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Slow-neutron cross sections of hafnium.*

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The slow-neutron scattering and related cross sections of hafnium pertinent to neutron diffraction study are the major subject of this paper. Nearly two dozen publications have dealt with cross sections of hafnium, since, apart from control and poison applications in nuclear reactors, the proton–neutron number correlation in hafnium isotopes provides an attractive subject for nuclear energy level studies. However, inconsistencies between the observed cross sections and those computed from the Breit–Wigner dispersion formula suggest further study on the topic (see Itkin, 1962, for reference summary).

The cross sections of naturally occurring hafnium at 293 ± 3 °K have been re-examined at $0\cdot0717 \pm 0\cdot0002$ eV ($\lambda = 1\cdot068 \pm 0\cdot002$ Å) and some at 0·0460 eV ($\lambda = 1\cdot333$ Å) using a newly constructed neutron diffractometer (Atoji, 1964). The standard deviations cited for our experimental values are obtained from not less than six independent observations. No suitable hafnium compound with reliable composition and structural parameters was available. Consequently, the absolute intensities of hafnium metal filings, with nickel powder as standard, were measured based on the method of substitution and that of mixtures. Lack of sufficient impurity analysis apparently interfered with some of the earlier cross section values. The hafnium metal used in the present work was 99·13 wt.% pure, and was subjected to three independent spectroscopic analyses, which revealed, as major impurities, zirconium 8000 ppm, zinc 440 ppm, titanium 150 ppm and boron 1 ppm. These impurity contributions were not entirely insignificant in the data processing. Transmission measurements with a double-pinhole 3 cm-path cell were made, to obtain the total cross section. The observed Debye temperatures, 420 ± 9 °K for Ni and 240 ± 6 °K for Hf, possess larger uncertainties than the calorimetric values, 440 °K for Ni (Rayne & Kemp, 1956) and 260 °K for Hf (Wolcott, 1957). Subsequently, the latter values were chosen and low-angle reflections were employed for the coherent intensity measurement.

The coherent scattering cross section of hafnium (13·2 barns for nickel) was then found to be $7\cdot59 \pm 0\cdot27$ barns at 0·0717 and 0·0460 eV, being significantly different from the previous value of 9·73 barns at about 0·046 eV (Sidhu, Heaton & Zauberis, 1956). The sign of the amplitude, $b = 0\cdot777 \pm 0\cdot014 \times 10^{-12}$ cm, was reconfirmed to be positive from the $HfC_{0\cdot95}$ data. For hafnium metal, the cross section values at 0·0717 eV for the total of coherent scattering with the finite diffraction effect (Bacon, 1962, p. 42). Debye thermal elastic incoherent scattering, and the sum of all other scattering are, respectively, $75\cdot3 \pm 0\cdot2$, 5·77, 1·61 and approximately 4·0 barns. The paramagnetic scattering cross section calculated from the magnetic susceptibility of Kriessman & Callen (1954) is less than 0·03 barn.

Using the multi-level Breit–Wigner formulae and the virtual-level resonance parameters as summarized by Itkin (1962)†, the resonance scattering amplitudes, b' and b'', in $b = R + b' + ib''$ (R, reaction nuclear radius) and the capture cross sections, σ_c, are computed for the hafnium isotopes. The resonance amplitudes of natural hafnium at 0·0460 eV are $b' = -0\cdot2966$ and $b'' = -0\cdot0032$ in 10^{-12} cm, which differ insignificantly from the 0·0717 eV values in Table 1.

