$\zeta_{\text{Yb}^{3+}}$ is also larger; the ratio of $\zeta_{\text{Tm}^{2+}}/\zeta_{\text{Yb}^{3+}}=0.875$. This ratio is very close to the ratio of the other known isoelectronic systems Sm^{2+} and Eu^{3+} where

$$\zeta_{\text{Sm}^{2+}}/\zeta_{\text{Eu}^{3+}}=0.85.$$

The absorption spectra of 0.03 weight percent trivalent cerium in CaF_2 are shown in Fig. 8. In the case of the $4f^1$ one-electron system, the lowest state is the $^2F_{5/2}$ state and in the cubic field the G level will be the lower, if it is the upper state in the f^{13} system. All the three transitions will be allowed to the three cubic-field split levels of the $^2F_{7/2}$ state whether they are of electric dipole or magnetic dipole origin. Here again, the total extent of the spectra is about 1000 cm^{-1}. At liquid-He temperature there are two broad bands at 2255 cm^{-1} and at 3200 cm^{-1}. These are separated by about 270 cm^{-1} from two sharp lines at 1992 cm^{-1} and at 2930 cm^{-1}, respectively. These sharp lines could possibly be two of the three crystal lines, each carrying the summation tones of the CaF_2 lattice. The position of the third line cannot be determined from the data above. The relative positions of the levels shown in Fig. 2 are certain to change since the crystal field mixing of the two spin-orbit split states becomes very important with the small separation of the two ^2F states. The oscillator strength of the band at liquid-N_2 temperature is $f=7\times10^{-6}$.

While the analysis of the $\text{Yb}^{3+}\!:\!\text{CaF}_2$ and $\text{Ce}^{3+}\!:\!\text{CaF}_2$ system is incomplete, it was presented to show that the proposed large crystal field splitting in $\text{CaF}_2\!:\!\text{Tm}^{2+}$ is not inconsistent with the absorption data of its isoelectronic systems.

ACKNOWLEDGMENTS

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Nuclear Magnetic Resonance in Cubic Sodium Tungsten Bronzes*

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The nuclear magnetic resonances of W^{183} (natural abundance) have been studied in samples of cubic sodium tungsten bronzes (Na_xWO_3) with x ranging from 0.56 to 0.89, in tungsten trioxide, and in tungsten metal. The bronze resonances exhibit appreciable diamagnetic shifts ($\sim$0.3%) with respect to tungsten trioxide, the shift increasing with increasing x. The spin-lattice relaxation time for Na^{23} in $\text{Na}_{0.89}\text{WO}_3$ was found to be 55 sec. These results provide evidence that the conduction band in the cubic sodium tungsten bronzes is based on tungsten $5d$ states.

I. INTRODUCTION

THE properties of transition metal oxides have been of much interest in recent years. A large number of these oxides, e.g., TiO, VO_2, etc., are metallic, and much effort has been devoted toward understanding the corresponding electronic transport mechanisms. Of particular interest is tungsten trioxide, WO_3. Although it is an insulator, a number of univalent metals can be added to its lattice to yield metal tungsten bronzes, $M_x\text{WO}_3$ $(0<x<1)$ which range from semiconductors to metals, depending on M and x.[1–3] The interest in these materials arises primarily from the fact that the number of conduction electrons can be controlled by adjusting the metal concentration. The most extensively studied bronzes are those for which $M=\text{Na}$. In the range of $0.45<x<1$ the sodium tungsten bronzes exhibit typical metallic characteristics such as high electrical conductivity.[1] They crystallize in the cubic perovskite structure in which the tungsten atoms are at the centers of the unit cell, the oxygen atoms at the cube face centers, and the sodium atoms are distributed essentially at random over the corner positions.[4] The WO_3 skeleton of these bronzes is, therefore, almost identical to that of pure WO_3 (which has a distorted cubic structure).[5]

A number of investigations of the electronic properties of Na_xWO_3 have already been reported.[1,3,6–8] In addi-

