

Transient Nuclear Magnetic Resonance Study of the Conduction Band of Metallic Na_xWO_3 : ^{23}Na Relaxation*

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The spin-lattice relaxation time T_1 of the ^{23}Na nuclear magnetization in the cubic sodium-tungsten bronzes Na_xWO_3 has been measured as a function of x value (0.56–0.89) and temperature (1.4–298°K). There is evidence that more than 10% of the sodium nuclei aggregate into sodium-vacancy-free ($x=1$) regions. The temperature dependence of the data shows that the relaxation rate of ^{23}Na nuclei outside the vacancy-free regions is determined largely by a conduction-electron mechanism at 20 and 76°K, but that a quadrupolar mechanism becomes important at 298°K and spin diffusion to paramagnetic impurities begins to limit T_1 at 4°K. For $x=0.73$, $T_1T=74$ min-°K for conduction-electron relaxation, $T_1=18$ min for spin-diffusion-limited paramagnetic-impurity relaxation, and $T_1=7.7$ sec at 298°K for quadrupolar relaxation. The relaxation rate for the conduction-electron mechanism does not vary markedly with x value; the relaxation rates for the quadrupolar and paramagnetic-impurity mechanisms tend to decrease with increasing x value. The measured value of the conduction-electron contribution to the sodium nuclear relaxation is combined with an estimate of T_1 for relaxation through sodium $3p$ conduction electrons to give a conservative upper limit estimate of 33% for the density of sodium states at the Fermi surface.

I. INTRODUCTION

THE cubic sodium tungsten bronzes (Na_xWO_3 , where $0.4 < x < 1.0$) are nonstoichiometric metallic compounds with the perovskite structure: The tungsten atom lies in the center of the unit cell, the oxygen atoms lie in the face centers, and the sodium atoms are distributed over the corner positions. The electrical resistivity at 20°C for the high- x samples is of the order¹ of $10 \mu\Omega\text{-cm}$, which compares favorably with that of metallic sodium² ($4.7 \mu\Omega\text{-cm}$), metallic copper² ($1.7 \mu\Omega\text{-cm}$), and metallic tungsten² ($5.5 \mu\Omega\text{-cm}$). Hall coefficient measurements³ have shown that the conductivity is electronic, and that each sodium atom contributes one electron to the conduction band. The density of states per tungsten atom as determined from measurements of the specific heat⁴ is a monotonically increasing function of x ; however, the density of states per sodium atom is nearly independent of x .

There has been a great deal of speculation concerning the conduction band⁵⁻⁷ of these compounds. It has been established on the basis of Knight shift measurements that s electrons do not contribute appreciably to the conduction band. An essentially zero Knight shift for the ^{23}Na resonance was observed by Jones, Garbaty, and Barnes,⁸ while a small negative ^{183}W Knight shift attributed to diamagnetic core polarization

was measured by Narath and Wallace.⁹ There are two conduction-band models which are consistent with these and other experimental results: (a) the tungsten $5d$ conduction band proposed by Sienko,⁶ in which the sodium atoms serve primarily in the capacity of electron donors to a band which is empty in WO_3 ($x=0$), and (b) the sodium $3p$ conduction band proposed by Mackintosh,⁷ in which the $3s$ electrons of sodium are promoted to $3p$ states with subsequent overlap to form a band. Many arguments^{6,7} can be proposed in favor of or against either of these two models, so that only definitive experimental measurements of the relative contribution of tungsten $5d$ and sodium $3p$ states to the conduction band can resolve the question.

Due to the cubic symmetry of the Na_xWO_3 structure, p and d bands do not produce direct spin-dipolar shifts of the nuclear resonance. Furthermore, the indirect negative shifts due to exchange polarization of the core s electrons by the p - and d -band spin magnetizations¹⁰ may be largely masked by positive orbital contributions of such bands.¹¹ Thus, on the basis of previous measurements one cannot reject with certainty the possibility that the small negative shifts ($\approx -0.2\%$) of the ^{183}W resonance in Na_xWO_3 are caused by a differential-core diamagnetism relative to the WF_6 reference.⁷ Therefore, our experimental approach for determining the character of the conduction band is based on a measurement of the relative contribution of the conduction electrons to the relaxation rates of the ^{23}Na and ^{183}W nuclei. Due to the r^{-6} dependence of dipolar nuclear spin-lattice relaxation on separation distance r , sodium $3p$ conduction electrons at the Fermi surface can provide a significant relaxation mechanism for ^{23}Na nuclei while providing only a small contribution to relaxation of the ^{183}W nuclei. Similarly, tungsten $5d$

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¹ L. D. Ellerbeck, H. R. Shanks, P. H. Sidles, and G. C. Danielson, *J. Chem. Phys.* **35**, 298 (1961).

