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Transient Nuclear-Magnetic-Resonance Study of Phase Transitions in Metallic Sodium Tungsten Bronzes

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Measurements of line shape and spin-lattice relaxation of Na^{23} in Na_xWO_3 have been performed by pulse techniques in the temperature range 100–700 °K for three samples with $x = 0.517$, 0.72, 0.855. It has been observed that below a certain temperature the sodium nuclei experience a nonzero electric field gradient which cannot be ascribed to the presence of sodium vacancies. The temperature dependence of the Na^{23} quadrupole coupling constant, obtained from an elaboration of the free-precession data, shows that a phase transition from the high-temperature ideal perovskite structure to a distorted structure occurs. The observation of an anomalous rise in the spin-lattice relaxation rate indicates that the phase transition is driven by microscopic critical dynamics. The transition temperatures T_c depend upon the sodium content and were found to be $\simeq 390$ °K for $x=0.517$, 400 °K for $x=0.72$, and 425 °K for $x=0.855$. The transition occurs in a continous way: From the experimental results it cannot be decided whether it is of second order, with a departure from the Landau behavior close to T_c, or of first order with a transition temperature close to the critical temperature.

I. INTRODUCTION

Sodium tungsten bronzes, Na_xWO_3, are nonstoichiometric compounds that for $0.4 < x < 1.0$ are metallic and have perovskite structure: The tungsten atom lies at the center of the unit cell, the oxygen atoms lie at the face centers, and the sodium atoms are distributed randomly over the corner positions. The electronic properties of these compounds have been studied by several authors by means of magnetic susceptibility,[1] resistivity,[2] Hall-coefficient,[2] and specific-heat[3] measurements and also by nuclear magnetic resonance[4] and relaxation both at the Na^{23} and at the W^{183} site.[5,6] The measurements provide strong support for a model of the crystal where each sodium atom contributes one conduction electron to a tungsten 5*d* conduction band.

Some evidence exists in the literature that the sodium metatungstates are not exactly cubic at room temperature and below. Optical measurements[7] have demonstrated the presence of a birefringent phase over a wide temperature range. Neutron scattering[8] has confirmed that the oxygen atoms are slightly displaced with respect to the ideal perovskite structure. Furthermore, anomalies have been observed in the coefficient of thermal expansion[9] and of thermal conductivity.[10] All the above measurements suggest the possibility of the occurrence in these compounds of structural phase transitions.

Structural phase transitions in Na_xWO_3 would be of particular interest, since these crystals belong to the perovskite family which includes many ferroelectric materials, and one is then faced with the possibility that Na_xWO_3 are "ferroelectric metals." The aim of this paper is to establish the existence of phase transitions in Na_xWO_3 by nuclear-magnetic-resonance (NMR) techniques and to study their characteristics.

The previous NMR measurements[4-6] were performed in order to probe into the electronic properties of these metallic compounds; the continuous-wave measurements,[4] at room temperature, have shown that the Na^{23} Knight shift is very small and that no reliable information on the line shape and linewidth could be obtained because of the poor and easily saturating signal. The pulse measurements[5] have shown that the main contribution to the Na^{23} spin-lattice relaxation in the explored temperature range (4–300 °K) is due to the conduction electrons.

In this paper we report conclusive[11] results of the Na^{23} line shape and spin-lattice relaxation in three samples of Na_xWO_3 ($x = 0.517$, 0.72, 0.855) in the temperature range 100–700 °K. The study of the shape of the resonance spectrum was performed by pulse techniques which have been proved to be most suitable in the case of lines strongly broadened by quadrupole interaction.[12] The measurements of free precession (fp) and echo shape are presented in Sec. III, where it is shown that by an appropriate analysis of the data one can evaluate the quadrupole coupling constant at the different temperatures and demonstrate the existence of a structural phase transition.

In Sec. IV measurements of spin-lattice relaxation by pulse techniques are presented; these measurements were performed particularly in the neighborhood of the observed phase transition. In fact it has been recently[13,14] shown that the critical

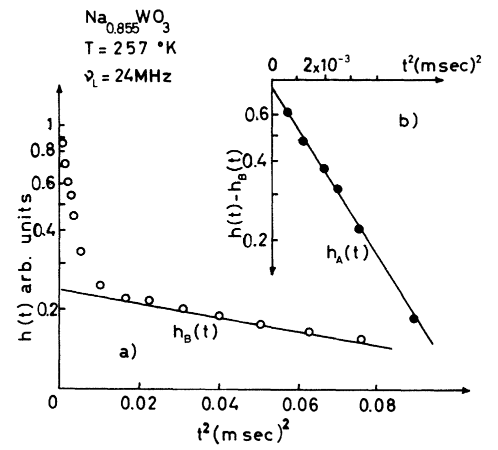

FIG. 1. (a) Semilogarithmic plot of the height $h(t)$ of the Na^{23} fp signal vs the square of the time elapsed after the end of the pulse. (b) Plot of the fp decay of the A component obtained by subtracting to the total fp height the height of the B component.

dynamics that drives the ferroelectric or purely structural transitions can be evidenced and studied through an anomalous contribution to the spin-lattice relaxation rate. The conclusions regarding the nature and the dynamics of the phase transition are discussed and summarized in Sec. V.