As previously pointed out by several authors (Hans & Sehgal, 1958; Egelstaff, 1959; Itkin, 1962), the observed

Table 1. *The coherent resonance scattering amplitudes in* 10^{-12} *cm at* 0·0717 *eV and the capture cross section in* 10^{-24} cm^2 *at* 0·0253 *eV*

The values including the assumed bound-level resonances are shown in parentheses

Isotope	Abundance	b'(calc.)	b''(calc.)	σ_c(obs.)	σ_c(calc.)
^{174}Hf	0·18%	−0·0664 (0·7722)	−0·0001 (−0·0129)	393 ± 55†	2·34 (393·0)
^{176}Hf	5·15	0 (0·1834)	0 (−0·0007)	15 ± 15	0 (15·0)
^{177}Hf	18·39	−0·7586 (−0·5452)*	−0·0126 (−0·0130)*	380 ± 30	392·0 (380·0)*
^{178}Hf	27·08	−0·5167 (−0·4000)	−0·0036 (−0·0039)	75 ± 10	71·3 (75·0)
^{179}Hf	13·78	−0·0937 (0·0433)	−0·0003 (−0·0015)	65 ± 15	8·23 (65·0)
^{180}Hf	35·44	−0·0179 (0·1114)	−0·0000 (−0·0005)	14 ± 5	0·26 (14·0)
Natural	100·00	−0·2988 (−0·1523)	−0·0033 (−0·0039)	105 ± 5	92·6 (105·6)

* Based on the adjusted parameters for the 1·10 and 2·38 eV resonances.

† Weighted average of Pomerance (1952) and Esch (1960).

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* Based on work performed under the auspices of the United States Atomic Energy Commission.

† In Itkin's report, the mean level spacing of ^{177}Hf should read 3·58 eV and the reduced neutron width at 1 eV of ^{177}Hf and ^{179}Hf should be corrected to 2·11 and 0·843 mV respectively.

and calculated σ_c (Table 1) suggest that some bound-levels contribute considerably to the thermal cross sections. A quantitative estimate of the bound-level parameters which are not discussed by previous authors is made here with the following assumptions. Firstly, average level parameters for the isotope or element in the virtual state are used for the bound-level resonances (Egelstaff, 1959). Secondly, only one bound-level is assigned for the even–even nuclei, since their level spacing near the binding energy is expected to be roughly 20 to 75 eV from the statistical hypothesis (Bollinger, 1960) and 70 to 110 eV from the virtual-level spacings. The bound-levels for ^{174}Hf, ^{176}Hf, ^{178}Hf and ^{180}Hf are then computed to meet the observed σ_c, as, $-E_0 = 2{\cdot}335$, 13·21, 34·05 and 10·17 eV, respectively. Here, the reduced neutron width for ^{176}Hf is taken as 10·7 mV, an average of those for ^{174}Hf, ^{178}Hf and ^{180}Hf. On the other hand, a number of bound-levels may be expected for ^{177}Hf and ^{179}Hf, because of their mean spacings, 3·58 and 4·17 eV, respectively. In order to estimate a maximum possible value for the b'' term, the major contributing resonance parameters of ^{177}Hf, (Γ_γ and $g\Gamma_n$ in mV) at 1·10 and 2·38 eV, are taken as (64, 1·0) and (58, 4·5), respectively. Although these are insignificantly different from Igo & Landon's data (1956), deduction in the resultant σ_c of 364·9 barns may be substantially meaningful. The statistically averaged bound levels in a range 0 to -110 eV are then assigned to $-E_0 = 6{\cdot}40 + 3{\cdot}58n$ eV for ^{177}Hf and $1{\cdot}64 + 4{\cdot}17n$ eV for ^{179}Hf, where n is a non-negative integer. Correspondingly, the coherent scattering amplitudes were computed including the bound-level effect (Table 1). The reaction nuclear radius to meet the observed amplitude is $0{\cdot}93 \times 10^{-12}$ cm. This is close to $0{\cdot}99 \times 10^{-12}$ cm of the cloudy crystal-ball model with a diffuse spherical potential but is deviated considerably from $0{\cdot}78 \times 10^{-12}$ cm of the one with a deformed potential or the strong interaction model (Chase, Wilets & Edmonds, 1958).