² O. W. Eshbach, *Handbook of Engineering Fundamentals* (John Wiley & Sons, Inc., New York, 1952), pp. 1-143, 1-144.

³ W. R. Gardner and G. C. Danielson, *Phys. Rev.* **93**, 46 (1954).

⁴ R. W. Vest, M. Griffel, and J. F. Smith, *J. Chem. Phys.* **28**, 293 (1958).

⁵ J. M. Keller, *J. Chem. Phys.* **33**, 232 (1960).

⁶ M. J. Sienko, *J. Am. Chem. Soc.* **81**, 5556 (1959).

⁷ A. R. Mackintosh, *J. Chem. Phys.* **38**, 1991 (1963).

⁸ W. H. Jones, Jr., E. A. Garbaty, and R. G. Barnes, *J. Chem. Phys.* **36**, 494 (1962).

⁹ A. Narath and D. C. Wallace, *Phys. Rev.* **127**, 724 (1962).

¹⁰ A. M. Clogston and V. Jaccarino, *Phys. Rev.* **121**, 1357 (1961).

¹¹ A. M. Clogston, V. Jaccarino, and Y. Yafet, *Phys. Rev.* **134**, A650 (1964).

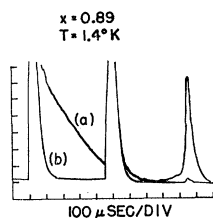


FIG. 1. Transient ^{23}Na nuclear magnetic resonance signals in Na_xWO_3 ($T_1 \approx 35$ min) in a uniform magnetic field obtained with a sequence of two equal-width (≈ 10 μsec) rf pulses at 9.0 Mc/sec: (a) 3 min and (b) 10 sec after a saturating rf comb.

conduction electrons can provide a significant relaxation mechanism for ^{183}W nuclei without appreciably affecting the relaxation of ^{23}Na nuclei.

The present paper¹² is concerned exclusively with relaxation measurements of the ^{23}Na ($I = \frac{3}{2}$) resonance as a function of temperature and x value. The details of our experimental results are presented in Sec. II. The experimental technique is described in IIA. The measured transverse relaxation rates are compared in IIB with predictions based on a random distribution of sodium vacancies. Although the transverse relaxation rates do not give information relevant to the conduction band in Na_xWO_3 , they demonstrate a clustering tendency which markedly affects the sodium distribution in these compounds. The spin-lattice relaxation measurements are presented in IIC. The significance of the spin lattice relaxation rates with respect to the Sienko and Mackintosh models is discussed in Sec. III.

II. EXPERIMENTAL RESULTS

A. Transient Nuclear-Magnetic Resonance Technique

A modified Arenberg model PG-650-C pulsed oscillator and Varian 12-in. magnet system were used for frequencies of 5 and 9 Mc/sec. The pulse sequence for the oscillator was produced by a Tektronix Type 162 waveform generator, a Hewlett Packard Model 218A delay generator, and DuMont Model 404 pulse generators. The pulsed oscillator output was fed into the tapped portion of a tuned coil containing the sample. The coil was mounted on a rigid probe and placed into a standard nitrogen-jacketed Dewar. Liquid-nitrogen, hydrogen, and helium baths were used to obtain temperatures of 76, 20, and 4°K, and cryogenic pumping on liquid helium was used to obtain temperatures between 4 and 1.4°K.

The receiver system consisted of a modified Arenberg Model PA-620 tunable preamplifier and an Arenberg Model WA-600B wide-band amplifier containing a video detector. Care was taken to keep the output signal within the linear range of the video detector. The recovery time of the system was approximately 50 μsec .

The signal was displayed on an oscilloscope, and data were recorded with a Polaroid camera.

A 10-sec saturating comb of 100 pulses, each 10–30 μsec in width, was used to destroy the nuclear magnetization. This comb was adequate to saturate even the quadrupolar-broadened levels, so that the subsequent recovery of the magnetization was essentially exponential.¹³ Two pulses of equal width were used to detect spin echoes, with the signal maximized with respect to pulse width. A single $\frac{1}{2}\pi$ pulse of approximately 30 μsec was used to detect the free-precession signal.

Each spin-lattice relaxation measurement consisted of 30–45 data points taken at time intervals following the saturating comb varying from a few seconds to several multiples of T_1 . Maximum signal to noise ratios of approximately 20 limited the precision of measurement at room temperature; extremely good signal to noise ratios were obtained at 4°K, so that precision in this region was limited only by slow tuning drifts of the apparatus.

The Na_xWO_3 samples were prepared by electrolytic reduction of a fused Na_2WO_4 - WO_3 mixture, crushed into particles smaller than 325-mesh, and suspended in solid paraffin. The same five samples ($x = 0.89, 0.81, 0.73, 0.65, 0.56$) have been used previously for specific heat⁴ and Knight shift⁹ measurements.