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tion, Jones *et al.*[9] have recently reported on a nuclear magnetic resonance (NMR) study of Na^{23} in cubic Na_xWO_3. They observed no paramagnetic Knight shift and concluded that the sodium atoms play the role of donors, giving up their 3*s* valence electron to a WO_3 conduction band, as had previously been proposed by Sienko.[10]

The present report describes the observation of the room temperature W^{183} NMR (natural abundance) in several samples of cubic Na_xWO_3 and WO_3. No paramagnetic Knight shifts were detected in the bronze samples. We have also remeasured the nuclear resonance frequency in metallic tungsten and find excellent agreement with the value reported by Sogo and Jeffries.[11]

A measurement of the spin-lattice relaxation time T_1 of Na^{23} in $Na_{0.89}WO_3$ confirms the ionic character of sodium in the WO_3 lattice.

In Sec. IV our results are discussed in terms of the various models for electrical conduction in Na_xWO_3.

II. EXPERIMENTAL

The samples of Na_xWO_3 ($x=0.89$, 0.81, 0.73, 0.65, 0.56) were kindly furnished us by Professor Danielson's group at Iowa State University. They were prepared by the electrolytic reduction of a fused $Na_2WO_4-WO_3$ mixture. Particle sizes were reduced by crushing so that the largest particles passed through a 325-mesh sieve. The powdered samples were then suspended in solid paraffin in order to eliminate rf penetration problems. The sample of tungsten metal (commercial 99.95%) was treated similarly. The WO_3 measurements were made on a commercial reagent grade sample. In their final form, our samples had tungsten concentrations of 1.9 g/cc in Na_xWO_3, 6.3 g/cc in W metal and 2.0 g/cc in WO_3.

All of our measurements were made at room temperature with a Varian Associates Wide-Line spectrometer and 12-in. magnet system. The W^{183} resonances were observed in fields of 11 and 14 kOe. Because of the small magnetic moment of the W^{183} nucleus and its low natural abundance (14%), special precautions were necessary to make the resonances in the bronzes and WO_3 observable. The longest available detector time constant (80 sec) was required. The magnetic field scanning rate was usually about 0.5 Oe/min and the modulation frequency 80 cps. A 10-mV recorder was substituted directly for the recommended 100-mV recorder, in order to obtain a reasonable signal amplitude on the recorder chart without saturating the output control unit with noise and modulation pickup components. The signals were generally unobservable with a 100-mV recorder. The nuclear resonance absorption mode, χ'', was only observable for tungsten metal. In all other samples only the dispersion mode, χ', under conditions of high rf power (≈ 1.2 Oe), was observable. These conditions correspond to a driving field considerably in excess of the saturation value. The nonsaturation of the dispersion signal for $(\gamma H_1)^2 T_1 T_2 > 1$ has been discussed by Redfield.[12] He finds that under this condition the dispersion derivative amplitude exceeds the predictions of the Bloch theory in solids by the factor T_1/T_2. This effect predicts dispersion signals which can be considerably stronger than the maximum obtainable absorption mode signals, in agreement with our observations. Under the above operating conditions, instrument warmup periods of several hours were required in order to reduce drift to a tolerable level. All resonances were observed in phase with the modulation.

Our initial searches for the W^{183} NMR in WO_3 were unsuccessful, presumably because of long relaxation times. The sample was therefore γ-irradiated (Co^{60}, 2×10^8 rad) in the hope that the introduction of a large number of paramagnetic centers might make the resonance observable. The resonance was finally detected in the irradiated sample, making it possible to optimize all instrument settings. The signal was then observed in pure WO_3, although its intensity and width were still considerably less than those of the irradiated specimen.

A search for the O^{17} NMR (natural abundance) in our samples was unsuccessful. This is not surprising since the interaction between the nonvanishing electric field gradients at the oxygen positions and the O^{17} nuclear electric quadrupole moment probably results in severe line broadening. This broadening mechanism is absent for W^{183} since it has no quadrupole moment ($I=1/2$).