II. EXPERIMENTAL

The measurements were performed with a Brüker B-KR 306 pulse spectrometer operating at 24 MHz in phase-sensitive detection mode with a radio-frequency field H_1 of about 15 Oe. Some measurements were also performed at 8 MHz ($H_1 = 30$ Oe). The signals were recorded with the aid of a box-car integrator (PAR model CW. 1).

The temperature was varied with a standard nitrogen-flow system, with the exception of the high-temperature measurements that were performed with the rf coil built in a water-cooled furnace. The samples were prepared at the Ames Laboratory of the Atomic Energy Commission, by electrolytic reduction of a fused Na_2WO_4-WO_3 mixture as described by Shanks *et al.*[15] Because of the rf skin effect the measurements had to be performed in finely powdered samples. The particles obtained by grounding the single-crystal fragments were sieved through a 250-mesh sieve; the thin oxide layer was enough to ensure electric insulation of the particles and consequently the rf penetration.

III. fp DECAY

The Na^{23} fp decay obtained at low temperatures in all the three samples investigated can be decomposed in two Gaussian components as shown in Fig. 1. We write

$$h(t) = h_A \exp(-t^2/\tau_A^2) + h_B \exp(-t^2/\tau_B^2), \tag{1}$$

where A and B refer to the fast and slow decaying components, respectively. The "dephasing time" τ is related to the second moment M_2 of the corresponding Gaussian absorption line:

$$M_2 = (2\pi^2\tau^2)^{-1} . \tag{2}$$

The study of the fp decay as a function of the temperature shows that the second moment M_2^A decreases with the temperature while M_2^B remains constant.

At a certain temperature, which depends on the x value of the sample, M_2^A reaches the same value as M_2^B, and no further variations take place at higher temperatures.

The second moment M_2^A of the A component is

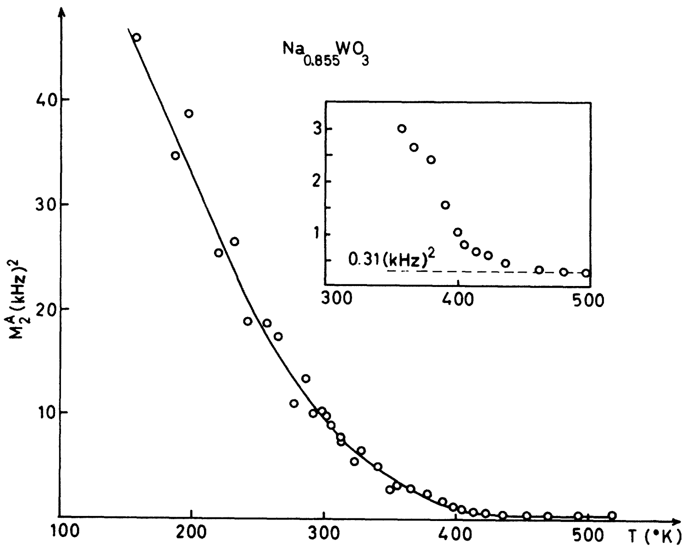

FIG. 2. Second moment of the A component of the Na^{23} signal as a function of temperature at 24 MHz. The enlarged portion of the figure shows that at high temperatures the second moment reaches the dipolar value.

TABLE I. Relative fraction of the B component in Na_xWO_3 evaluated from the extrapolated value of the Na^{23} fp at $t = 0$. The values in the first column yield the relative fraction of nuclei contributing to the B component in the assumption that only the central transition contributes to both the A and B signals; the second column refers to the case where to the B signal would contribute also the satellite transitions. The data listed in the second half of the table refer to Fromhold and Narath's measurements and will be discussed in Sec. III B.

x value (Our samples)	$\frac{h_B}{h_A + h_B}$	$\frac{h_B}{\frac{5}{2}h_A + h_B}$	x value (Ref. 5)	$\frac{h_B}{h_A + h_B}$
0.855	0.22	0.10	0.89	0.32
0.72	0.28	0.135	0.73	0.29
0.517	0.25	0.12	0.56	0.22

plotted in Fig. 2 as a function of temperature for the sample with $x = 0.855$. A similar behavior has been observed for the samples with $x = 0.517$ and 0.72. The relative weights of the A and B components were found to be constant, within the 10% estimated error, in the whole temperature range, and their mean values are given in Table I.

