6$ Å^{-1}, and they were corrected for thermal diffuse scattering by the application of the formula derived by Chipman and Paskin (1959). The thermal diffuse scattering corrections ranged from a few tenths per cent to about 2 per cent, and they were estimated to be accurate to within 20 per cent.

The absolute structure factor $F(111)$ of NbC was determined relative to the recent absolute measurement of the (111) reflection of aluminium (Järvinen *et al.* 1969). Aluminium was selected as the standard material because the results of three independent absolute measurements (Batterman *et al.* 1961, DeMarco 1967, Järvinen *et al.* 1969) for $F_s(111)$ agree to within 0·6%. Since thin foils of NbC were not available, its mass absorption coefficient μ_ρ for Cu Kα radiation was determined as a mass weighted mean of the values of the elemental constituents. By adopting the values $\mu_\rho(\mathrm{Nb}) = 148{\cdot}8$ cm^2 g^{-1} (Hughes *et al.* 1968) and $\mu_\rho(\mathrm{C}) = 4{\cdot}60$ cm^2 g^{-1} (International Tables for X-ray Crystallography 1962, table 3.2.2A), the outcome will be $\mu_\rho(\mathrm{NbC}) = 137{\cdot}0$ cm^2 g^{-1}, which corresponds to the value $\mu = 1068$ cm^{-1}. There are great variations in the experimental results for the mass absorption coefficient of carbon (International Tables for X-ray Crystallography 1962, table 3.2.1). Fortunately, the contribution of carbon to the total absorption of NbC is small, a 20% error in μ_ρ(C) only affecting the value μ_ρ(NbC) by about 0·6%. For aluminium the value $\mu_s = 133{\cdot}2$ cm^{-1} was measured.

On inserting into equation (2) the above values of μ and μ_s, the result 0·8578 obtained for the ratio $E(111)/E_s(111)$ of the thermal diffuse scattering corrected energies, and other quantities, the absolute structure factor $F(111) = 106{\cdot}4 \pm 1{\cdot}4$ is obtained for Cu Kα radiation. The estimate of the error in $F(111)$ includes the inaccuracies attributable to the following factors: $F_s(111)$ of aluminium (0·7%), absorption coefficients of aluminium (0·3%) and NbC (1·0%), and ratio of the diffracted energies (0·4%). Thus the total error (square root of sum of squares) is about 1·3%.

4. The structure factors

The theoretical structure factors of NbC are given by

$$F_{\mathrm{theor}}(hkl) = 4\{(f_0 + \Delta f' + \mathrm{i}\Delta f'')_{\mathrm{Nb}} \exp(-M_{\mathrm{Nb}}) \pm (f_0 + \Delta f' + \mathrm{i}\Delta f'')_{\mathrm{C}} \exp(-M_{\mathrm{C}})\} \tag{3}$$

where the plus and minus signs apply to reflections with indices *hkl* all even and all odd respectively. The expression $\exp(-M)$, with $M = B(\sin\theta/\lambda)^2$, is the Debye–Waller temperature factor, f_0 is the scattering factor which is independent of the x-ray wavelength, and $\Delta f'$, $\Delta f''$ are the real and imaginary components of the anomalous dispersion correction.

For interpretation of the experimental data, a lattice model of neutral niobium and carbon atoms will be considered as a basis. The free-atom form factors computed by Cromer and Waber (1968, private communication) from relativistic Hartree–Fock wave functions were employed for niobium; for carbon, use was made of Hartree–Fock free-atom scattering factors calculated from Clementi's (1965) wave functions. In the region $\sin\theta/\lambda < 0{\cdot}5$ Å^{-1} the relativistic Hartree–Fock values are about 1% lower than the form factors calculated from Dirac–Slater (Cromer and Waber 1965) and Hartree–Fock–Slater (Hanson *et al.* 1964) wave functions.