B. Transverse Relaxation

Figure 1 shows the ^{23}Na nuclear signals obtained from Na_xWO_3 in a *uniform* magnetic field using a 2-pulse sequence. These signals consist of a free-precession signal following the first rf pulse and a narrow spin echo after the second rf pulse. There are two related features which are especially noteworthy: (a) The dephasing time T_2^* of the echo is approximately 40 μsec compared with a T_2^* of 200–300 μsec for the free-precession signal, and (b) the broader free-precession signal is not refocused by the second rf pulse. It is apparent that the damping of the transverse nuclear magnetization is due to inhomogeneity effects in the case of the spin echo and an intrinsic relaxation mechanism in the case of the free-precession signal. The spin-spin relaxation time T_2 of the free-precession signal [$T_2(\text{FP})$] must be very nearly the same as its T_2^* in order to explain the observation that no refocusing occurs for this signal after the second rf pulse. The T_2 of the spin echo is much longer; it was measured and found to lie between 700 and 1400 μsec . The decay curves used to obtain T_2 were nonexponential for both signals. Consequently, the quoted values are based on estimates of the time required for the signals to decay to $1/e$ of their maximum value. The resulting T_2 's were found to be essentially independent of x value and temperature and are evidently due to dipolar spin-spin interactions. Static quadrupolar broadening in our powdered samples can account for the difference

¹² For a preliminary report of this work, see A. T. Fromhold, Jr. and A. Narath, *Bull. Am. Phys. Soc.* 8, 592 (1963).

¹³ W. W. Simmons, W. J. O'Sullivan, and W. A. Robinson, *Phys. Rev.* 127, 1168 (1962).

in T_2^* for the two signals, provided one assumes that the signals arise from two different types of sodium sites or regions in the sample: ^{23}Na spins experiencing severe static quadrupolar broadening with a relatively long T_2 and ^{23}Na spins experiencing very little quadrupolar broadening with a relatively short T_2 .

At this point it seems appropriate to speculate on the origin of the two distinct transient responses of the ^{23}Na spin system. Because of the rapid r^{-3} and r^{-6} dependences¹⁴ of first- and second-order quadrupolar broadening, respectively, it is important to consider the effect of vacancies in the six nearest-neighbor sodium positions surrounding a given sodium site. If these positions are either completely occupied or completely empty, the resulting nearest-neighbor cubic symmetry leads to a zero contribution to quadrupolar broadening from the nearest-neighbor shell. Conceivably, the occurrence of these two configurations could account for the free-precession signal ($T_2^* \simeq T_2$) since vacancies outside the nearest-neighbor shell lead to a second-order quadrupolar broadening of the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition which is, on the average, smaller than that due to nuclear spin-spin interactions. One or more vacancies in nearest-neighbor positions, on the other hand, would give rise to significant second-order broadening so that the transient signal from such nuclei would appear as an echo ($T_2^* < T_2$) even in a uniform external field. A single sodium vacancy in a nearest-neighbor position, for example, gives a direct contribution to the electric field gradient of 5.06×10^{15} V/cm², assuming a lattice constant¹⁵⁻¹⁷ $a_0 = 3.846$ Å. Applying standard formulas¹⁴ for powdered samples, we calculate a resulting first-order separation of the peaks corresponding to the $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transitions of 338 kc/sec, and a second-order spread in the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition of 6.62 kc/sec for a Larmor frequency of 9.00 Mc/sec. (This assumes a nuclear quadrupole moment¹⁴ $Q = 0.100 \times 10^{-24}$ cm² and an antishielding factor¹⁸ $\gamma_\infty = -4.53$.) From these considerations it follows that the $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transitions would be unobservable in our experiments for sodium nuclei having even a single vacancy within a radius of $\simeq 3a_0$. The $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition, which is broadened only in second order, would exhibit a $T_2^* \simeq 80$ μsec [assuming $T_2^* = (2\Delta\nu)^{-1}$] for a single nearest-neighbor vacancy and correspondingly shorter dephasing times for two or three vacancies.