Before drawing any conclusion about the origin of the two components A and B let us consider separately the measurements of second moment at high temperature (where $M_2^A \simeq M_2^B$) and the temperature dependence of M_2^A.

A. High-Temperature Second Moment

Above 500 °K all three samples display a Gaussian fp decay with a single dephasing time. The ratios of the fp heights extrapolated at $t = 0$ for the different samples were found to correspond to the ratios of the number of sodium atoms present in the sample. The second moments of the absorption signal at 24 MHz are reported in Table II. The good agreement between experimental and theoretical values suggests that at high temperatures the resonance signal is broadened practically only by nuclear magnetic dipolar interaction. This conclusion is supported by high-temperature measurements performed at 8 MHz; the lack of variation of the second moment rules out the existence of second-order quadrupole broadening which depends on the reciprocal of the resonance frequency.

TABLE II. High-temperature experimental values $M_2^A \simeq M_2^B$ and theoretical values for the Na^{23} second moment in Na_xWO_3. The experimental values, evaluated from Eq. (2), have been corrected for magnetic field inhomogeneity. The theoretical values are the Van Vleck dipolar second moments.

x value	M_2(expt) (kHz^2)	M_2(theor) (kHz^2)
0.517	0.24 ± 0.05	0.22
0.72	0.29 ± 0.05	0.30
0.855	0.31 ± 0.03	0.34

TABLE III. Greatest component $V_{zz} \equiv eq$ of the axially symmetric efg tensor, quadrupole coupling constant e^2qQ/h, and second-order quadrupole splitting of the central line in powder $\Delta\nu_{\pm 1/2} = (25/192\,\nu_L)\,(e^2qQ/h)^2$ as calculated for different potentials associated to the sodium vacancy. The quadrupole moment of Na^{23} is $Q = 0.1 \times 10^{-24}$ cm^2 and the antishielding factor $(1 - \gamma_\infty) \simeq 5$. The quadrupole splitting was calculated for a resonance frequency $\nu_L = 24$ MHz.

Model	eq (10^{12} esu)	e^2qQ/h (kHz)	$\Delta\nu_{\pm 1/2}$(kHz)
Point charge	85	620	2.1
Thomas-Fermi screening	3.4	25	3.3×10^{-3}
Friedel screening	8.8	64	22×10^{-3}

The absence of second-order quadrupole effects is surprising in these cubic but nonstoichiometric compounds: One could infer *either* that the sodium vacancies diffuse fast enough to average out the electric field gradient (efg) *or* that the presence of the conduction electrons drastically reduces the efg associated to the sodium vacancies.

Measurements of sodium diffusivity in Na_xWO_3 show that the diffusion takes place at a measurable rate only at very high temperature. By extrapolating at 500 °K the temperature dependence of the diffusion constant D given by Smith and Danielson[16] one obtains $D \simeq 8 \times 10^{-25}$ cm^2/sec which corresponds to a jumping time of 6×10^6 sec which clearly cannot explain an averaging of the efg due to diffusion of the sodium vacancies.

The efg due to a sodium vacancy can be estimated approximately by treating the vacancy as an effective negative charge imbedded in a sea of conduction electrons. As shown in Table III the efg produced by a vacancy on a nearest-neighbor Na^{23} nucleus is quite different if it is assumed that the conduction electrons have a uniform distribution or if screening effects are taken into account. The Thomas-Fermi screening length, $\lambda^2 = 4\pi e^2 N(E_F)$, was calculated by using the experimental values[1,3] of the density of states at the Fermi level, $N(E_F)$. In the case of Friedel screening, the efg was calculated as indicated by Kohn and Vosko[17] using for the amplitude and phase of the oscillatory electron density the values obtained by Langer and Vosko[18] in first-order perturbation theory and using the electron density of the $x = 0.72$ sample.

Even though the efg calculated by using a single-screened impurity model can be only indicative in view of the high vacancy concentration, the tabulated data show that a nonuniform distribution of the conduction electrons strongly reduces the efg associated to the sodium vacancies. In view of the 5*d* character of the conduction band[19] the reduction of the efg due to a sodium vacancy should be considered in terms of a more complex redistribution of the electronic charge rather than in terms of simple screening effects in a uniform sea of conduction electrons.