Anomalous dispersion contributions to the form factors of niobium were calculated with the values $\Delta f' = -0{\cdot}58$, $\Delta f'' = 2{\cdot}68$ reported by Cromer (1965). For carbon, use was made of the value $\Delta f' = 0{\cdot}02$ ($\Delta f''$ is negligible) extrapolated from Cromer's data. The results of Cromer for niobium compare favourably with the values $\Delta f' = -0{\cdot}6$, $\Delta f'' = 2{\cdot}8$ calculated by Dauben and Templeton (1955), so that the uncertainty in the dispersion corrections hardly exceeds 20%.

The temperature parameters, B_{Nb} and B_{C}, of the individual atoms were determined by employing the difference Fourier method (see e.g. Kurki-Suonio and Fontell 1964, Järvinen and Inkinen 1967). The results obtained were $B_{\mathrm{Nb}} = (0{\cdot}52 \pm 0{\cdot}08)$ Å^2 and $B_{\mathrm{C}} = (0{\cdot}75 \pm 0{\cdot}08)$ Å^2. After the B values had been fixed, the dispersion corrections were applied to the experimental F values. The resulting experimental structure factors F_{exp} are listed in table 1, along with the theoretical values F_{theor} and the differences $\Delta F = F_{\mathrm{exp}} - F_{\mathrm{theor}}$. The limits of error of the values F_{exp} include the inaccuracies attributable to the following factors: counting statistics, background subtraction, thermal diffuse scattering correction, polarization ratio of the monochromator, and dispersion correction. All the values will have an additional uncertainty of 1·3%, corresponding to the estimated error in the absolute scale.

Table 1

(*hkl*)	$\sin\theta/\lambda$	F_{exp}	F_{theor}	ΔF
(111)	0·194	108·3 ±0·3	113·7	−5·4
(200)	0·224	128·4 ±0·5	133·9	−5·5
(220)	0·316	109·1 ±0·4	111·5	−2·4
(311)	0·371	84·6 ±0·4	85·7	−1·1
(222)	0·387	96·9 ±0·6	97·8	−0·9
(400)	0·447	88·3 ±1·1	88·1	0·2
(331)	0·487	71·5 ±0·6	70·9	0·6
(420)	0·500	81·7 ±0·7	80·6	1·1
(422)	0·548	74·3 ±0·6	74·5	−0·2
(511) (333)	0·581	61·0 ±0·6	60·8	0·2

5. Analysis and discussion

The electron distributions of the atoms were studied in terms of lattice harmonics $K_{n\alpha}$, in this case cubic harmonics (Kurki-Suonio and Merisalo 1967). Accordingly, the electron density and the scattering factor of the atoms were expressed as expansions:

$$\rho(\boldsymbol{r}) = \sum_{n\alpha} \rho_{n\alpha}(r) K_{n\alpha}(\theta, \phi)$$

$$f(\boldsymbol{b}) = \sum_{n\alpha} f_{n\alpha}(b) K_{n\alpha}(u, v).$$

Here, r, θ, ϕ and b, u, v are the spherical coordinates of the vectors in the real and reciprocal space, $\boldsymbol{r}$ and $\boldsymbol{b}$, respectively, n is the order of harmonics, and α runs through all independent harmonics of the same order. The radial functions are then given by the

series (Kurki-Suonio 1967)

$$\rho_{n\alpha}(r) = \frac{4\pi(-\mathrm{i})^n}{VA_{n\alpha}} \sum_v F_v \mathrm{j}_n(2\pi b_v r) K_{n\alpha}^*(u_v, v_v) \tag{4}$$

$$f_{n\alpha}(b; R) = \frac{(4\pi)^2 R^3}{VA_{n\alpha}} \sum_v F_v K_{n\alpha}^*(u_v, v_v) \times \frac{x\mathrm{j}_{n+1}(x)\mathrm{j}_n(x_v) - x_v \mathrm{j}_{n+1}(x_v)\mathrm{j}_n(x)}{x^2 - x_v^2} \tag{5}$$

where V is the volume of the unit cell, R is the radius of the sphere which separates the atom from its surroundings as completely as possible, $x = 2\pi Rb$, $x_v = 2\pi Rb_v$, j_n is the spherical Bessel function of nth order, and

$$A_{n\alpha} = \int_0^{\pi} \int_0^{2\pi} K_{n\alpha}^* K_{n\alpha} \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi.$$

