effects of the embrittling of the AgCl cannot be too great. However, in the present work, there must be pressure gradients because of the large sample, and the NMR will result from nuclei subjected to a distribution of pressures.

The nuclear resonance was observed by use of a single-coil coherent pulsed spectrometer, the ^{51}V free-induction decay signal being observed at a frequency of 6.9 MHz. With transmitter pulses of 200-W peak rf power, a maximum free-induction signal resulted from pulses of 3-μsec duration. The integrated amplitude of the initial free-induction signal on repetitive pulsing was stored in a boxcar integrator and was recorded as a function of magnetic field. In later experiments, the ^{51}V spin echo following a pair of transmitted pulses was also measured and recorded. Spin-lattice relaxation measurements were made by measuring the recovery of the free induction and echo signals following a train of 1 to ~100 rapidly repeated saturating pulses. The pulse technique was especially suitable to the high-pressure measurements since it obviated the need of bringing separate field-modulation coils in the already crowded geometry of the cryostat, and since the use of the short 200-W pulses enabled a width $\Delta\omega \sim 1/\tau \sim 300$ kHz of the spectrum to be covered with each pulse.

The magnet was calibrated by observing the ^{27}Al resonance in Al filings both at 1 atm and 10 kbar as a function of field. This calibration was performed on two different samples with no change within experimental error. As a further check on the calibration, one sample of V_2O_3 was run together with Nb as a field marker. Using the Al resonance calibration of the magnet, the 26-kbar Knight shift of ^{93}Nb in Nb metal was observed to be $+1.01 \pm 0.20\%$ in comparison with its atmospheric pressure value of $+0.85\%$.

II. RESULTS

In the first experiment the pressure was increased to 26 kbar at room temperature and the system was then cooled to 4.2 °K. The ^{51}V nuclear resonance was observed by free-induction decay. The pressure was decreased and the intensity of the resonance decreased until it was no longer observable at ≈ 13 kbar (see inset Fig. 2). With a new sample of V_2O_3 plus Nb, the pressure was then increased slowly up to ≈ 65 kbar and the shift in the resonant frequency followed as a function of pressure by sweeping through the resonance with field. The load was then released slowly to ≈ 25 kbar and the frequency shift with pressure was found to be reversible. After holding 48 h at 25 kbar the apparatus was recooled to 4.2 °K and the pressure cycled up to ≈ 65 kbar and back again. Cracking sounds which are usually associated with the partial failure of the tungsten carbide were heard during the first release of pressure from 65 kbar. If the die had cracked then it is probable that the pressure calibration would change. However, the die is more efficient on a recycling of the pressure in that it takes a smaller applied load to reach the Bi *I*-*II* transition. Since it is not possible to account for these opposite effects accurately, the data from the second pressure cycle to 65 kbar are plotted using the same

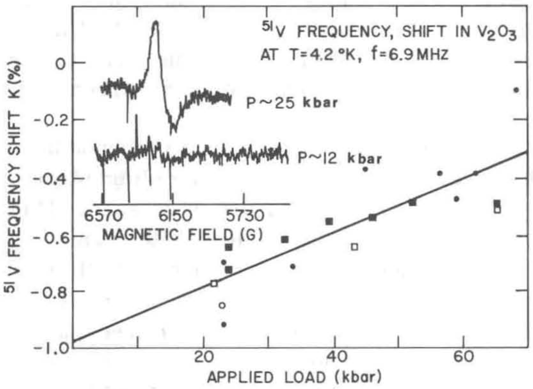

FIG. 2. ^{51}V frequency shifts in V_2O_3 at $T = 4.2$ °K and $f = 6.9$ MHz. Circles and squares refer to measurements taken, respectively, on the initial application of load and on a second application of load two days later. Closed data points refer to measurements made with increasing load and open data points to measurements with decreasing load. A later measurement on a third sample using spin-echo amplitude measurements at 26 kbar gave $K(26\ \text{kbar}) = -0.92\% \pm 0.20\%$. The calibration of the load was obtained from the 25.5-kbar transition of bismuth on the initial loading, as described in the text. During the second loading (square data points) it was noted that the bismuth transition was reached under ~20% less load than on the initial loading. For this reason, the pressure on the V_2O_3 sample in the 20- to 30-kbar regime is as much as 5 kbar greater than indicated for the square points. Conversely, in the regime above 50 kbar, cracking of the girdle may have resulted in a reduction of pressure. Correction for these two effects would *raise* the already anomalously high slope shown for the frequency shift versus pressure. It is also probable that in the presence of pressure inhomogeneities in the 20- to 30-kbar regime the portions of the sample in the higher-pressure regions would contribute more strongly to the observed resonance than would those portions of sample in lower-pressure regions. This phenomenon would result from the rapid falloff in resonance intensity at low pressures demonstrated in Fig. 3 and in the inset of this figure. For this reason, also, the data points in the 20- to 30-kbar regime may represent pressures up to 5 kbar greater than shown. Consideration of such a correction would also increase the frequency-shift–versus–pressure slope. The inset of the figure shows free-induction-decay nuclear-resonance amplitudes as measured with phase-coherent detection at 25 and 12 kbar. The greatly reduced amplitude at 12 kbar results from the fact that the sample is antiferromagnetically ordered at this pressure, and the nuclear resonance is consequently shifted out of the region of observability to a much higher frequency.

pressure calibration. The ^{51}V frequency shifts (relative to a reference gyromagnetic ratio[8] of 1.1193 kHz/G) as a function of pressure are shown in Fig. 2. The estimated accuracy of the Knight-shift measurements is ±0.20%. The intensity of the resonance as a function of pressure is shown in Fig. 3. The break in the curve at 26 kbar is interpreted as arising from the transition from the nonmagnetic to magnetic state with decreasing pressure. The earlier resistivity measurements showed a sharp transition as a function of pressure at 4.2 °K. It is assumed that the width of the transition to zero intensity reflects the large pressure gradients in the present experiment with decreasing pressure.