As can be seen in Table III, the egf due to a screened impurity is large enough to produce first-order quadrupole effects; in fact the satellite transition is spread in a powder sample over a frequency range of the order of

$$\nu_Q = \tfrac{1}{2} e^2 qQ/h \;, \tag{3}$$

which, even for screened impurities, is larger than the dipolar linewidth. First-order quadrupole effects have been indeed detected experimentally; an echo characteristic of first-order quadrupole broadening[20] can be observed at high temperature. In agreement with the calculated values (Table III), the width of the echo is larger than 10 kHz, but no further information about the width of the satellite line distribution could be obtained.

B. Temperature Dependence of Quadrupole Interaction

Let us consider the temperature region where the fp decay can be decomposed in two components and analyze the temperature dependence of M_2^A (Fig. 2). The broadening of the *A* component is due to second-order quadrupole effects: In fact the corresponding fp signal can be refocused into an echo by a subsequent 180° pulse; moreover measurements performed at 8 MHz indicate that the dephasing time (evaluated from the width of the echo) is about three times smaller than at 24 MHz, in agreement with the frequency dependence of the second-order quadrupole interaction.

The theoretical shape of the fp decay of the central line in a powdered sample, in presence of second-order quadrupole broadening, is approximately Gaussian for the first part and is followed by beats. Experimentally, it was found that the decay is practically Gaussian but the beats were not detected probably because of the damping effect of the dipolar interaction and the small signal-to-noise ratio.

The dephasing time of the fp can be related to the quadrupole coupling constant by

$$\tau = f(\eta)\,\nu_L/\nu_Q^2 \;. \tag{4}$$

A numerical evaluation of the fp decays for different values of the asymmetry parameter η has given for $f(\eta)$ the approximate expression

$$f(\eta) = 0.25 + 0.8\exp(-\eta^2/0.26) \;.$$

Taking into account Eqs. (4) and (2) we can write, for small η:

$$e^2qQ/h \simeq 4\nu_L^{1/2}(M_2^*)^{1/4} \,, \tag{5}$$

where M_2^* is given by the experimental *A*-component second moment after subtracting the dipolar contribution. By using Eq. (5), for $\nu_L = 24$ MHz, one obtains the temperature dependence of the quadrupole coupling constant which is shown in Fig. 3(a).

The temperature dependence of the quadrupole coupling constant can be fitted by a $(T_0 - T)^{1/2}$ law with a critical temperature T_0 which depends upon the x value of the samples; the proportionality constant is practically the same for all the samples, as it appears from Fig. 3(b). From a least-squares fit of the experimental data one obtains for the critical temperature:

$x = 0.517, \quad T_0 = 401$ °K,

$x = 0.72, \quad T_0 = 408$ °K,

$x = 0.855, \quad T_0 = 446.5$ °K.

Our measurements can be reconciled with the earlier NMR measurements which, however, were not interpreted in the same way. Jones *et al.*[4] reported a Na^{23} resonance linewidth at room temperature of 1.11 Oe in $Na_{0.89}WO_3$. This value corresponds to a second moment of 0.345 kHz², in good agreement with the second moment M_2^B of the temperature-independent *B* component (see Table II). One can deduce that the above authors observed only the *B* component of the total line.[21] Fromhold and Narath[5] also have reported that the fp signal in several sodium tungsten bronzes reveals a fast and a slow decaying component. The slow decaying component has a dephasing time of the order of 200–300 μsec, in good agreement with the one observed by us; the fact that Fromhold and Narath's measurements were performed at 4 °K and 9 MHz confirms our observation that the *B* component is temperature and frequency independent. The fast decaying component gives a narrow echo having a dephasing time $\tau \simeq 40$ μsec. If one extrapolates our results at 4.2 °K and 9 MHz one obtains $\tau \simeq 9$ μsec. However, because of the low intensity of the rf field the width of the echo observed by Fromhold and Narath is probably not the true width but the spectral width of the pulse used which is indeed of the order of 40 μsec. This fact should explain also the slight discrepancy observed between Fromhold and Narath's data and ours regarding the relative percentage of the *A* and *B* components (Table I).