The relative abundance of sodium nuclei which give rise to the free-precession signals can be obtained from our experiments for two limiting cases: (1) An upper limit is obtained if we assume a small cluster model (i.e., if there are sodium vacancies sufficiently close to

TABLE I. Relative abundances of ^{23}Na nuclei within vacancy-free regions in Na_xWO_3 .

x value	Predictions for random distribution	Values obtained from experimental data	
		Small cluster model	Large cluster model
0.89	0.50	0.32	0.16
0.73	0.15	0.29	0.14
0.56	0.04	0.22	0.10

the nuclei in question so that the resulting quadrupolar interaction causes only the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition to contribute to the observed free-precession signal). (2) A lower limit is obtained if we assume a large cluster model (i.e., if the nuclei are surrounded by a sufficient number of filled or empty sodium shells so that the quadrupolar interaction is small enough for all three transitions to contribute to the free-precession signal). For the small-cluster model the relative abundances are obtained directly from the observed signal intensities after correcting for differences in the relaxation times by extrapolating the measured intensities to the thermal equilibrium values. For the large-cluster model, the relative abundances differ from the values for the small-cluster model by normalizing factors which arise from the fact that only the central transition would contribute to the echo intensity whereas all three transitions would contribute to the free-precession amplitude.

If the sodium vacancies are randomly distributed over the appropriate lattice positions, the relative abundances can be predicted from the probability of finding the nearest-neighbor shell of a given sodium site either completely filled or empty. For a sodium concentration x , these probabilities are x^6 and $(1-x)^6$, respectively. Over the range of x values studied, the statistical probability of having vacancy-free regions with radius larger than a_0 is vanishingly small. Thus, only the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition would be observable in our experiments because of the large first-order quadrupolar interaction to which essentially all sodium nuclei are subjected. The relative abundances predicted for a random vacancy distribution are given in Table I together with the relative abundances obtained from the signal intensities in the limit of small and large cluster models. It can be seen clearly that the experimental results are inconsistent with a random vacancy distribution. The outstanding feature of the experimental results, interpreted on the basis of either cluster model, is the lack of a marked x dependence. This indicates a decided tendency for sodium clustering in the low- x samples.

A distinction cannot be made between the large- and small-cluster models on the basis of the transverse relaxation rates. There is evidence, however, that many of the sodium clusters are large enough to result in a vanishing first-order quadrupole effect for a substantial number of sodium spins. For example, the postulate of relatively large vacancy-free regions explains the dif-

¹⁴ M. H. Cohen and F. Reif, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, pp. 339, 350, 400.

¹⁵ M. E. Straumanis, *J. Am. Chem. Soc.* **71**, 679 (1949).

¹⁶ E. W. Brimm, J. C. Brantley, J. H. Lorenz, and M. H. Jellinek, *J. Am. Chem. Soc.* **73**, 5427 (1951).

¹⁷ Bruno Morosin (private communication).

¹⁸ T. P. Das and R. Bersohn, *Phys. Rev.* **102**, 733 (1956).

ficulty which was encountered in obtaining an exponential recovery of the echo amplitude following saturation of the spin system, and the ease with which exponential recoveries of the free-precession signal were obtained. The strong nuclear quadrupole interactions in the disordered regions make it difficult to saturate the $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transitions. Although these transitions are presumably not observed in our experiments, they can affect the recovery of the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition as a result of spin exchange among the various spin levels. An exponential recovery is expected only after a Boltzmann distribution has been established¹⁸; this is expected to take a considerable length of time since spin diffusion is a slow process in the disordered regions. The initial recovery rates were found to be considerably faster than the asymptotic rates unless care was taken (narrow rf pulses, long saturating comb) to saturate all three transitions initially (i.e., unless the initial distribution among the four spin levels corresponded to an infinite spin temperature). The recoveries of the free-precession amplitude, on the other hand, were always exponential within our experimental uncertainty. This behavior is expected in a large ordered region ($x=1$) because of the equidistant nuclear spin levels.

In principle it should be possible to observe the characteristic spin-lattice relaxation times for both types of region at sufficiently high temperatures because of the slow exchange of energy between these regions resulting from the absence of rapid spin diffusion in the disordered regions. At temperatures sufficiently low to make spin diffusion to paramagnetic impurities the rate limiting step, however, the regions are expected to relax at a common rate. Experimentally the echo relaxation time at 20°K is found to be only half as long as that for the free-precession signal. This difference becomes smaller on lowering the temperature and essentially disappears below 4°K. These observations are consistent with the existence of large clusters. Since no evidence of sodium vacancy-free clusters appears in x-ray diffraction measurements,¹⁷ it is possible to estimate an upper limit of $\sim 1000 \text{ \AA}$ for the mean cluster diameter. Since our T_1 measurements were based on observations following saturation of all three transitions, the observed differences between $T_1(\text{FP})$ and $T_1(\text{Echo})$ support our contention that the two transient signals arise from spatially distinct regions. If the echo were due to $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transitions (rather than $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions in disordered regions as we have assumed) it would be necessary for the observed free-precession intensity to be due entirely to $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions in the *same* regions which give rise to the echo. (This requirement follows from the fact that the echo accounts for at least 60% of the total intensity observed in our experiments.) Hence, the measured echo and free-precession T_1 's would be identical, in disagreement with our results. Any contribution to the measured echo intensity from $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transitions must therefore be small. Moreover, such contribution

would necessitate a proportional increase in the estimated abundances of sodium nuclei in vacancy-free regions which we have given in Table I.