The radii of the atomic spheres needed in calculating the radial components f_n were determined by computing the average spherical electron densities ρ_0 of niobium and carbon atoms by means of series (4) with coefficients F_{exp} given in table 1 (figure 1). Evaluation of

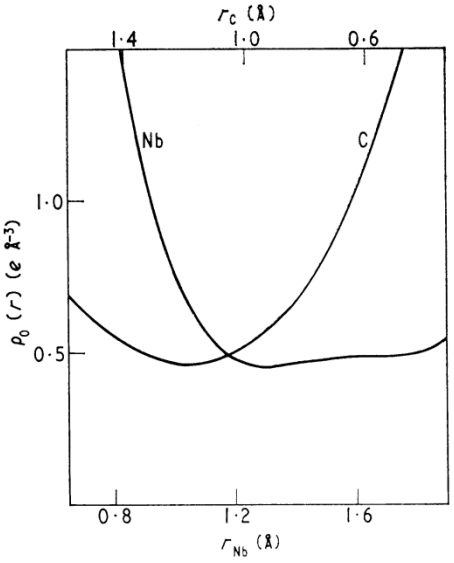

Figure 1. Average spherical electron densities at Nb and C in NbC.

the residual term was effected through Gaussian representations of the theoretical scattering factors. From figure 1 the radii $R_{\mathrm{Nb}} = 1{\cdot}3$ Å, $R_{\mathrm{C}} = 1{\cdot}2$ Å were chosen corresponding to the minima of the curves. This choice is motivated by the intuitive idea that the neighbours give no essential contribution as far as the curve is declining, and by the model calculation of Kurki-Suonio (1968) showing that the neighbouring atoms affect the results Δf_n little even for moderately large spheres and, moreover, to obtain a reasonable interpretation in terms of separate atoms in a case where the atoms overlap the use of overlapping spheres is necessary.

The differences between experimental and theoretical values of the radial functions f_n for $n = 0, 4, 6, 8, 10$ were calculated by means of series (5) with coefficients ΔF reported in

table 1, and with radii of spheres given above. The results are illustrated in figure 2. The spherical components Δf_0 show marked deviations between experimental and theoretical electron distributions in both atoms. The outer-electron charge density of the niobium atom is more widely spread in the crystal than in the free atom, while the carbon atom is contracted compared with the free-atom states. In other words, the results indicate a

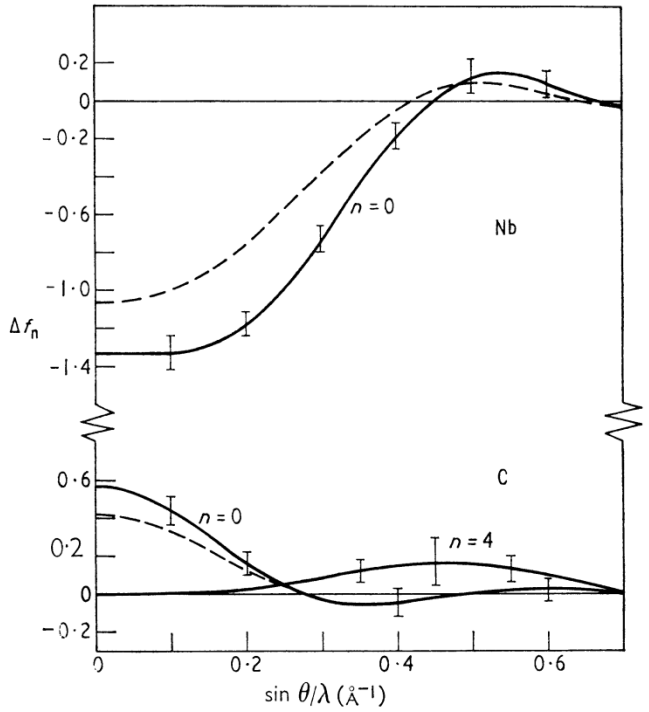

Figure 2. Radial scattering factors Δf_n for cubic harmonic components of Nb and C. The broken curves correspond to a scale factor higher by 2%.