In concluding, since the sodium vacancies are not responsible for the strong quadrupole effects displayed by the *A* component, this component must then arise from sodium nuclei which experi-

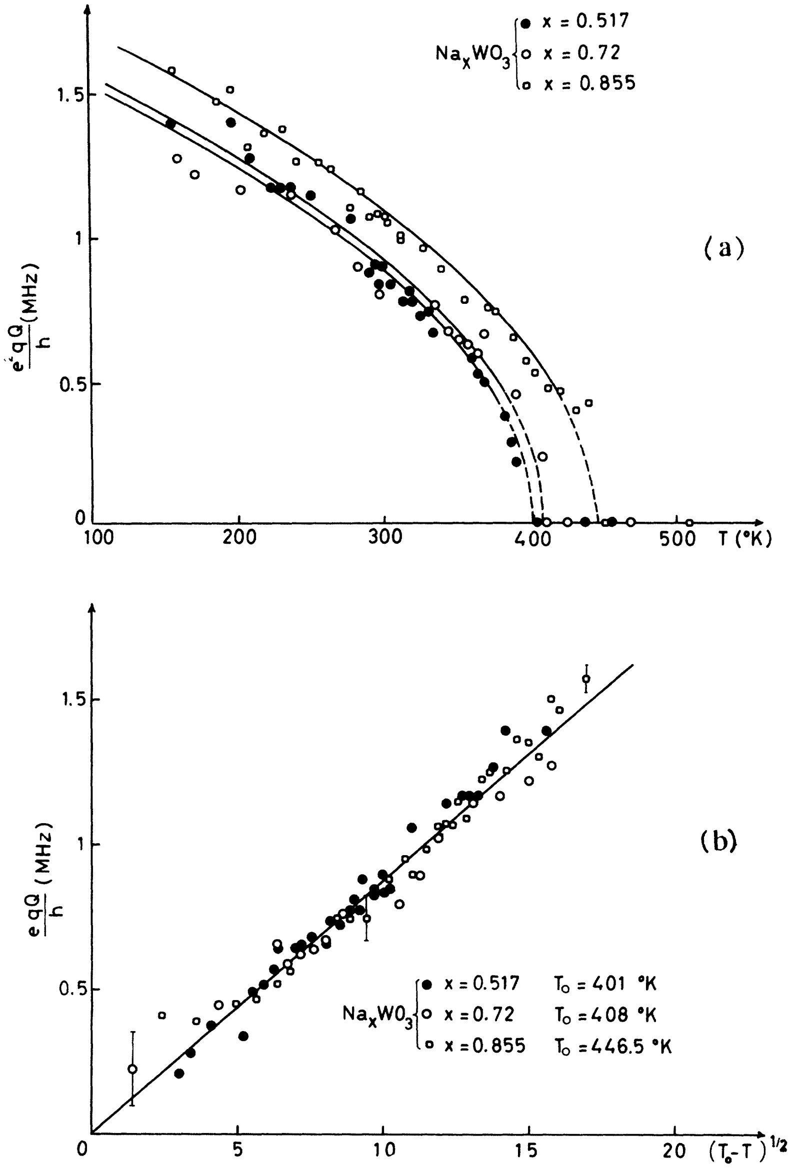

FIG. 3. Na^{23} quadrupole coupling constant for Na_xWO_3: (a) as a function of temperature, (b) as a function of $(T_0 - T)^{1/2}$. The solid lines represent best fits of the experimental data according to the law $e^2q\,Q/h = 0.0874 \times (T_0 - T)^{1/2}$ MHz. Some representative estimated errors are indicated in (b). The large error near T_0 is due to the fact that the quadrupole broadening becomes of the order of the dipolar linewidth.

ence an efg due to a noncubic crystal environment. Therefore a phase transition from the cubic high-temperature phase to a distorted structure must occur. Moreover, the presence of a B component which is not broadened could suggest that in the distorted structure there are also sodium sites which have a short-range environment with "quasi-cubic" symmetry. However, one cannot rule out the possibility that the two components arise from two different regions present in all samples with constant relative weight.

IV. SPIN-LATTICE RELAXATION

The spin-lattice relaxation rate was measured by testing with a 90° pulse the recovery of the nuclear magnetization $M(t)$ following the saturation obtained with a comb of about 100 pulses, each 10 μsec long. This comb should be adequate to saturate both central and satellite transitions at room temperature and above, while at low temperatures, where quadrupole effects are strongest, the saturation of the satellite transitions could be incomplete.

