

taken to have the same values at high pressure as were estimated by Jones for 1 atm,<sup>13</sup> namely,  $\chi_{VV} \approx 210 \times 10^{-6}$  emu/mole (of  $\text{VO}_{1.5}$ ),  $\chi_{dia} \approx 0$ . The temperature and pressure dependence of the susceptibilities and frequency shifts evidently result primarily from the  $d$ -spin terms. Figure 4 shows the deduced temperature and pressure variation of the  $d$ -spin term of the frequency shift in a three-dimensional plot. The  $d$ -spin susceptibility is then proportional to the  $d$ -spin frequency shift. The shaded surface indicates the transition to the insulating antiferromagnetic state, where the resonances become unobservable. It is seen that in the high-pressure regime studied here the resonance frequency shifts lie in the same range as the higher-temperature 1-atm values.<sup>13</sup>

The pressure dependence of the frequency shift is quite strong, however. The slope of  $K$  versus  $P$  shown in Fig. 2 is  $dK/dP = 0.0095 + 0.0050\%/kbar$ . Taken with a value of the bulk compressibility<sup>15</sup>  $d \ln V/dP = 2140 \pm 500 \text{ kbar}^{-1}$ , it yields the unusually large value of  $d \ln K/d \ln V = 19 \pm 10$ . Expressing  $K$  as  $K = \alpha_d \chi_d + \beta \chi_{VV}$ , we isolate the only significant factor in producing the observed volume dependence by noting that the volume dependence of the three factors,  $A_{orb}$ ,  $\chi_{VV}$ , and  $A_{d-spin}$ , can only be of order unity. This is because (i)  $A_{orb}$  is proportional to the mean value of  $r^{-3}$  for the  $3d$  wave functions,<sup>16</sup> so would not be expected to vary more strongly than the volume; (ii)  $\chi_{VV}$ , as mentioned above, depends on the over-all features of all the degenerate bands, so would also vary approximately as the volume; and (iii) measured values of  $A_{3d}$  in  $V$  and in the ferromagnetic transition metals vary only roughly linearly in volume.<sup>17</sup> We thus deduce that the volume dependence of the  $d$ -spin susceptibility  $\chi_d$  is primarily responsible for the large pressure and volume dependence of the Knight shift. Hence,

$$\frac{d \ln \chi^{spin}}{d \ln V} \approx \frac{d \ln K^{spin}}{d \ln V} \approx \frac{K}{K^{spin}} \frac{d \ln K}{d \ln V} \approx 8 \pm 5.$$

This value for  $d \ln \chi_d/d \ln V$  is larger than the usual value near unity found in most other metals. For comparison, a value of 0.8 is found for  $V$  metal.<sup>18</sup> Apparently, metallic  $\text{V}_2\text{O}_3$  is very nearly critical with respect to forming a magnetic state and as a result the susceptibility is strongly volume dependent. It is, however, definitely not yet magnetically ordered, as indicated above by the absence of any frequency shifts of the order of 300 MHz.

In view of the absence of ordering, it is apparent that  $\text{V}_2\text{O}_3$  must be described by an unmagnetized band in the high-pressure metallic state at  $4.2^\circ\text{K}$ . An estimate of the minimum electron spin fluctuation frequency  $\omega_f$  can be obtained from the nuclear relaxation rates. In the absence of exchange enhancement and for  $kT < \hbar\omega_f$ , one expects the nu-

clear spin-lattice relaxation rate to be of order<sup>19</sup>

$$(T_1)^{-1} \sim A^2 kT / \hbar^3 \omega_f^2.$$

From the experimental result  $(T_1)^{-1} \leq 200 \text{ sec}^{-1}$  at  $4.2^\circ\text{K}$  and  $A/\hbar = 3 \times 10^8 \text{ sec}^{-1}$ , we find that  $\hbar\omega_f \gtrsim 300^\circ\text{K}$ .

A consistent estimate of  $\hbar\omega_f$  can also be obtained from the static spin susceptibility. One expects

$$\chi^{spin} \sim \mu_B^2 / \hbar\omega_f$$

for a band which may be exchange enhanced.<sup>20</sup> For  $\chi^{spin} = 12.3 \times 10^{-6} \text{ emu/g}$ , we obtain  $\hbar\omega_f \sim 400^\circ\text{K}$  in order-of-magnitude agreement with the estimate from nuclear relaxation.

The pressure dependence of the resonance frequency shift at  $4.2^\circ\text{K}$  implies that the resonance frequency shift may also be somewhat pressure dependent at  $T > 170^\circ\text{K}$ . From observations at  $170^\circ\text{K}$ ,<sup>13</sup> however, there is unfortunately no means of distinguishing between localized magnetic moments and spin fluctuations with frequency below  $kT/\hbar$ . The significance of the present work is that the metal-to-insulator transition can occur at low temperature between a high-pressure metallic state which unambiguously is paramagnetic and a lower-pressure antiferromagnetic-insulating state.

