

metals which occlude hydrogen more strongly than Pd.

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¹⁴An APW calculation for hypothetical Pd₄H₃ gives a similar result, with about 0.35 *s-p* electron state falling below the top of the *d* bands. The structure assumed for Pd₄H₃ is a cubic unit cell containing four palladiums in the original fcc positions and hydrogens in three of the four octahedral sites in the unit cell.

Sign of the Nuclear Quadrupole Interaction in Rhenium Metal

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The sign and magnitude of the nuclear quadrupole splitting in rhenium metal have been determined by heat-capacity measurements down to 19 mK. We find an average coupling constant $e^2qQ/h = -246 \pm 2$ MHz for the two rhenium isotopes. This gives an electric field gradient at the nucleus of $q = -100 q_{\text{lat}}$, where q_{lat} is the source gradient produced by the Re⁷⁺ ion cores in the hcp lattice.

In recent years hyperfine quantities, such as the electric field gradient (EFG) at the nucleus, have become increasingly important as a means of studying the spatial behavior of conduction electrons in metals. The EFG originating from the charged ion cores in a noncubic lattice experiences a major enhancement from the screening effect of the conduction electrons, which involves the total electron charge density and thus all the states in the occupied volume within the Fermi surface. This effect has been shown¹ to produce considerable antishielding in the only case fully calculated, that of antimony, where the semi-metallic nature allowed the small Fermi-surface overlaps to be ignored and only filled Brillouin zones to be considered. On the other hand, the calculations of Watson, Gossard, and Yafet² predict that in heavy metals with high densities of states at the Fermi level the free carriers will contribute a gradient which may be two orders of magnitude greater than the source gradient and which will have the opposite sign, i.e., a shielding rather than an antishielding effect.

While there exists a great deal of experimental data on quadrupole coupling constants and nuclear quadrupole moments, which allow the magnitude of the EFG at the nucleus to be obtained with fair accuracy in many metals, the lack of knowledge of the sign of the EFG is apparent. Obviously in treating a quantity such as the EFG which is made up of several canceling contributions, it is as desirable to know the sign as it is to know the magnitude. Except for γ resonance experiments involving transitions between different nuclear excitation levels, the sign of the quadrupole interaction can only be determined directly if some means are available for producing nuclear alignment. This is not straightforward as the splittings are of the order of 1 mK.

In the present work we report results from nuclear heat-capacity measurements on rhenium metal down to 19 mK, from which the sign of the quadrupole coupling has been unambiguously obtained. The net contribution to the EFG from the conduction electrons turns out to be one of substantial shielding, which is in agreement with the

Table I. Experimental values of the average nuclear quadrupole coupling e^2qQ_{av}/h in rhenium metal and some characteristics of the respective specimens.

Ref.	Experimental method (K)	e^2qQ_{av}/h (MHz)	Specimen	$\rho_{300}/\rho_{4.2}$	Width of superconducting transition (mK)	Purity (%)
5	Specific heat down to 0.37	279 ± 5	Polycrystal	38	50	99.96
6	Specific heat down to 0.13	302 ± 5	Single crystal ^a	20 000		
7	Specific heat down to 0.16	270 ± 5	Single crystal	417	7	99.995
3	Nuclear acoustic resonance 4.2	261 ± 2	Single crystal ^a	20 000		
This work	Specific heat down to 0.019	-246 ± 2	Polycrystal ^b	66 169	7	99.96

^aThe same specimen was used in the measurements of Refs. 6 and 3.

^bThe 0.6-mole specimen consisted of two arc-melted buttons. The quoted purity from a mass spectrometric analysis is an average for both buttons, and the width of the superconducting transition from a heat-capacity measurement at higher temperatures is the total width of the two together.

theory of the Fermi-surface contribution, although this is contradicted by the little experimental evidence available for other metals.

Natural rhenium has two isotopes, 37.07% of Re^{185} and 62.93% of Re^{187} . Both have nuclear spin $I = \frac{5}{2}$ and sizable quadrupole moments differing³ by only 6%: $Q(\text{Re}^{185}) = +2.3 \pm 0.9$ b and $Q(\text{Re}^{187}) = +2.2 \pm 0.9$ b.⁴ The nuclear quadrupole interaction is among the largest for the nonmagnetic metals, which makes rhenium attractive for calorimetric hyperfine studies as evidenced by the number of previous measurements compiled in Table I. The Schottky anomaly in the heat capacity arising from the axially symmetric quadrupole interaction can be expanded in powers of T^{-1} on the high-temperature side to give the two leading terms:

$$C_Q = \frac{R(2I+2)(2I+3)}{(80)2I(2I-1)} \left(\frac{e^2qQ}{k_B} \right)^2 T^{-2} - \frac{R}{1120} \frac{(2I-3)(2I+2)(2I+3)(2I+5)}{(2I)^2(2I-1)^2} \left(\frac{e^2qQ}{k_B} \right)^3 T^{-3}. \quad (1)$$