Because of the presence of the quadrupole interaction, the Zeeman levels are not equally spaced and therefore the recovery can be nonexponential. By considering a quadrupole contribution to the relaxation characterized by $\Delta m = 1, 2$ transition probabilities W_1 and W_2 and a magnetic contribution characterized by a $\Delta m = 1$ transition probability W_M one finds from the solution of the appropriate master equations that in the case of saturation of all lines the recovery of the central transition is of the form:

$$\frac{M(t)-M(\infty)}{M(\infty)} = -(1+a)e^{-\lambda^- t} + a e^{-\lambda^+ t}, \qquad (6)$$

while for saturation of the central component only one has

$$\frac{M(t)-M(\infty)}{M(\infty)} = -(b+\tfrac{1}{2})e^{-\lambda^- t} + (b-\tfrac{1}{2})e^{-\lambda^+ t}, \qquad (6')$$

where

$$\lambda^{\pm} = W_1 + W_2 + 7W_M \pm [(W_1 - W_2 + 3W_M)^2 + 16W_M^2]^{1/2}$$

and

$$a = \frac{4W_2 - 2W_1 + 2W_M - \lambda^-}{\lambda^- - \lambda^+}; \quad b = \frac{4W_M}{\lambda^+ - \lambda^-}.$$

Since the recovery $M(t)$ of the magnetization was found to be exponential for a long saturating comb, we can deduce from Eq. (6) that the quadrupole contribution is small or that $W_1 \simeq W_2$. Then we will speak in terms of a relaxation time T_1 where $1/T_1 \equiv 2W_M + 2W_{1,2}$. On the other hand, for a short saturating comb, which at low temperature should not saturate the satellite transitions, the recovery of the magnetization was found to be nonexponential in agreement with Eq. (6′).

The exponential recovery of the nuclear magnetization indicates also that the sodium nuclei contributing to the A and B components of the fp decay have practically the same relaxation rate; this fact is consistent with the hypothesis that the two low-temperature components of the signal arise from nuclei in nonequivalent sites rather than from the existence of two different regions of the sample.

The temperature behavior of the relaxation rate is shown in Fig. 4. There are three relaxation mechanisms that, in principle, can contribute to the Na^{23} relaxation rate in Na_xWO_3: relaxation by magnetic impurities, by conduction electrons, and by lattice vibrations. The low-temperature measurements by Fromhold and Narath[5] show that the contribution due to magnetic impurities is negligible and that there is, instead, a sizable contribution due to the conduction electrons via magnetic hyperfine interaction which follows the Korringa relation $T_1TK^2 = \text{const}$. Since we have found that the small Knight Shift K does not show any appreciable variation as a function of temperature, we can assume that the magnetic contribution goes as $1/T_1 \propto T$ over the whole temperature range.

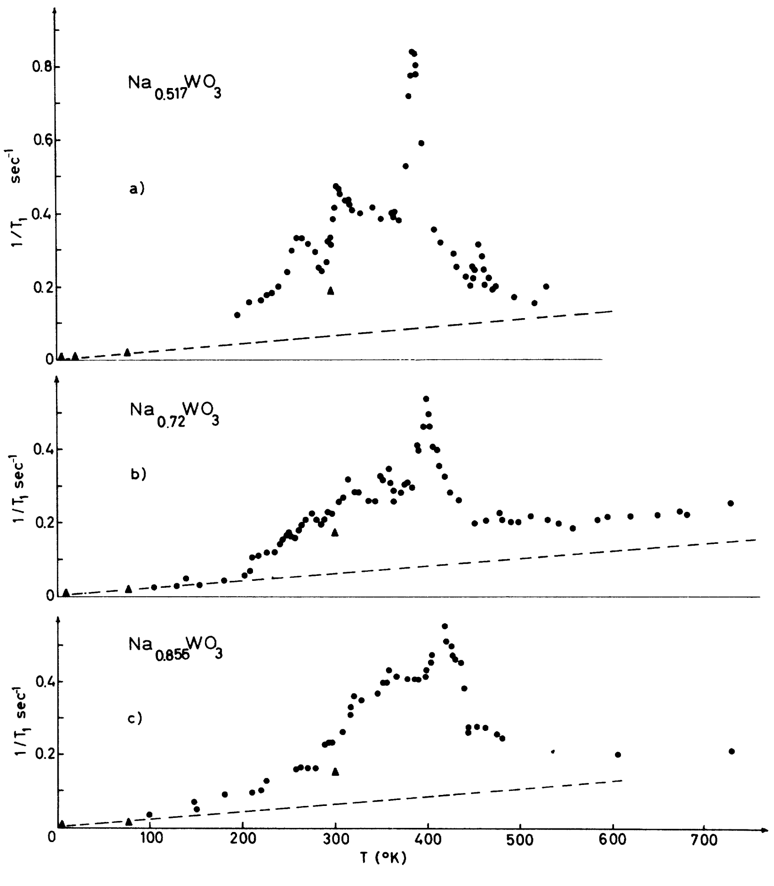

FIG. 4. Na^{23} relaxation rate at 24 MHz in Na_xWO_3 as a function of temperature. Measurements from Ref. 5 (solid triangle). Conduction-electron contribution to the relaxation according to the Korringa relation obtained by fitting the low-temperature data (dashed line).

