Comment on the "compressibility collapse" transition in ReO_3

J. E. Schirber, L. J. Azevedo, and A. Narath
Sandia Laboratories, Albuquerque, New Mexico 87185*
(Received 19 June 1979)

First- and second-order quadrupolar effects on the Re NMR in ReO_3 have been used to show that the "compressibility collapse" transition results in a high-pressure phase of symmetry lower than cubic and to map out the phase boundary from 1 to 300 K.

In a recent Letter[1] Schirber and Morosin presented evidence for an unusual second-order phase change in ReO_3 in which the compressibility increased discontinuously by a factor of about 7 in the high-pressure phase. Single-crystal x-ray studies to 4.3 kbar at room temperature did not show any change in symmetry even though simple volume considerations based on the low-temperature transition pressure and the thermal expansion indicated the transition should occur below 3.5 kbar at room temperature.

We have used first- and second-order quadrupole effects on the Re nuclear magnetic resonance (NMR) in the high-pressure phase to (i) establish that the symmetry is lowered by the transition and (ii) to determine the phase boundary between 1 and 300 K.

Samples were taken from powder passed through 325 mesh from crushed single crystals grown by vapor transport which were used in the original NMR studies of Narath and Barham.[2] A small amount of Al powder was mixed with the sample to provide an *in situ* field calibration. Below 250 K, pressures were generated in He gas. The 1-K data were taken by careful isobaric freezing[3] of the He. Above 250 K kerosene was used as the pressure medium. In all cases the pressure was monitored by a 0–100 000-psi Heise gauge. The high-pressure vessel and the rf coil and lead-in arrangement were described earlier.[4] A phase coherent transient spectrometer[5] was employed to detect the nuclear magnetic resonances of ^{187}Re and ^{185}Re in a single-coil geometry. Data were taken in both a superconducting solenoid at fields from 10 to 35 kOe and in an electromagnet at ~20 kOe.

The lowest-field experiments were conducted to demonstrate the change in symmetry across the transition as evidenced by second-order quadrupole splitting of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition. While the line shape was somewhat distorted in both the free-induction and pulse echo modes, features corresponding to the edges of the second-order split line could be identified. This splitting in field is given by

$$\Delta H = \frac{25}{144} \frac{\nu_Q^2}{\gamma \nu_0} [I(I+1) - \tfrac{3}{4}] \quad , \tag{1}$$

where γ is the gyromagnetic ratio; ν_Q is the quadrupole frequency; ν_0 is the resonant frequency; and I is the spin ($\frac{5}{2}$ for Re). ΔH was shown at several pressures at 1 K to be proportional to $1/\nu_0$. A plot of ν_Q versus pressure at 1 K is shown in Fig. 1 as determined from Eq. (1). Within the scatter ν_0 appears to extrapolate linearly to zero near 2.5 kbar, consistent with the transition pressure at liquid-He temperatures determined from the de Haas–van Alphen data in Ref. 1. These data clearly show the reduction in symmetry in the high-pressure phase but the splitting could not be resolved, even at the lowest frequencies, closer than ~1 kbar above the transition.

Because of this inaccuracy of determining the transition from the second-order quadrupole splitting, we instead used the diminuation of the amplitude of the resonance when the $2I$ first-order satellites moved out from under the central $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ line. This has the advantage that the diminuation is not dependent upon frequency. For $I = \frac{5}{2}$ the expected[6] amplitude

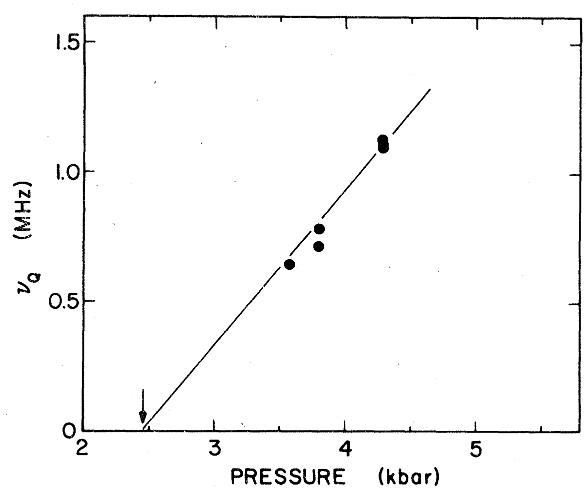

FIG. 1. Quadrupole frequency ν_Q vs pressure at 1 K for ReO_3 determined by the splitting of the central ^{187}Re resonance. Data were taken at frequencies of 10, 21, and 34 MHz. The vertical arrow corresponds to the transition pressure determined in Ref. 1 from the de Haas–van Alphen data.