The determination of T_1 for Na^{23} in $Na_{0.89}WO_3$ was made using the standard c.w. saturation technique.[13] A modulation frequency of 20 cps and a modulation amplitude much smaller than the linewidth were used. The rf field settings H_1 were calibrated by measuring the voltage induced in a small wire loop with a high-impedance rf voltmeter (Hewlett Packard Model 411-A).

Magnetic field strengths were measured by calibrating the field scanning unit against the H^2 resonance in 20% D_2O-H_2O, 0.5*M* $MnSO_4$, using $\mu_D=0.85738$ nm. Frequency measurements were made with a digital counter.

III. RESULTS

The results of our W^{183} measurements are summarized in TABLE I. For purposes of comparison, we have also listed the moments reported by Sogo and Jeffries[11] for metallic tungsten and those of Klein and Happe[14] for WF_6. The most striking feature of our results is the absence of a paramagnetic Knight shift in the Na_xWO_3 samples. Instead, the resonances exhibit appreciable diamagnetic shifts with respect to WO_3 as well as WF_6.

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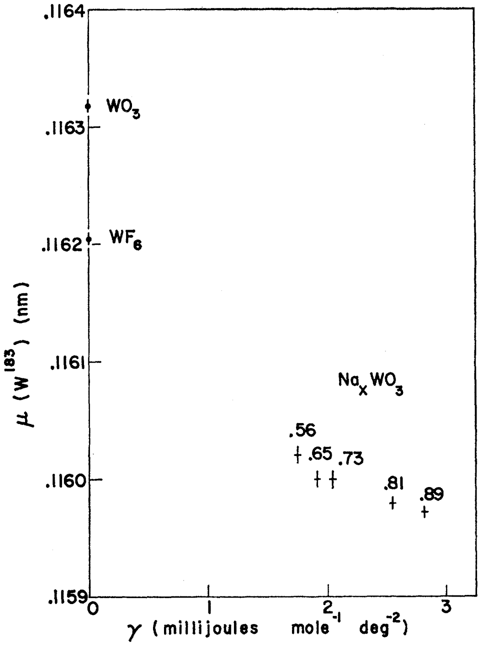

FIG. 1. Variation of the W^{183} resonance shifts in cubic sodium tungsten bronzes with the electronic specific heat. The insulators WO_3 and WF_6 are also shown for purposes of comparison.

It seems unlikely that the magnitude of the observed shifts could be accounted for by conduction electron diamagnetism. A more plausible explanation is an exchange polarization of the core s electrons at the tungsten sites by conduction electrons near the top of the Fermi distribution. This mechanism, which has been discussed by Clogston and Jaccarino[15] in connection with negative Knight shifts in some intermetallic compounds, predicts a linear dependence of the resonance shift on the conduction electron spin susceptibility. In Fig. 1 we have plotted the measured W^{183} moments against the electronic specific heat coefficients $\gamma(x)$ as determined by Vest *et al.*[7] on the same samples as those used in the present study. The electronic specific heat coefficients are directly proportional to the density of states $N(\zeta)$ at the Fermi surface, and to zeroth order in $KT/N(\zeta)$ to the paramagnetic spin susceptibility. It is seen that the observed x dependence of the shifts is in qualitative agreement with the model, suggesting that non-s tungsten states contribute significantly to the conduction band. A model in which the conduction electrons are confined to sodium states could not easily account for our observations.

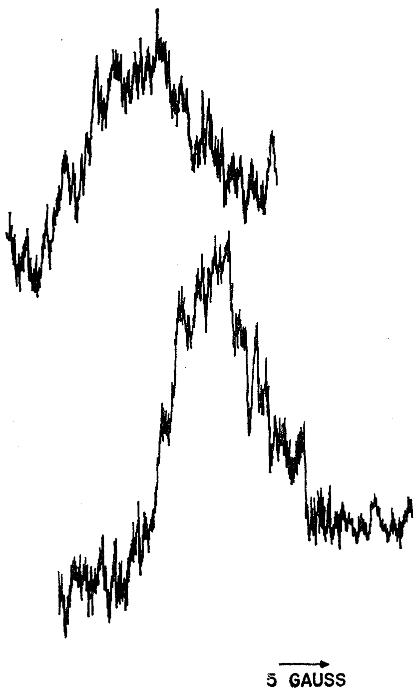

FIG. 2. Apparent dispersion derivative signals for W^{183} in Na_xWO_3. The observations were made at 14 kOe using a modulation of 2 Oe at 80 cps and a rf field strength of 1.2 Oe. Upper trace: $x=0.56$. Lower trace: $x=0.89$.