The calculated σ_c of natural hafnium, 63·9 barns at 0·0717 eV, with the bound-level contribution, reduces to a self-consistent value of 11·4 barns for the total scattering cross section at 0·0717 eV. The isotropic disorder-scattering cross section of the element is calculated as 1·04 barns and the multiple scattering cross section of the hafnium sample used in the present work (0·005 mm in average diameter) is estimated as about 1 barn (Atoji, 1961). Hence, the spin incoherent scattering cross section should be less than two barns, a reasonable value for ^{177}Hf and ^{179}Hf. In our discussion, relatively large experimental errors in σ_c and the radiation widths are not rigorously treated and an experimental verification similar to that of Peterson & Smith (1962) is not presented. Nevertheless, it may well be concluded that the imaginary part of the scattering amplitude of natural hafnium can be neglected in diffraction study at subcadmium neutron energies.

References

Atoji, M. (1961). *J. Chem. Phys.* **35**, 1950.

Bacon, G. E. (1962). *Neutron Diffraction*. 2nd ed. Oxford: Clarendon Press.

Bollinger, L. M. (1960). *Nuclear Spectroscopy*. Part A, p. 424. New York: Academic Press.

Chase, D. M., Wilets, L. & Edmonds, A. R. (1958). *Phys. Rev.* **110**, 1080.

Egelstaff, P. A. (1959). *Phys. Rev.* **115**, 182.

Esch, L. J. (1960). Reactor Technology Report No. 15, Physics, Report No. KAPL–2000–12, Knolls Atomic Power Laboratory.

Hans, H. S. & Sehgal, M. L. (1958). *Indian J. Phys.* **32**, 276.

Igo, G. & Landon, H. H. (1956). *Phys. Rev.* **101**, 726.

Itkin, I. (1962). *Analysis of the Neutron Capture Cross Section and Resonance Integral of Hafnium.* Report No. WAPD–TM–324, Bettis Atomic Power Laboratory.

Kriessman, C. J. & Callen, H. B. (1954). *Phys. Rev.* **94**, 837.

Peterson, S. W. & Smith, H. G. (1962). *J. Phys. Soc. Japan*, **17**, Supplement B-II, 335.

Pomerance, H. (1952). *Phys. Rev.* **88**, 412.

Rayne, J. A. & Kemp, W. R. G. (1956). *Phil. Mag.* **1**, (8) 918.

Sidhu, S. S., Heaton, L. & Zauberis, D. D. (1956). *Acta Cryst.* **9**, 607.

Wolcott, N. M. (1957). *Phil. Mag.* **2**, (8) 1246.

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$(NH_4)_2Mn_2(SeO_4)_3$, Ein Doppelselenat mit Langbeinitstruktur.

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Aus der Gruppe der isomorphen Doppelsulfate

$$A_2^{+}B_2^{2+}(SO_4)_3$$

(A = K, Rb, NH_4, Cs, Tl; B = Mg, Ca, Mn, Fe, Co, Ni, Zn, Cd)

sind durch die Arbeiten von Gattow & Zemann (1958) bisher 26 Verbindungen bekannt. Die Strukturuntersuchung durch Zemann & Zemann (1957) führte zur Raumgruppe $P2_13$ (T^4) (kubisch). Entsprechende Doppelselenate sind noch nicht beschrieben.

Durch thermischen Abbau von $(NH_4)_2Mn(SeO_4)_2 . 6\,H_2O$ bei 100 °C und 20 Torr–H_2O-Dampfdruck erhielten wir ein äquimolares Gemisch von $(NH_4)_2Mn_2(SeO_4)_3$ mit Ammoniumselenat. Nach Extraktion mit absolutem Alkohol lag das reine Doppelselenat vor. Die kubische Indizierung des Pulverdiagramms ergab eine Gitterkonstante von $a_0 = 10{,}53_3$ Å. d-Werte und relative Intensitäten der Tabelle 1 wurden einer Zählrohr-Diffraktometer-Aufnahme mit Fe $K\alpha$-Strahlung entnommen. Ein Vergleich der Intensitätsverhältnisse und der systemati-

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