The measured values of T_2 for the two transient signals can be accounted for readily on the basis of a cluster model. The decay of the transverse nuclear magnetization within clusters should be characteristic of dipolar broadening in a simple cubic lattice.¹⁹ The estimate of $T_2(\text{FP}) \simeq 200\text{--}300 \text{ \mu sec}$ is in excellent agreement with such a model. The spin-spin relaxation in the disordered regions, on the other hand, proceeds much more slowly because: (a) there are fewer neighbors than in the ordered regions for participation in the relaxation process, (b) the second-order quadrupolar broadening of the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition decreases the probability of spin-exchange, and (c) the first-order interaction makes the $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transitions unavailable for spin exchange with the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition.

In the foregoing discussion the tacit assumption was made that the observed quadrupole effects are due only to point defects of effective charge $-|e|$. Contributions from nonuniform conduction-electron distributions and lattice strains were ignored because the magnitude of these effects cannot be assessed accurately. Since the resulting modification of the electric field gradient is expected to occur primarily near sodium vacancy sites, our conclusions regarding the presence of vacancy-free clusters in our samples are not influenced.

It should be pointed out that our results provide no support for the structure proposed by Atoji and Rundle²⁰ on the basis of their neutron-diffraction study. From their measurements a superlattice structure containing eight WO_3 complexes per unit cell (resulting from a doubling of the cubic lattice constants) was obtained. Evidence for ordering of the sodium positions over a range of x values from 0.6–0.9 also was obtained. The proposed ordering is complete at $x=0.75$ with sodium vacancies at all (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ positions of the enlarged cell. For this structure ($x=0.75$) we calculate an electric field gradient at each sodium site which is 1.34 times as large as the gradient produced by one nearest-neighbor vacancy. Hence, our observations of free-precession decays with $T_2^* \simeq T_2$ at low x values suggests that ordering of the type proposed by Atoji and Rundle is not important in our samples. This conclusion is supported by the fact that we observed no anomalous behavior in our measurements on an $x=0.73$ sample.

Finally, we should remark that the CW ^{23}Na resonances previously reported^{8,9} evidently originated from vacancy-free regions, thus explaining the agreement between the observed linewidth ($x=0.89$) of 1.11 ± 0.09 Oe and the calculated Gaussian dipolar linewidth of 1.06 Oe. The observed CW absorption thus corresponds to our free-precession signal, whereas the much broader

¹⁹ I. J. Lowe and R. E. Norberg, *Phys. Rev.* **107**, 46 (1957).

²⁰ M. Atoji and R. E. Rundle, *J. Chem. Phys.* **32**, 627 (1960).

CW absorption in the disordered regions probably was not observed.

C. Spin-Lattice Relaxation

The spin-lattice relaxation time T_1 has been measured as a function of temperature, magnetic field, and x value for the two types of nuclear signal. The recovery of the free-precession signal (^{23}Na nuclei in vacancy-free regions) was exponential, and the recovery of the spin-echo signal (disordered regions) was essentially exponential, as discussed in the preceding section. The T_1 values range from a few seconds at room temperature to tens of minutes at liquid-helium temperatures. There is no measurable dependence of T_1 on the magnetic field strength. This is illustrated in Fig. 2 which shows the recovery of the free-precession signal at 4°K after a saturating comb at frequencies of 5 and 9 Mc/sec. The recovery of the magnetization is exponential within experimental error and the slope is independent of frequency.

Figure 3 is a logarithmic plot of the T_1 data versus temperature for the two nuclear signals at three x values. Each data point is the average of approximately three determinations except for data below 4°K, for which several days were required to measure a single value of T_1 . The variation of T_1 with temperature is quite large as expected; T_1 for $x=0.89$, for example, has values of 0.125, 1.10, 4.4, and 13.9 min at temperatures of 298, 76, 20, and 4°K, respectively.

It is found that $T_1(\text{Echo})$ at a given temperature increases with increasing x value; furthermore, the relaxation time for the free-precession signal, $T_1(\text{FP})$, at a given temperature is longer than the corresponding $T_1(\text{Echo})$. At 4°K, for example, $T_1(\text{Echo})$ is 2.7, 10.5, and 13.9 min for x values of 0.56, 0.73, and 0.89, respectively, and $T_1(\text{FP})$ is 15.3 and 18.9 min for x values of 0.73 and 0.89, respectively.