TABLE I. Summary of W^{183} resonance shifts. The nominal temperature is 300°K and the nominal field strength is 14kOe. The reference compound is WF_6.

Substance		μ (nm)	$\Delta H/H(\%)$
Na_xWO_3	$x=0.56$	0.116020 ± 0.000010	-0.159
	$x=0.65$	0.116000 ± 0.000010	-0.176
	$x=0.73$	0.116000 ± 0.000010	-0.176
	$x=0.81$	0.115979 ± 0.000005	-0.194
	$x=0.89$	0.115972 ± 0.000005	-0.201
WO_3		0.116321 ± 0.000005	$+0.100$
		0.11630 ± 0.00001[a]	$+0.08$
WF_6		0.116205 ± 0.000002[b]	0
W		0.117439 ± 0.000002	$+1.062$
		0.11744 ± 0.00001[c]	$+1.06$

[a] Value for γ-irradiated sample (Co^{60}, 2×10^8 rad).
[b] Taken from Klein and Happe, reference 14.
[c] Taken from Sogo and Jeffries, reference 11.

A second interesting feature of the bronze tungsten resonances is the behavior of the observed intensities as a function of x. In Fig. 2 we show representative tracings of two Na_xWO_3 resonances. Within experimental error the apparent derivative intensities increase with increasing x value while the widths remain approximately constant. Furthermore, within the range of H_1 amplitudes available to us (≤ 1.2 Oe) the observed signal intensities decrease with decreasing rf field. The rate of decrease is greatest for the $x=0.89$ sample. Unfortunately, the poor signal-to-noise ratio together with the extreme conditions of high rf power and high modulation frequency and amplitude make it impossible to interpret the line shapes and intensities quantitatively. However, our observations are consistent with Redfield's theory,[12] if we assume that the intensity variations are caused by a dependence of the local fields

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at the tungsten nuclei on the x value. The calculated Gaussian dipolar width[16] for $x=1$ is 1.1 G($\langle \Delta H^2\rangle = 0.32$ G^2) which is comparable to our maximum rf fields. Redfield predicts a nearly constant $\partial\chi'/\partial H_0$, proportional to $\langle \Delta H^2\rangle^{-1}$, for $2H_1^2 < \langle \Delta H^2\rangle$ and a decreasing $\partial\chi'/\partial H_0$ for $2H_1^2 > \langle \Delta H^2\rangle$, where $\langle \Delta H^2\rangle$ is the usual second moment of the absorption line shape. Since the dipolar width of the tungsten resonance in Na_xWO_3 is primarily determined by interactions with the Na^{23} moments, we expect $\langle \Delta H^2\rangle$ to be approximately proportional to x. Therefore, over the range of H_1 amplitudes in which we could detect the resonances ($0.5-1.2$ Oe) the theory predicts an increasing degree of saturation of $\partial\chi'/\partial H_0$ with decreasing x value, in agreement with observation. Furthermore, the increase of the intensities with H_1 suggests that the experimental conditions correspond to H_1 amplitudes only slightly larger than $\langle \Delta H^2\rangle$.

The extreme width of the bronze resonances when compared to the calculated dipolar width is characteristic of dispersion signals under high power conditions. Figure 3 shows signals obtained in tungsten metal at two different power levels. The 4-Oe width of the high-power signal compares with a width of ~0.5 Oe which we obtained for an absorption mode signal below saturation. If a similar saturation broadening factor is applied to the calculated second moments of the Na_xW0_3 tungsten resonances, reasonable agreement is obtained with our experimental observations. A simple correlation between true linewidths below saturation and apparent derivative dispersion widths for different samples at high power levels is of course not to be expected.