If both terms can be resolved, then the magnitude and also the sign of the interaction are determined. At the lowest temperatures of the present measurement the T^{-3} term corresponds to 5% of the first term. The other contributions from the electronic and lattice heat capacity rapidly become insignificant below 0.1 K and moreover can be accurately taken into account, being well known from earlier measurements at higher temperatures.⁷

The heat capacity was measured with the conventional heat-burst method in an adiabatic-demagnetization cryostat.⁸ Temperatures were determined by a cerium magnesium nitrate thermometer thermally attached to the specimen, the accuracy being $\pm 0.5\%$ with a further ± 0.08 mK arising from the uncertainty in the thermometer shape factor.⁹ The small addenda correction due to the heat capacity of the thermometer was measured separately and amounted to only 1% of the T^{-2} part of the heat capacity of the specimen. The overall accuracy of an individual heat-capacity point is believed to be within $\pm 1\%$ below 0.15 K. At higher temperatures the accu-

racy gradually falls owing to the increasing contribution to the heat capacity from the 14 g of copper in the wires and foils used for thermal links, which was calculated rather than measured. Thermal diffusion within the calorimeter presented no problem, the time constant for approaching the steady temperature drift after a heating pulse being $650T^{-3} \mu\text{sec K}^{-3}$.

To quench the superconductivity of the rhenium the measurements were made in various homogeneous fields up to 600 G. Above the transition field of about 200 G no field dependence of the heat capacity was detected. In the superconducting state a nonreproducible small fraction of the normal-state nuclear heat capacity was observed. This was attributed to normal regions in the specimen arising from flux trapped during the demagnetization process although care was taken to limit the field on the specimen to a few tens of gauss. No nuclear heat capacity is to be expected in the superconducting state since the slow spin-lattice relaxation thermally isolates the nuclear spin system.

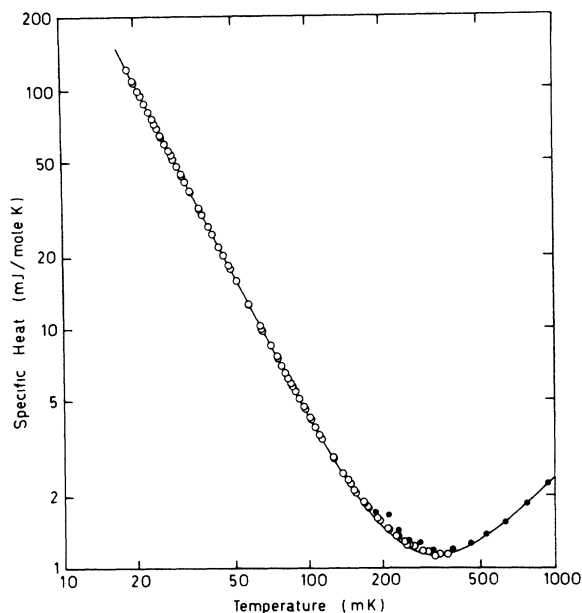


FIG. 1. Heat capacity of rhenium metal: closed circles, Smith and Keesom (Ref. 7); open circles, present work. The solid curve represents the best fit, $C_p (\mu\text{J mole}^{-1} \text{K}^{-1}) = 40.6 T^{-2} + 0.0342 T^{-3} + 2290 T + 27 T^3$.

The results for the normal state are plotted in Fig. 1 together with measurements at higher temperatures by Smith and Keesom.⁷ The best least-squares fit to our data, represented by the continuous curve, is given by

$$C_p (\mu\text{J mole}^{-1} \text{K}^{-1}) = (40.6 \pm 0.6) T^{-2} + 0.034 T^{-3} + 2290 T + 27 T^3, \quad (2)$$

where the first two terms represent the nuclear quadrupole contribution and the last two are the electronic and lattice contributions, respectively, for which the values of Ref. 7 are assumed. The quoted error in the T^{-2} term includes the uncertainty in the temperature scale and the statistical variances of the data for both the specimen and the empty calorimeter. As the absolute magnitude of the T^{-3} term is fixed by the T^{-2} term, which is quite accurately determined from the higher-temperature data, the low-temperature data essentially serve only to determine the sign of the interaction. This is illustrated in Fig. 2 where $C_p T^2$ is plotted against temperature. The two solid curves correspond to a negative and a positive interaction, the magnitude being determined by the higher-temperature points. The interaction is clearly negative.