The width of the ^{51}V resonance response between half-power points of spin-echo amplitude tracings was (300 ± 50) G at a pressure of 26 kbar. This width is apparently the result of either an inhomogeneous magnetic field or frequency-shift distribution resulting from pressure inhomogeneities. Measurement of the width from the free-induction-decay tracings was more difficult because of the oscillations in the recorded tracings resulting from the phase coherent mode of detection.

The decay of the spin-echo amplitude gave an approximate dynamic microscopic phase-memory time T_2 of (20 ± 5) μsec at 26 kbar. This is approximately 20 times longer than the static macroscopic phase-memory time associated with the linewidth of 300 G and confirms that the observed linewidth results from inhomogeneous, rather than dynamic, broadening. The value of T_2 is of the order expected from nuclear dipolar interactions.[9] This indicates that there are no indirect nuclear exchange (Ruderman-Kittel) interactions[10] significantly greater than the dipolar interaction present, since the motional narrowing effect of such nuclear exchange interactions would be to lengthen T_2 beyond the normal dipolar value.[11] Further, as will be shown later, the observed T_2 is much too short to result from nuclear spin-lattice relaxation. The spin-lattice relaxation-time measurement of the recovery of the signal following saturation of the resonance was restricted in accuracy by the limited signal to noise and by difficulty in saturating the entire ^{51}V resonance spectrum. A recovery time of 5 msec was measured, but it is felt that this is a lower limit on the true T_1. This is because equilibration of the level populations involved in transitions near the center of the resonance profile would be expected to occur faster than equilibration of the entire set of nuclear states.[12] It is probable that the measured rate is accurate within one order of magnitude. In any event, the limit $T_1 \gtrsim 5$ msec is more than two orders of magnitude longer than T_2, and confirms that spin-lattice relaxation is not an important contribution to the T_2 process.

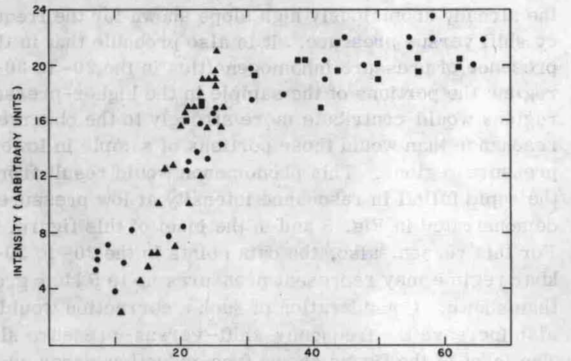

FIG. 3. Intensity of the nuclear-resonance free-induction-decay amplitude versus applied load at 6.9 MHz and $T = 4.2$ °K. The triangles refer to an initial loading to 26 kbar, the circles to a loading of a new sample to 65 kbar, and the squares to a first loading two days later.

III. INTERPRETATION

Because of the hyperfine interaction $A_d \vec{I} \cdot \vec{S}^d$ between the nuclear spins $\vec{I}$ and the d-electron spins $\vec{S}^d$, the NMR gives information about the spin magnetization $\vec{S}^d(q, \omega)$. An especially sensitive test is provided for static $(\omega = 0)$ configurations of magnetic ordering in that magnetically ordered d-electron spins $\langle S_z^d(q_0, 0)\rangle$ would shift the nuclear resonance frequency by $\sim A_d \langle S_z^d(q_0, 0)\rangle / h$. For[13] $A_d/h = 3 \times 10^8$ sec^{-1} and $\langle S_z^d(q_0, 0)\rangle = 1$, this is a frequency shift of ~300 MHz. The fact that ^{51}V resonance is observed at 4.2 °K in metallic (high-pressure) V_2O_3 with a shift and linewidth $\sim 10^3$ times smaller than 300 MHz is the most important result of the present investigation, and puts an upper limit of $\sim 10^{-3} \mu_B$ on any statically ordered moments under the experimentally observed conditions.

In order to make a more detailed interpretation of the nuclear-resonance frequency shifts and linewidths, we may partition the magnetic susceptibilities and the frequency shifts into component parts.[13, 14] The susceptibility can be expressed as

$$\chi(T) = \chi_d(T) + \chi_{VV} + \chi_{dia},$$

and the frequency shift can be expressed as

$$\begin{aligned} K(T) &= K_d(T) + K_{VV} + K_{dia} \\ &= \alpha_d \chi_d(T) + \beta' \chi_{VV}. \end{aligned}$$

$\chi_d(T)$ refers to the temperature-dependent d-spin susceptibility, χ_{VV} refers to the Van Vleck field-induced paramagnetism, and χ_{dia} refers to the ion core and orbital diamagnetism. For reasons which will be detailed in the following discussion of the pressure dependence of the frequency shifts, it is felt that the Van Vleck and diamagnetic terms are substantially pressure independent. They may be