Another feature of the high power dispersion signals is the inversion of the central portion of the apparent derivative as compared to low power signals. The resonances in metallic tungsten clearly demonstrates this effect. Whereas the resonance at low power approximates a true dispersion derivative quite well, the one at high power obviously does not (Fig. 3). In Na_xWO_3 and WO_3, the center of the line has apparently disappeared completely. An intermediate case is the resonance in irradiated WO_3 as shown in Fig. 4. An explanation of this effect is at present not possible.

The result of our T_1 determination for Na^{23} in $Na_{0.89}WO_3$ is 55 sec. We also measured the Na^{23} T_1 in NaCl (reagent grade, polycrystalline) and obtained 2.3 sec. Our modulation conditions corresponded to $\omega_M T_1 \gg 1$. The analysis of the saturation behavior of $\partial\chi''/\partial\omega$ was, therefore, based on $\partial\chi''/\partial\omega \propto [\partial g(\omega)/\partial\omega] \times S(\omega)$, where $S(\omega)=[1+\frac{1}{2}(\gamma H_1)^2 T_1 g(\omega)]^{-1}$. In both measurements we assumed a Gaussian line shape $g(\omega)$. Our result for NaCl compares with $T_1 = 13$ sec obtained by Wikner *et al.*,[17] on an optically pure single crystal.

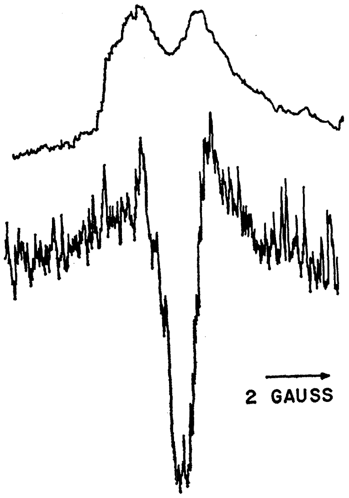

FIG. 3. Apparent dispersion derivative signals for W^{183} in tungsten metal. Upper trace: $H_1 = 1.0$ Oe. Lower trace: $H_1 = 0.05$ Oe. Both resonances were recorded at 14 kOe using a modulation of 1 Oe at 20 cps and a detector time constant of 25 sec.

IV. DISCUSSION

Several models have been proposed to describe the conduction electrons in Na_xW0_3. In order to explain the absence of a positive Knight shift of the sodium resonance, these models have been concerned with wave functions which have nodes at the sodium sites. Sienko[2,10] proposed that the conduction band is based on tungsten $5d(t_{2g})$ functions. He suggested [10] that these wave functions have angular nodes in the directions of the nearest-neighbor sodium sites. Although these functions do not in fact have such angular nodes [the three tungsten $5d(t_{2g})$ functions each have angular nodes on two of the planes $x=0$, $y=0$, and $z=0$], the electron density at the sodium sites should nevertheless be negligibly small. In Appendix I we discuss some properties of conduction electrons based on tungsten $5d(t_{2g})$ functions, in the approximation of tight-binding. We find there that such conduction electrons have nodes at the sodium sites when the wave vector lies along the

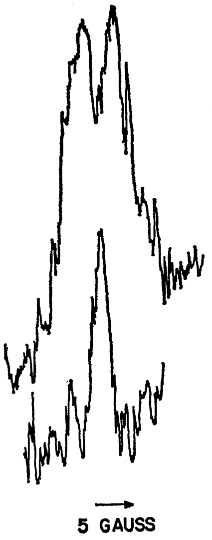

FIG. 4. Apparent dispersion derivative signals for W^{183} in WO_3 at 14 kOe. The rf field strength was 1.2 Oe. The modulation was 2 Oe at 80 cps and detector time constant was 80 sec. Upper trace: Irradiated sample (Co^{60}, 2×10^8 rad). Lower trace: pure WO_3.

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x, y, or z axis, or is at a corner of the first Brillouin zone. We also estimate an upper bound for the sodium Knight shift in Na_xWO_3 to be $5\times 10^{-5}\%$, which is much smaller than the error of the measurement.[9] We thus conclude that the absence of a sodium Knight shift does not depend on the presence of nodes for the tungsten $5d$ model.