The contribution to the relaxation rate due to the lattice phonon vibrations via quadrupole interaction should behave as $1/T_1 \propto T^2$, in the high-temperature region.[22] From the inspection of Figs. 4(b) and 4(c) it can be seen that the low-temperature measurements ($T < 200$ °K) can be matched to the high-temperature measurements ($T > 550$ °K) by assuming a magnetic contribution $T_1 T \simeq 4.5 \times 10^3$ sec °K (in agreement with the results of Ref. 5) and a quadrupole contribution $T_1 T^2 \simeq 6 \times 10^6$ sec °K^2.

Over the intermediate temperature range (200–550 °K) the behavior of the relaxation rate is very anomalous. In particular in the neighborhood of the critical temperature T_0 determined from the fp measurements (Sec. III) the relaxation rate shows a peak similar to those recently observed in the neighborhood of the ferroelectric transition temperature.[13,14] On the low-temperature side of the transition the relaxation rate presents additional small anomalies whose origin cannot yet be explained in a satisfactory way.

In the above cited works[13,14] it has been shown that in presence of a sufficiently strong coupling of the nuclear spin system with the "lattice" the relaxation rate is a parameter sensitive to the existence of the microscopic critical dynamics which drives the phase transitions and that a maximum in the relaxation rate occurs at the transition temperature T_c.

In the sodium tungsten bronzes the coupling of the nuclear spin system with the "lattice" should be the electric interaction of the Na^{23} nuclear quadrupole moment with the time-dependent efg associated to phonon vibrations (or to a more complex lattice dynamics). However, because of the presence of a sizable magnetic contribution to the relaxation, one cannot rule out the possibility that the critical slowing down and the associated enhancement of the fluctuations is felt by the nuclei through the magnetic hyperfine interaction with the conduction electrons.

The transition temperatures in Na_xWO_3 estimated from temperature behavior of the relaxation rate are

$x = 0.517$, $T_c \simeq 390$ °K,

$x = 0.72$, $T_c \simeq 400$ °K,

$x = 0.855$, $T_c \simeq 425$ °K.

V. CONCLUSIONS

The relevant result obtained by the present investigation is that in Na_xWO_3 a phase transition occurs from a cubic to a distorted structure and that the transition is accompanied by microscopic critical dynamics.

An attempt can be made to draw some conclusions about the structure of the low-temperature phase and about the nature and the dynamics of the transition. These conclusions will be mostly qualitative since the only data at present available regarding the transition are our NMR results and moreover these measurements were taken in powdered samples (no single-crystal experiment is possible in these conducting compounds).

The smooth temperature variation of the quadrupole coupling constant near the transition is indicative of a continuous (i.e., second-order or nearly second-order) phase transition. In this case the classical Landau approach or mean-field approximation, which is a good approximation far enough from the transition, predicts for the order parameter a temperature behavior of the form $\propto (T_0 - T)^{1/2}$.

The quadrupole coupling constant behaves over a wide temperature range as $(T_0 - T)^{1/2}$ (see Fig. 3), as it must if the efg is linear in the order parameter. However, for a small deformation of the ideal perovskite structure, like the one occurring in $BaTiO_3$ and $LaAlO_3$, one finds that the leading contribution to the efg at the Ba and La sites is quadratic in the order parameter. Therefore, in the assumption that also in Na_xWO_3 the leading term of the efg is the one related to the order parameter (at least near the transition), one has to conclude that the deformation of the cell in Na_xWO_3 must be more complex, like, for example, that occurring in some of the noncubic phases of $NaNbO_3$.[23] The complexity of the structure of the noncubic phase in Na_xWO_3 is supported by the observation of two nonequivalent sodium sites, similarly to what has been recently observed in the Na^{23} NMR spectrum in powdered $NaNbO_3$.[24]

Regarding the nature of the transition one has to point out that the temperatures T_0 obtained from the fp measurements are higher than the temperatures T_c obtained from the maximum of the relaxation rates. Since the transition temperature should be T_c, one could infer *either* that a small unobservable discontinuity occurs in the quadrupole coupling constant at T_c *or* that the Landau behavior of the order parameter changes into critical behavior close to T_c. In the first case it would mean that the phase transition is really a first-order transition even if close to a second-order one; in the second case the order parameter and therefore the quadrupole coupling constant should behave near T_c as $(T_c - T)^{1/3}$.[25]

Unfortunately both the above interpretations are consistent with the experimental behavior of the quadrupole coupling constant close to the transition in view of the rapid increase, in this region, of the error in the evaluation of this quantity from the fp signal.