The data at 76°K and below for the $x=0.89$ sample follow the relation $T_1 \propto T^{-1}$, while the data for $x=0.73$ and 0.56 progressively deviate towards a temperature-independent behavior with decreasing temperature. The T^{-1} dependence of T_1 on temperature indicates a conduc-

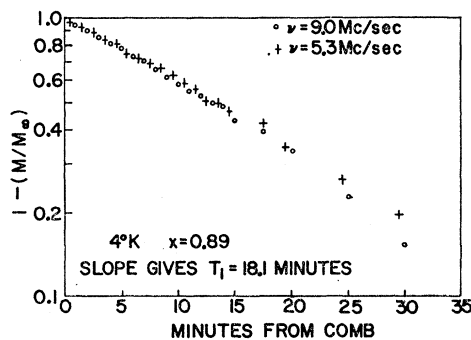


FIG. 2. Recovery of the ^{23}Na free-precession signal at 4°K in $\text{Na}_{0.89}\text{WO}_3$ following a saturating rf comb.

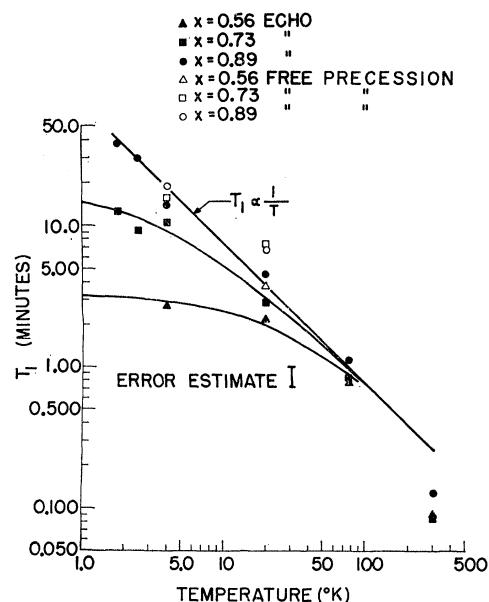


FIG. 3. Experimental results of T_1 versus temperature for three x values. The solid lines were computed from a fit to the data of a combination of conduction electron and paramagnetic impurity relaxation mechanisms with magnitudes listed in Table II.

tion-electron relaxation process. The data begin to deviate from the $T_1 \propto T^{-1}$ curve at low temperatures due to spin diffusion to paramagnetic impurities, which provides a relaxation process which is essentially temperature-independent. The deviation is more pronounced for the lower x value samples, since the concentration of paramagnetic impurities in these samples is probably higher. The fact that T_1 is independent of magnetic field, as illustrated in Fig. 2, shows that the rate-limiting step for relaxation is spin diffusion to paramagnetic impurities rather than relaxation through the paramagnetic impurities. The solid curves in Fig. 3 were obtained by fitting the experimental spin-echo data (1.4–76°K) to the expression $1/T_1 = A + BT$, where A and B are constants which determine the effectiveness of the paramagnetic impurity and conduction electron relaxation processes, respectively.

The T_1 's at 298°K are shorter than would be obtained by extrapolating the $T_1 \propto T^{-1}$ relation from lower temperatures. The Debye temperature for these compounds⁴ is of the order of 450–500°K, so that quadrupolar coupling to lattice vibrations should be effective at 298°K, but not at 76°K and below. The fact that the 298°K data in Fig. 3 fall below the $T_1 \propto T^{-1}$ curve is undoubtedly due to the quadrupolar mechanism. This quadrupolar contribution can be calculated from the difference between the extrapolated curves in Fig. 3 and the experimental data at 298°K.

Table II shows the results of the above analysis at 298°K. Note that T_1 for the paramagnetic impurity mechanism has values of the order of minutes, and increases markedly with increasing x value. No contribu-

TABLE II. Contributions to the spin-lattice relaxation time T_1 (Echo) from the three relaxation processes in Na_xWO_3 at 298°K.

x value	Electric quadrupole (sec)	Mechanism Conduction electron (sec)	Paramagnetic impurity (min)
0.89	15.1	14.8	>40
0.73	7.7	14.8	18
0.56	7.7	18.1	3.3

tion from this process could be observed in the $x=0.89$ sample even at 1.4°K. The quadrupolar process also becomes less efficient at higher x values. This is reasonable, since the magnitude of the fluctuations in the electric field gradient should be less for higher x values. The large impurity relaxation contribution to the measured T_1 's for $x=0.56$ makes it difficult to obtain an accurate value for the conduction electron contribution in this sample. Hence the increase in T_1T from 74 min-°K ($x=0.89$) to 90 min-°K ($x=0.56$) is probably not very meaningful. It appears therefore that T_1T (due to conduction electrons) is essentially independent of x value. It is significant that the values of T_1T are approximately three orders of magnitude larger than the values obtained²¹ for other good electrical conductors such as metallic ^{23}Na ($T_1T=5.1$ sec-°K) and metallic ^{63}Cu ($T_1T=1.27$ sec-°K).