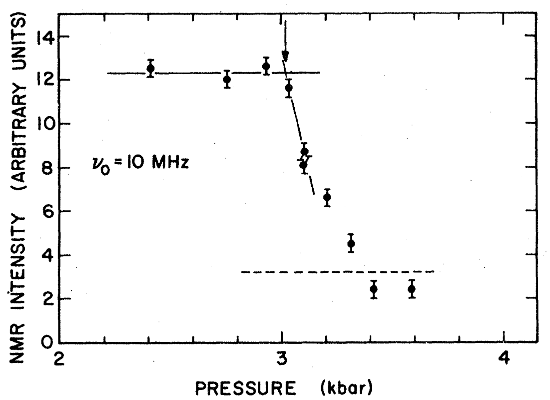

FIG. 2. Amplitude in arbitrary units of the ^{187}Re nuclear magnetic resonance vs pressure at 76 K. The dashed horizontal line represents $\frac{9}{35}$ of the low-pressure amplitude as discussed in the text. The vertical arrow indicates our definition of the transition pressure.

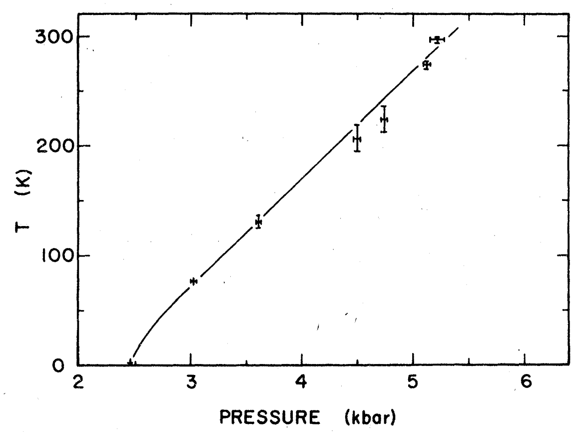

FIG. 3. Temperature-pressure dependence of "compressibility collapse" transition in ReO_3 as determined by data such as shown in Fig. 2. The 1-K point is from the de Haas–van Alphen data of Ref. 1 but is consistent with the extrapolation shown in Fig. 1. The line is shown as a guide to the eye.

ratio is $\frac{35}{9}$. This assumes we are observing all five transitions in the low-pressure phase.[2] Figure 2 shows a plot of the ^{187}Re NMR amplitude in arbitrary units versus pressure at 76 K. The transitions were found to be extremely sharp and reproducible on cycling to within ~10 bar. Data were always taken with increasing pressure because of hysteresis in the Heise gauge and in the piston of the separator. The temperatures were all achieved by immersion in fluids (liquid N_2, various freons, ice water, and ambient water) and the temperature monitored by a Cu-Constantan thermocouple, except in water where a mercury thermometer was used. The scatter in the temperature points shown stems from drifts in temperature of the fluids which had to be heated to prevent cooling by the superconducting magnet cryogens. The points near room temperature were taken in an electromagnet so do not suffer from this difficulty. Using this technique we have mapped out the phase boundary up to 300 K as shown in Fig. 3. The transition pressure of 5.4 kbar at 300 K explains why the room-temperature single-crystal x-ray studies to 4.2 kbar of Ref. 1 detected no change in the structure.

In summary, we have shown using NMR as a function of temperature and pressure that the "compressibility collapse" transition results in a lowering of the symmetry from cubic and have determined the phase boundary from 1 to 300 K.

We gratefully acknowledge the technical assistance of R. L. White and D. L. Overmyer. This work was supported by the U. S. DOE, under Contract No. DE-AC04-76-DP00789.

*A U.S. DOE facility.

[1]J. E. Schirber and B. Morosin, Phys. Rev. Lett. 42, 1485 (1979).
[2]A. Narath and D. C. Barham, Phys. Rev. 176, 479 (1968).
[3]J. E. Schirber, Cryogenics 10, 418 (1970).
[4]H. T. Weaver, J. E. Schirber, and A. Narath, Phys. Rev. B 8, 5443 (1973).
[5]A. Narath and D. C. Barham, Rev. Sci. Instrum. 45, 100 (1974).
[6]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University, London, 1961), p. 239.