The average quadrupole interaction for the two

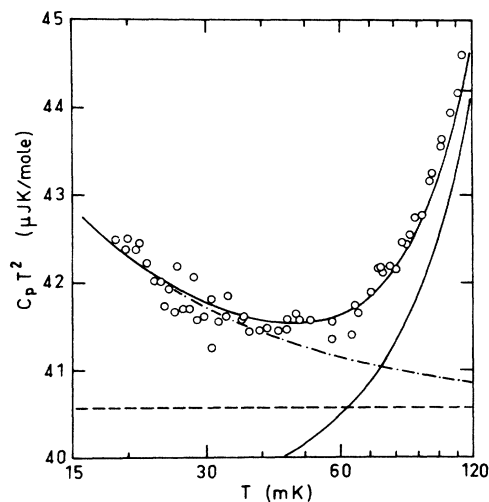


FIG. 2. Heat capacity plotted as $C_p T^2$ vs T . The upper solid curve corresponds to a negative interaction and the lower to a positive interaction of the same magnitude. The dashed line with constant value represents the first term, and the dashed-dotted curve represents the first two terms of the quadrupole heat-capacity expansion with a negative coupling constant.

isotopes has the value

$$e^2 q Q_{av} / h = -246 \pm 2 \text{ MHz, or} \\ -11.81 \pm 0.09 \text{ mK}, \quad (3)$$

where Q_{av} is weighted by the relative abundances of the two isotopes. The present result is compared with earlier measurements^{3,5-7} in Table I. There is a considerable spread in the parameters determined calorimetrically. However, as the present measurement extended a factor of 10 lower in temperature, the result is unambiguous, being virtually uninfluenced by the subtraction of lattice and electronic contributions. We observed a small anomaly centered at 0.3 K, probably caused by transition-metal impurities,¹⁰ which, if general, would confuse the nuclear heat capacity deduced from measurements above 0.2 K. Better agreement is obtained between the present result and a recent nuclear-acoustic-resonance measurement.³ However, the difference still lies well outside our experimental error. Although the correlation between the quality of the specimen and the magnitude of the coupling is not clear, a part of the difference may be accounted for by lattice defects and charge impurities arising as a result of metallurgical difficulties with a high-melting-point material.

For purposes of interpretation it is convenient to divide the EFG into an ionic and electronic

component,

$$q = q_{\text{lat}}(1 - \gamma_{\infty}) + q_{\text{el}}(1 - R), \quad (4)$$

where q_{lat} is the gradient due to all other ions (considered as point charges at the appropriate lattice sites), γ_{∞} is the Sternheimer antishielding factor with the polarization of the host core by q_{lat} taken into account, q_{el} is the valence-electron contribution, and R is the corresponding antishielding factor with $(1 - R)$ approximately unity.

Assuming a charge of $+7e$ on the ion cores corresponding to the $5d^56s^2$ electrons of the free atom⁴ and using the tabulated lattice sums of de Wette,¹¹ we obtain for the lattice gradient in rhenium $eq_{\text{lat}} = +4.57 \times 10^{15}$ V/cm². From Sternheimer's calculations of the antishielding factors for several heavy ions,¹² γ_{∞} for Re is estimated to be -50 . This gives a value of $+2.3 \times 10^{17}$ V/cm² for the ionic contribution to the EFG. Taking into account the total experimental gradient of -4.6×10^{17} V/cm² calculated from Eq. (3), we obtain a valence-electron contribution of -6.9×10^{17} V/cm². This is a striking result. The source gradient from the lattice experiences a net shielding effect from the valence electrons, which overshields by 150 times, i.e., $q_{\text{el}} = -150q_{\text{lat}}$. There are two other comparable cases of nonmagnetic metals where the sign of the EFG is known, and in both cases the net valence-electron gradient antishields as is conventionally expected. These are hafnium,¹³ which has been studied by several groups using Mössbauer techniques, and indium,¹⁴ where the sign was inferred from a comparison of NMR data on the metal and its alloys with the screening theory of charge impurities of Kohn and Vosko.¹⁵ The valence-electron contribution is $q_{\text{el}} = +170q_{\text{lat}}$ for hafnium and $+70q_{\text{lat}}$ for indium.

One negative contribution to q_{el} has been studied by Watson, Gossard, and Yafet² who considered the charge redistribution at the Fermi level under the influence of the perturbing lattice potential $V(r) = -\frac{1}{2}e^2q_{\text{lat}}r^2P_2^0(\cos\theta)$. The calculation was prompted by the observation of a correlation between the EFG and the density of states $\eta(E_F)$ at the Fermi level in a series of V_3X intermetallic compounds. The contribution to the gradient linear in both $\eta(E_F)$ and q_{lat} when separated turns out to be strongly shielding. Watson,

Gossard, and Yafet predict a value of $-60q_{\text{lat}}$ for this contribution in rhenium and $(-50 \text{ to } -70)q_{\text{lat}}$ in indium.¹⁶ While this is certainly a significant negative contribution it is not big enough to explain the large shielding gradient arising from the valence electrons in rhenium.

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