It is interesting to compare the properties of me-

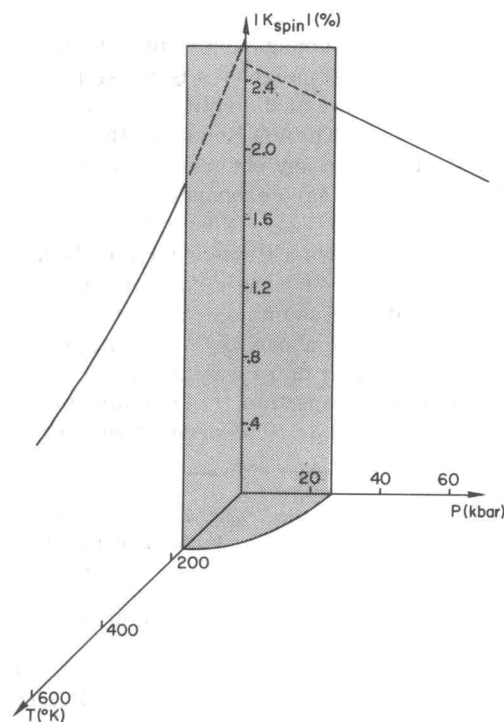


FIG. 4.  $d$ -spin components of  $^{51}\text{V}$  NMR frequency shifts as a function of pressure at  $T = 4.2^\circ\text{K}$  and as a function of temperature at  $P = 1 \text{ atm}$ . The solid lines are linear and Curie-Weiss fits, respectively, of the data. The broken lines are continuations of the fits in the antiferromagnetic region where no resonances were observed.

talic  $V_2O_3$  with those of V metal. As seen above, the  $d$ -spin frequency shift varies from  $-1.8$  to  $-2.3\%$  under the experimental conditions for  $V_2O_3$ , and, from the hyperfine coupling constant used above, corresponds to a  $d$ -spin susceptibility of  $9.6 \times 10^{-6}$  to  $12.3 \times 10^{-6}$  emu/g. (In making this correspondence, we should note that the proportionality of the  $d$ -spin Knight shift and  $d$ -spin susceptibility occurs even though the  $d$ -spin Knight shift results from some combination of core polarization, conduction electron polarization, and unquenched orbital polarization effects. We require only that these several contributions preserve their relative contributions to the  $d$ -spin Knight shift as the temperature or pressure is varied.)

Comparisons should also be made with other vanadium oxides. Vanadium "monoxide," although originally reported to undergo a metal-insulator transition similar to that of  $V_2O_3$ , has now been shown to have no transition for compositions ranging from  $VO_{0.79}$  to  $VO_{1.30}$ .<sup>21</sup> Nuclear resonances were observed in samples of composition  $VO_{0.86}$ ,  $VO_{1.02}$ , and  $VO_{1.23}$  between 1.4 and 300 °K with no evidence of a sharp transition.<sup>22</sup> A frequency shift of  $+0.4\%$ , independent of composition and temperature, was observed. A resonance linewidth increasing with O content and decreasing temperature was found, however, and interpreted in terms of increased susceptibility on a minority of V atoms with few V neighbors. The suppression of magnetism by the presence of V near neighbors is consistent with the pressure reduction of the spin susceptibility of  $V_2O_3$  inferred above. The VO Knight shifts are somewhat more positive than any observed in  $V_2O_3$ . The magnetic site VO nuclear resonances were not observed, however.

$VO_2$ , which shows a first-order metal-insulator transition at  $\sim 345$  °K, has also been studied.<sup>23</sup> Umeda, Ashida, Kusumoto, and Narita observed nuclear resonance above and below this transition, demonstrating that there was no onset of magnetic ordering at the transition.<sup>24</sup> They further discovered an intermediate first-order structural trans-

formation at  $\sim 325$  °K. In the insulating state, the  $^{51}V$  frequency shift was  $+0.28\%$  and in the metallic state the shift was  $-0.38\%$ , reflecting a sevenfold increase in magnetic susceptibility<sup>25</sup> on passing from the insulating to metallic states. The  $VO_2$  nuclear resonance was observed in this laboratory down to  $T = 1.7$  °K, indicating no magnetic ordering to this temperature. The metallic range shift lies in the same range as the  $V_2O_3$  shifts, and the metallic susceptibilities of  $VO_2$  and  $V_2O_3$  are very similar.

#### CONCLUSIONS

The most important result of this study is that a nuclear-resonance signal is observable in metallic  $V_2O_3$  at 4.2 °K with a relatively small frequency shift and linewidth. This reveals immediately that the metallic state does not order magnetically and that the transition from insulator-to-metal is accompanied by a transition from localized magnetic moment behavior to band magnetism. It thus precludes superlattice spin-density wave states in the metallic state at  $P > 26$  kbar, as might occur in Kohn's theory of the Mott transition.<sup>26</sup> Whether the band mass is enhanced by polaron formation and whether exchange enhancement is important is not resolved, although in either case a lower limit of  $10^{13}$  sec<sup>-1</sup> or  $\sim 300$  ° can be placed on the spin fluctuation frequency. The strong dependence of the susceptibility on volume for metallic  $V_2O_3$  might result either from a strongly volume-dependent state density or strongly volume-dependent exchange enhancement. Again, the resonance results do not determine the choice between the two possibilities.

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