Regarding the dynamics of the transition, the anomalous increase observed in the relaxation rate shows evidence of large fluctuations of the order parameter even quite far from the transition temperature. Recently we have shown that for ferroelectric phase transitions, in the mean-field approximation region and taking into account the anisotropy of the long-range dipolar forces, $1/T_1$ behaves as $\ln(T-T_0)$ in the assumption of a direct relaxation mechanism and of a critical dynamics described by a generalized damped soft mode.[13] In effect in Na_xWO_3 the anomalous contribution to the relaxation rate can be fitted above T_c by a logarithmic law with a critical temperature T_0 close to T_c. This fact would confirm the nearly second-order nature of the phase transition. However, since the sodium tungsten bronzes present particular complications, such as the nonstoichiometry and the metallic character, and since no clues are available regarding the nature of the interactions driving the phase transition, one cannot attach much meaning to the fitting of the anomalous relaxation rate by a logarithmic law.

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[1] J. D. Greiner, H. R. Shanks, and D. C. Wallace, J. Chem. Phys. 36, 772 (1962).

[2] W. R. Gardner and G. C. Danielson, Phys. Rev. 93, 46 (1954).

[3] R. W. Vest, M. Griffel, and J. F. Smith, J. Chem. Phys. 28, 293 (1958); B. G. Gerstein, A. K. Klein, and H. R. Shanks, J. Phys. Chem. Solids 25, 177 (1964).

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

[5] A. T. Fromhold, Jr., and A. Narath, Phys. Rev. 136, A487 (1964).

[6] A. T. Fromhold, Jr., and A. Narath, Phys. Rev. 152, 585 (1966).

[7] J. H. Ingold and R. C. De Vries, Acta Met. 6, 736 (1958).

[8] M. Atoji and R. E. Rundle, J. Chem. Phys. 32, 627 (1960).

[9] C. C. Rosen, B. Post, and E. Banks, Acta Cryst. 9, 447 (1956).

[10] H. R. Shanks and R. D. Redin, J. Phys. Chem. Solids 27, 75 (1966).

[11] Preliminary measurements suggesting the existence of a phase transition at a critical temperature dependent on the sodium content have been previously published: G. Bonera, F. Borsa, M. L. Crippa, and A. Rigamonti, in *Magnetic Resonance and Radiofrequency Spectroscopy*, edited by P. Averbuch (North-Holland, Amsterdam, 1969), p. 520; Proceedings of the Sixteenth Colloque AMPERE, Bucharest, September 1970 (unpublished).

[12] G. Bonera, A. Avogadro, and F. Borsa, Phys. Rev. 165, 391 (1968).

[13] A. Rigamonti, Phys. Rev. Letters 19, 436 (1967); G. Bonera, F. Borsa, and A. Rigamonti, Phys. Rev. B 2, 2784 (1970).

[14] R. Blinc, S. Zumer, and G. Lahajnar, Phys. Rev. B 1, 4456 (1970).

[15] H. R. Shanks, P. H. Sidles, and G. C. Danielson, Advan. Chem. Ser. 39, 237 (1963).

[16] J. F. Smith and G. C. Danielson, J. Chem. Phys. 22, 226 (1954).

[17] W. Kohn and S. H. Vosko, Phys. Rev. 119, 912 (1960).

[18] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids 12, 196 (1959).

[19] M. J. Sienko, J. Am. Chem. Soc. 81, 5556 (1959); A. Ferretti, D. B. Rogers, and J. B. Goodenough, J. Phys. Chem. Solids 26, 2007 (1965).

[20] G. Bonera and M. Galimberti, Solid State Commun. 4, 589 (1966).

[21] An investigation with a Varian wide-line spectrometer in the dispersion mode with high rf field intensities (see, for example, Ref. 12) has confirmed that the resonance signal is the superposition of a narrow component and an inhomogenously broadened component.

[22] J. Van Kranendonk, Physica 20, 781 (1954).

[23] I. Lefkowitz, K. Lukaszewicz, and H. D. Megaw, Acta Cryst. 20, 670 (1966).

[24] F. Wolf, D. Kline, and H. S. Story, J. Chem. Phys. 53, 3538 (1970).

[25] Critical behavior of the order parameter of this form has been recently observed by K. A. Müller and W. Berlinger [Phys. Rev. Letters 26, 13 (1971)] for the first time in purely structural (i. e., order-order) transitions.