Unfortunately, the signal-to-noise ratio was too poor to measure T_1 (FP) reliably at 76 and 298°K. Thus an analysis similar to the one carried out above for T_1 (Echo) could not be made. It is apparent, however, that the conduction-electron process is slightly less efficient for the free-precession signal than for the spin echo.

Samples for which $x=0.81$ and $x=0.65$ were studied also, but not so extensively as the three x values used to obtain the data in Fig. 3. The results were consistent with the data which have been presented.

III. DISCUSSION

The most important experimental result of the present study is the observation that conduction electrons contribute significantly to the ^{23}Na nuclear spin-lattice relaxation rate in metallic Na_xWO_3 .

The measured conduction electron contributions can arise from the following magnetic interactions:

- Fermi contact interaction with partly filled s shells ($l=0$).
- Contact interaction resulting from core polarization of filled s shells.
- Spin-dipolar interaction with partly filled non- s shells ($l \neq 0$).
- Orbital interaction with partly filled non- s shells.

All four mechanisms involve only those conduction-

electron states that lie near the Fermi level. Interactions a and b give rise to the well-known positive²² and negative²³ Knight shifts of the nuclear resonance frequency, respectively, and also give contributions to the nuclear spin-lattice relaxation which are separately related to the corresponding Knight shift contributions according to Korringa-like²⁴ relations [$T_1T \propto (\Delta H/H)^{-2}$]. The resonance shift produced by the spin-dipolar interaction c vanishes when the point group symmetry is cubic as in Na_xWO_3 ; its contribution to the relaxation, however, does not vanish. In general, the total nuclear-relaxation rate is given by the sum of the individual rates associated with interactions $a-d$. The net shift of the resonance frequency, on the other hand, can be reduced through mutual cancellation when interactions a and b are present simultaneously.

In addition to the magnetic interactions there exists a contribution to nuclear relaxation (for $I > \frac{1}{2}$) due to quadrupole interactions with electric field gradients arising from non- s conduction electrons.²⁵ This process may be neglected in the present case because of the relatively small quadrupole moment of ^{23}Na .

In its simplest form the Mackintosh model⁷ for the Na_xWO_3 conduction band consists of overlapping sodium $3p$ wave functions. The resulting band has essentially pure p character and hence the direct ^{23}Na contact interaction a is entirely absent. Neglecting for the moment the possibility of core polarization, the only important contributions to the sodium relaxation would come from the spin-dipolar and orbital mechanisms c and d . These contributions can be calculated using the results of Obata²⁶ who obtained the following expression for a p band in the tight-binding approximation:

$$1/T_1 = (52\pi kT/5\hbar) [\gamma_e \gamma_N \hbar^2 N(\zeta_0) \langle r^{-3} \rangle]^2.$$

Here $\langle r^{-3} \rangle$ is the average of r^{-3} over the appropriate atomic sodium $3p$ function and $N(\zeta_0)$ is the density of electronic states at the Fermi energy ζ_0 per unit energy normalized in such a way that the total density per state per atomic volume is unity. Since the atomic p states have twofold spin degeneracy and threefold orbital degeneracy, the value of $N(\zeta_0)$ is just $\frac{1}{6}$ of the measured⁴ density of states. Also γ_e and γ_N are the appropriate electronic and nuclear gyromagnetic ratios, k is Boltzmann's constant, and $2\pi\hbar$ is Planck's constant. The free-atom value of $\langle r^{-3} \rangle$ can be obtained from the ^{23}Na hyperfine constants in the $^2P_{1/2}$ and $^2P_{3/2}$ states as

²² C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

²³ V. Heine, Phys. Rev. **107**, 1002 (1957); J. H. Wood and G. W. Pratt, Jr., *ibid.* **107**, 995 (1957).

²⁴ J. Korringa, Physica **16**, 601 (1950); See also R. Hecht and A. G. Redfield, Phys. Rev. **132**, 972 (1963); **133**, 12 (1964) for corrections of Korringa's expression for spin-dipolar and orbital relaxation.

²⁵ A. H. Mitchell, J. Chem. Phys. **26**, 1714 (1957).

²⁶ Y. Obata, J. Phys. Soc. Japan **18**, 1020 (1963).