Keller[18] suggested that the conduction band might be composed of tungsten $6s$ functions, and that the band may be inverted (minimum energy when the wave vector is at a zone corner). For such a band the electrons of lowest energy would have nodes at the sodium sites, and electrons near the bottom of the band would have correspondingly small densities at the sodium sites. Mackintosh[19] proposed that the conduction electrons are based on sodium $3p$ functions. Such functions should also lead to a negligible Knight shift of the sodium resonance.

The results of the present investigation strongly suggest that the conduction electrons in cubic Na_xWO_3 are largely of tungsten $5d$ character. Regarding the sodium p-band model, Jones *et al.*,[9] have argued that any conduction band based on sodium states should have a significant contribution from sodium $3s$ states. However, such a $3s$ contribution would give a positive Knight shift for sodium, in contrast to the observations.[9] The present result of approximately 55 sec for the sodium T_1 appears to rule out the sodium $3p$ model for conduction electrons. In Appendix II, following the methods of Korringa[20] and Masuda,[21] we estimate T_1 for sodium due to dipolar interactions with conduction electrons based on sodium $3p$ states. This involves making use of the spin-orbit interaction in the free atom to calculate $\langle r^{-3}\rangle$ for the sodium $3p$ wave function. The calculated relaxation time for $x=0.89$ is 2.3 sec. Thus, it seems unlikely that sodium $3p$ states are actually important in the conduction band of cubic Na_xWO_3.

The absence of a positive Knight shift for tungsten in the bronzes rules out any major contribution of tungsten $6s$ states to the conduction band. We would expect that the energies of the tungsten $6s$ and $5d(e_g)$ states (and perhaps also the tungsten $6p$ states) are lowered, with respect to the tungsten $5d(t_{2g})$ states, in bonding with oxygen states to form a valence band. The observed small diamagnetic shift of the tungsten resonance frequency, and the increase of this shift with increasing density of states at the Fermi energy, serve as direct evidence that the conduction electrons in Na_xWO_3 can be considered as based on tungsten states other than tungsten $6s$.

ACKNOWLEDGMENTS

We wish to express our appreciation to David C. Barham for his expert operation of the NMR spectrometer. We also wish to thank H. R. Shanks, P. H. Sidles, and G. C. Danielson at Iowa State University for providing us with the Na_xWO_3 samples.

APPENDIX I. SOME PROPERTIES OF TIGHT-BINDING WAVE FUNCTIONS IN Na_xWO_3

Consider a crystal with N unit cells. The position vectors of the tungsten sites are $\mathbf{r}_n$ and the origin of coordinates is taken at some tungsten site. The conduction band functions are based on the three tungsten $5d(t_{2g})$ functions $\phi_j(\mathbf{r})$:

$$\phi_{xy}(\mathbf{r})=(15/4\pi)^{\frac{1}{2}}(xy/r^2)f(r), \tag{1.1}$$

and similarly for ϕ_{yz} and ϕ_{zx}, where r is the distance from the tungsten nucleus and where $\int_0^\infty[f(r)]^2r^2dr=1$. $\phi_{xy}(\mathbf{r})$ has angular nodes on the planes $x=0$ and $y=0$. When the overlap integrals are limited to nearest neighbors, these functions do not combine in the Na_xWO_3 lattice. That is, if $U(\mathbf{r})$ is a function which has the periodicity of the lattice, the integral $\int\phi_{j'}(\mathbf{r}-\mathbf{r}_n)U(\mathbf{r})\phi_j(\mathbf{r})\,d\mathbf{r}$ vanishes unless $j'=j$ for $\mathbf{r}_n$ a vector connecting nearest-neighbor tungsten sites. Since the $5d(t_{2g})$ functions for different j do not mix, the Bloch functions can be formed for a given j independently of the others[22]:

$$\psi_{j\mathbf{k}}(\mathbf{r})=N^{-\frac{1}{2}}\sum_n e^{i\mathbf{k}\cdot\mathbf{r}_n}\phi_j(\mathbf{r}-\mathbf{r}_n), \tag{1.2}$$

where $\mathbf{k}$ is the wave vector which takes any allowed value in the first Brillouin zone $(-\pi/a<k_x, k_y, k_z\leq\pi/a)$ and a is the lattice parameter. The functions (1.2) are nearly normalized; the departure from normality will be negligible in the following calculations.