transfer of charge from the niobium to the carbon atoms in NbC crystal compared with the free-atom model. The non-spherical components are very small, of the order of 10^{-2}, except the K_4 component of the carbon atom. If the observed Δf_4 of the carbon atom is real, it indicates electron transfer from [111] to [100] directions, that is towards nearest neighbours. As shown by the error bars its significance is not quite clear. Moreover, the large Δf_0 of the neighbouring Nb atoms adds some uncertainty to its interpretation. On the other hand, the smallness of higher order components indicates good internal consistency of the experimental values. We are therefore inclined to regard this result as a trace of covalent bond formation with no observable contribution from the side of niobium atoms. This non-sphericity would cause the structure factors of the coincident reflections (511) and (333) to differ slightly. The values $F(511) = 60{\cdot}97$, $F(333) = 61{\cdot}28$ would be consistent with the results of figure 2. This change in the starting values of analysis has a negligible effect on the results Δf_n.

The structure of NbC may be dissected into cubic sub-units—Wigner–Seitz cells—of edge $a/2$ such that the niobium and carbon atoms lie in the centres of such cubes. One effect of the strong contraction of the carbon atom is a substantial increase in the electron count taken over the volume of its Wigner–Seitz cell. This electron count is insensitive to the choice of Debye–Waller factors since, on the average, the thermal motion does not alter the total charge in the cell. Consequently, it constitutes a useful quantity for obtaining quantitative information on the degree of electron transfer.

The number of electrons in the Wigner–Seitz cell surrounding an atom at the origin is given by

$$N = \sum_{hkl} F(hkl) \frac{\sin \frac{1}{2}\pi ha}{\pi h} \frac{\sin \frac{1}{2}\pi ka}{\pi k} \frac{\sin \frac{1}{2}\pi la}{\pi l}. \quad (6)$$

With the differences ΔF as coefficients, the series (6) gives the result $\Delta N = -1{\cdot}0 \pm 0{\cdot}2$; the error estimate includes the uncertainties of the relative F_{exp} values and the scale factor. Thus the experimental number of electrons in the niobium Wigner–Seitz cell is significantly smaller than that corresponding to the superposition of free-atom charge densities, showing a charge transfer of about one electron from the metal to the carbon atoms when NbC is formed.

Evidence that there is a charge transfer from the niobium to the carbon atom can also be found in spectroscopic works: (i) The binding energy of the 1s level of carbon is lower in NbC than in graphite, which implies negative carbon atoms in carbide (Ramqvist 1969). (ii) The binding energy of the $3d_{5/2}$ level of the niobium atom is higher for the carbide than for the metal, which indicates that the metal atoms are positive in NbC (Ramqvist 1969). (iii) Korsunskii (1960) examined the $L\beta_2$ and $L\gamma_1$ lines of niobium and concluded that in the formation of stoichiometric niobium monocarbide there is a decrease in the filling of the metal 4d states. Thus it appears safe to conclude that in NbC the metal atoms are positive and the carbon atoms negative.

The question whether the metal atom is an electron donor or acceptor with respect to the carbon atom in refractory carbides has been discussed in several works. A number of them indicate that the metal atom acts as electron acceptor (Lye and Logothetis 1966, Holliday 1967, Fischer and Baun 1968). On the other hand, the spectroscopic measurements of Ramqvist *et al.* (Ramqvist 1969) on pure and well-defined samples, and the quantum-mechanical calculations made using linear combination of atomic orbitals (Bilz 1958) and augmented plane wave (Ern and Switendick 1965, Conklin and Silversmith 1968) methods give support for the positive character of the metal atom. Furthermore, the works in the last group indicate that in cubic carbides the electron transfer consists mainly of metal d electrons which are going into carbon 2p levels, so that the bonding is a mixture of ionic bonding and interactions between the metal d and carbon 2p levels.

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