²¹ A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

determined by Perl, Rabi, and Senitzky²⁷ using the atomic-beam resonance technique. The average for the two states is found to be $\langle r^{-3} \rangle = 1.70 \times 10^{24} \text{ cm}^{-3}$. The computed value of T_1 at 298°K is thus 0.90 sec for $x=0.89$. This compares with an earlier upper limit estimate of 2.3 sec⁹ based on the work of Korringa²⁴ and a value of $\langle r^{-3} \rangle$ obtained from the fine-structure splitting of the sodium $3p$ term. It is probable that the largest error in the calculation of T_1 arises from the uncertainty in the value of $\langle r^{-3} \rangle$. If we assume, somewhat arbitrarily,²⁸ that a 25% reduction occurs in going from the free atom to the solid, the calculated T_1 increases to 1.6 sec compared with an observed conduction electron contribution of 14.8 sec. Hence, in this approximation we can attribute only 33% of the measured density of states at the Fermi level to sodium $3p$ states.

It is very unlikely that a sodium band in the cubic environment of Na_xWO_3 could exhibit 100% p character at the Fermi level, independent of x value. Mackintosh⁷ has attempted to overcome this difficulty by postulating that the s character is small and is accompanied by sufficient core polarization to lead to the observed small diamagnetic shift⁸ of the ^{23}Na resonance. This shift is very small, having an absolute magnitude which is typically about 5% (relative to aqueous NaCl) of the paramagnetic shift in sodium metal. Since the contact interactions are much more effective in producing nuclear relaxation than the spin-dipolar and orbital interactions, even a small admixture of sodium s states into the conduction band would drastically reduce our estimate of the density of sodium states at the Fermi level. Thus our estimate of 33% must be regarded as a very conservative upper limit to the contribution of sodium states to the conduction band in Na_xWO_3 .

A more plausible explanation for the observed conduction electron contribution to the ^{23}Na spin-lattice relaxation is provided by the Sienko model.⁶ In this model the conduction band is based on tungsten $5d(t_{2g})$ states with a possible admixture of oxygen $2p$ states. The triply degenerate $5d(t_{2g})$ orbitals have an appreciable density near the sodium core. Hence, it is possible that the slight diamagnetic ^{23}Na shifts are a result of an exchange polarization of the sodium ion core due to overlap with the tungsten conduction electrons.¹⁰ It is significant that the magnitude of the measured shifts is consistent with the observed relaxation rates if core polarization²⁸ is the only important conduction-electron perturbation acting on the ^{23}Na spin system. This conclusion follows if we make the reasonable assumption that the Korringa-

like relation

$$T_1 T = \frac{\hbar}{4\pi k q} \left(\frac{\gamma_e}{\gamma_N} \right)^2 \left(\frac{\Delta H}{H} \right)_{\text{cp}}^{-2}$$

obtained by Yafet and Jaccarino²⁸ gives an adequate estimate of the relationship between the core polarization shift and the corresponding relaxation rate for our case. In this expression q is a reduction factor which is given by the reciprocal of the orbital degeneracy of the conduction band. For $x=0.73$ we obtain $T_1 T = 52 \text{ min} \cdot ^\circ\text{K}$ using the measured⁸ shift of -0.006% and $q = \frac{1}{3}$. This compares with our experimental value of 73 $\text{min} \cdot ^\circ\text{K}$ for the conduction-electron contribution to the echo relaxation. The free-precession relaxation due to conduction electrons is probably slightly longer as can be seen from our T_1 measurements at 4 and 20°K. Furthermore, with the exception of the $x=0.89$ case, the shifts⁸ exhibit the same lack of x dependence as do the relaxation rates. The shift for the $x=0.89$ sample was found to be somewhat lower ($\Delta H/H_{(\text{NaCl})} = -0.0022\%$) than the average for the other x values ($\Delta H/H_{(\text{NaCl})} = -0.0058\%$); this reduction, however, is qualitatively consistent with the longer relaxation times measured for the $x=0.89$ free-precession signal.

The absence of a definite x dependence for the measured ^{23}Na relaxation times (and frequency shifts) is not understood on the basis of either model. For example, if the measured relaxation times were related to the square of the density of states per unit volume at the Fermi surface⁴ one would expect T_1 to decrease by a factor of 2.6 in going from $x=0.56$ to $x=0.89$. This trend, however, is not observed.

Although our results do not rule out the possibility of a small contribution of sodium states to the conduction band of Na_xWO_3 , they provide convincing evidence that such an admixture is not very important. As regards the Sienko model, it has the virtue of not being in disagreement with the nuclear resonance measurements which have been carried out to date. In fact, it finds support in the negative Knight shift of the ^{183}W resonance,⁹ which moreover exhibits the expected increase with increasing x value. Definite conclusions, however, must await measurements of the ^{183}W relaxation times.

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²⁷ M. L. Perl, I. I. Rabi, and B. Senitzky, Phys. Rev. **98**, 611 (1955).

²⁸ Y. Yafet and V. Jaccarino, Phys. Rev. **133**, A1630 (1964).