The electron density at a particular sodium site (whose location is $\mathbf{s}$) is given by

$$\psi_{j\mathbf{k}}^*(\mathbf{s})\psi_{j\mathbf{k}}(\mathbf{s})=\phi_j(\mathbf{s})\sum_n\cos(\mathbf{k}\cdot\mathbf{r}_n)\phi_j(\mathbf{s}-\mathbf{r}_n). \tag{1.3}$$

This density is studied by limiting the sum over $\mathbf{r}_n$ to the eight tungsten sites which are nearest neighbors to the sodium at $\mathbf{s}$. The expression (1.3) then vanishes for $\mathbf{k}$ along the x, y, or z axes in k-space, and also for the eight equivalent points when $\mathbf{k}$ is at a zone corner.

An upper limit for the sodium Knight shift due to conduction electrons based on tungsten $5d(t_{2g})$ states can now be estimated by means of the equation[23]

$$\Delta H/H=(8\pi/3)(\chi_pM)\langle|\psi_F(0)|^2\rangle, \tag{1.4}$$

where χ_pM is the average electronic susceptibility per atom and $\langle|\psi_F(0)|^2\rangle$ is the probability density for electrons at the nucleus, averaged over electrons near the Fermi surface. The paramagnetic susceptibility can be

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calculated from the measured electronic specific heat.[7,8] For $x=0.89$, $(\chi_p M)$ is found to be 6.4×10^{-29} cm³/atom. The density of conduction electrons at the sodium nucleus can be estimated with the aid of (1.3). For this purpose the Hartree wave functions for atomic tungsten[24] have been used. For any of the $5d(t_{2g})$ functions located on a tungsten site, the density at the position of a nearest-neighbor sodium site is $\gamma^2=1.7\times 10^{-5}a_H^{-3}$, where $a_H=$ the Bohr radius. According to (1.3) (with the sum restricted to nearest neighbors), the maximum electron density contributed by a single state is $8\gamma^2$. An upper limit on the electron density at the sodium nucleus is then obtained by taking $8\gamma^2$ for the contribution by every conduction electron which contributes to the average $\langle|\psi_F(0)|^2\rangle$. For $x=0.89$, (1.4) then gives $\Delta H/H=5\times 10^{-7}$. This upper limit decreases with decreasing x, since the electronic susceptibility decreases with decreasing x.

APPENDIX II. SODIUM SPIN-LATTICE RELAXATION BY SODIUM 3*p* ELECTRONS

Nuclear spin-lattice relaxation by conduction electrons has been discussed by Korringa.[20] Following Korringa's method, T_1 for sodium nuclei in $\mathrm{Na}_x\mathrm{W0}_3$, due to dipolar interactions with p-type conduction electrons, can be estimated. For this purpose a tight-binding band is constructed of the three sodium $3p$ functions $\theta_l(\mathbf{r})$ ($l=x$, y, or z):

$$\theta_x(\mathbf{r})=\hat{x}g(r), \tag{2.1}$$

and similarly for $\theta_y(r)$ and $\theta_z(r)$, where $\hat{x}$ is a unit vector in the x-direction. When overlap integrals are limited to nearest neighbors, the three $3p$ functions do not mix for the simple cubic array of sodium sites in $\mathrm{Na}_x\mathrm{W0}_3$.[25] The Bloch functions are again linear combinations of functions of the type (2.1) located at each of the sodium sites in the crystal. However, since the dipolar interaction of a given sodium nucleus with the conduction electrons depends mainly on the electronic wave function near the nucleus, it is a good approximation to neglect all the terms in the Bloch function except the function located on the sodium site under consideration. The slight departure from normality of the Bloch function will also be neglected. The Bloch function for the state with wave vector $\mathbf{k}$ then becomes, in the region near the sodium site located at $\mathbf{s}_n$,

$$\psi_{x\mathbf{k}}(\mathbf{r}-\mathbf{s}_n)=N^{-\frac{1}{2}}e^{i\mathbf{k}\cdot\mathbf{s}_n}\hat{x}g(r), \tag{2.2}$$

and similarly for $\psi_{y\mathbf{k}}$ and $\psi_{z\mathbf{k}}$.

If a spin temperature can be defined for the system of sodium nuclei, which is true to a good approximation for the present case, a relaxation time can be calculated. Three independent processes contribute to the relaxation, corresponding to interactions of the nuclei with the three independent p bands. Thus[20]

$$\begin{aligned}1/T_1=&(4\pi KT/\hbar)v^2[\tfrac{1}{3}N(\zeta)]^2g^2\mu_0{}^4[\tfrac{3}{5}\langle r^{-3}\rangle_\theta]^2\\ &\sum_{l=1}^{3}\{(17/90)\langle 3|\boldsymbol{\alpha}_{l\mathbf{k}}|^2|\boldsymbol{\alpha}_{l\mathbf{k}'}|^2+|\boldsymbol{\alpha}_{l\mathbf{k}}\cdot\boldsymbol{\alpha}_{l\mathbf{k}'}|^2\rangle+(50/27)\\ &\times\langle|\boldsymbol{\alpha}_{l\mathbf{k}}|^2|\boldsymbol{\alpha}_{l\mathbf{k}'}|^2-|\boldsymbol{\alpha}_{l\mathbf{k}}\cdot\boldsymbol{\alpha}_{l\mathbf{k}'}|^2\rangle\},\end{aligned} \tag{2.3}$$

where K is Boltzmann's constant, T the absolute temperature, $2\pi\hbar$ is Planck's constant, v is the volume of a unit cell, $N(\zeta)$ is the density of electronic states per unit volume per unit energy evaluated at the Fermi energy, μ_0 is the Bohr magneton, g is the nuclear g factor expressed in Bohr units, $\langle r^{-3}\rangle_\theta$ is the average of r^{-3} over the atomic function (2.1), and where $\boldsymbol{\alpha}_{x\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{s}_n}\hat{x}$, and similarly for $\boldsymbol{\alpha}_{y\mathbf{k}}$ and $\boldsymbol{\alpha}_{z\mathbf{k}}$. Since the p bands are completely degenerate, $\frac{1}{3}N(\zeta)$ corresponds to the density of states at the Fermi energy for any one band. The indicated averages of the α vectors are over all values of $\mathbf{k}$ and $\mathbf{k}'$ over the Fermi surface. These averages are carried out by assuming that the Fermi surface is a sphere in k space.

The value of $\langle r^{-3}\rangle_\theta$ can be obtained approximately from the atomic spin-orbit interaction energy, which is given by[26]

$$H'=(1/2m^2c^2)(1/r)(\partial V/\partial r)\mathbf{l}\cdot\mathbf{s}. \tag{2.4}$$

As an approximation $V(r)$ can be taken to be $-Ze^2/r$. This leads to an expression for the fine-structure splitting of the sodium $3p$ term

$$\Delta E(^2P_{1/2}-{}^2P_{3/2})=(3Ze^2\hbar^2/4m^2c^2)\langle r^{-3}\rangle_\theta.$$

Within this approximation, a lower limit for $\langle r^{-3}\rangle_\theta$ (and hence an upper limit for T_1) is obtained by taking $Z=11$. With tabulated value[27] $\Delta E=17.2$ cm⁻¹, $\langle r^{-3}\rangle_\theta$ is found to be 1.20×10^{24} cm⁻³.

The density of electronic states was taken from the measured values[7] for $x=0.89$. T_1 was computed from (2.3) and was found to be 2.3 sec.

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[24] Millard F. Manning and Jacob Millman, Phys. Rev. **49**, 848 (1936).

[25] See reference 22.

[26] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 286.

[27] *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1.