

Nuclear spin–lattice relaxation in the metal-oxide system Na_xWO_3

E. L. Vavilova, I. A. Garifullin, N. N. Garif'yanov, V. Yu. Maramzin,
G. B. Teitel'baum, and G. G. Khaliullin

*Kazan Physicotechnical Institute, Kazan Science Center, Russian Academy of Sciences,
420029 Kazan, Russia*

(Submitted 5 August 1993; resubmitted 13 September 1993)

Pis'ma Zh. Eksp. Teor. Fiz. **58**, No. 8, 645–648 (25 October 1993)

A qualitative difference has been found between the temperature dependence of the rate of spin relaxation of sodium nuclei in a Na_xWO_3 sample with a superconducting composition ($x=0.2$) and that in a sample with a nonsuperconducting composition ($x=0.4$). The difference is attributed to antiferromagnetic correlations in the conduction band of the sample with a superconducting composition.

Research on the high- T_c superconducting systems has forced a reexamination of the properties of superconducting oxides synthesized previously, in particular, the sodium–tungsten bronzes. The old ideas (Ref. 1, for example), which had the superconductivity in these bronzes arising because of a lattice instability, ran into a contradiction with recent experimental data from ESR measurements² and measurements of the magnetic susceptibility.³ It was suggested in Refs. 2 and 3 that antiferromagnetic fluctuations play an important role in the onset of the superconductivity, as in high- T_c systems. It is thus natural to use NMR analysis to study this system. When applied to high- T_c systems, the NMR method has proved an exceedingly sensitive detector of magnetic fluctuations. Since the sodium ions in the lattice of this compound occupy two nonequivalent sites, with symmetric and asymmetric tungsten-ion surroundings, the existence of two types of relaxation would lead to an unambiguous conclusion about the nature of the magnetic correlations in the tungsten d -wave band. In this letter we are reporting preliminary results on the spin–lattice relaxation of ^{23}Na nuclei in Na_xWO_3 samples of superconducting composition ($x=0.2$) and of nonsuperconducting composition ($x=0.4$).

The test samples were prepared by a method of solid-phase synthesis⁴ in which sodium tungstate (Na_2WO_4), tungsten trioxide (WO_3), and a fine-grain powder of metallic tungsten are mixed and thoroughly reground. The resulting mixture is heated at $T=800^\circ\text{C}$ for 48 h in an inert atmosphere. A study of the resulting samples by x-ray diffraction revealed that they consist of a single phase, having a tetragonal structure with lattice constants $a=b=1.25$ nm and $c=0.4$ nm. Measurements of the superconducting transition temperature by an rf magnetic susceptibility method showed that the sample with $x=0.2$ has $T_c=2.5$ K, while the sample with $x=0.4$ shows no traces of superconductivity down to 1.3 K.

The spin–lattice relaxation rate was measured on a Bruker SXP-100 NMR spectrometer over the temperature range from 20 to 100 K at a frequency of 16.05 MHz. The test samples for the NMR measurements were powders fixed in paraffin. The

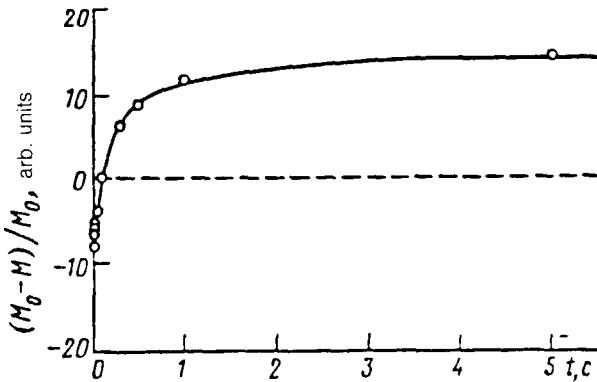


FIG. 1. Change in the height of the echo signal versus the time between pulses for the sample with $x=0.2$ at a temperature of 20 K. Solid line—The two-exponential law $(M_0 - M)/M_0 = 14.8 - 15 \times \exp(-t/0.15) - 7.5 \exp(-t/1.3)$. The time is in seconds.

average grain size was no greater than $50 \mu\text{m}$. The spin-lattice relaxation time was found by the stimulated-echo method and from restoration of the spin-echo signal after a train of three pulses, $180^\circ\text{-}90^\circ\text{-}180^\circ$.

Figure 1 shows the amplitude of the echo signal versus the time interval between pulses for the sample with $x=0.2$ at a temperature of 20 K. This behavior cannot be described by a single exponential function. On the other hand, the experimental results for both samples, at this and other temperatures, can be described satisfactorily by a superposition of two exponential functions, with very different times. The relative weights of the exponential functions with the short and long relaxation times are approximately 2:1.

Figure 2 shows the temperature dependence of the relaxation rates T_1^{-1} found through this decomposition for rapidly relaxing centers for samples with sodium concentrations $x=0.2$ and $x=0.4$. For a sample with $x=0.2$, the spin-lattice relax-

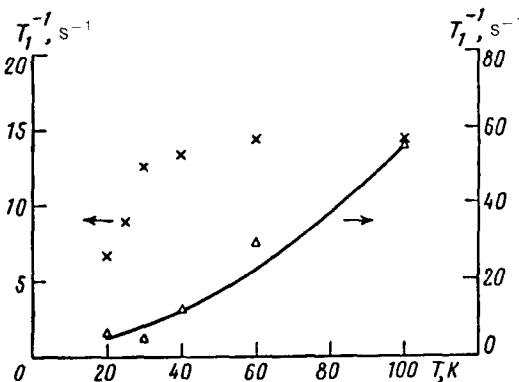


FIG. 2. Relaxation rate of fast-relaxing centers versus the temperature for samples with $x=0.2$ (crosses) and $x=0.4$ (triangles). The solid line was calculated with the model density of states in (1).

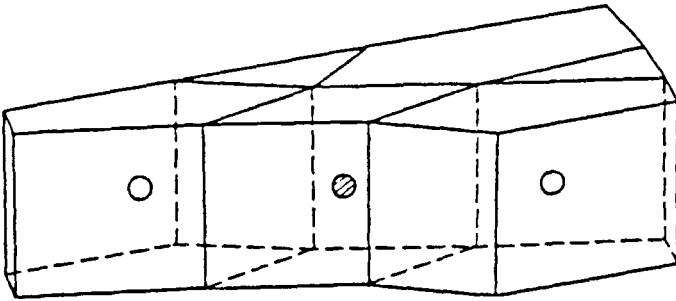


FIG. 3. Fragment of the structure of tetragonal sodium-tungsten bronze. The circles are sodium ions in pentagonal channels (open circles) and tetragonal channels (hatched circle). The vertices are occupied by tungsten ions. There are oxygen ions at the midpoints of all edges.

ation rate increases with the temperature in the interval from 20 to 40 K, and then remains essentially constant at higher temperatures. For the sample with $x=0.4$ we observe a monotonic increase in the relaxation rate T_1^{-1} above 25 K, up to the highest temperatures. The relaxation rate of the slow-relaxing centers turns out to be on the order of 1 s^{-1} for both samples. Measurements of the spin-spin relaxation time T_2 yielded values on the order of 1 ms.

In the crystal lattice of the tetragonal phase of the sodium-tungsten bonds, the sodium ions occupy two distinct crystallographic sites⁵ (Fig. 3). In the sites of the first type, the sodium ions are in pentagonal channels formed by oxygen, and they have asymmetric surroundings of tungsten ions. In the sites of the second type the sodium ions are in tetragonal oxygen channels and are surrounded symmetrically by tungsten ions. The ratio of the numbers of possible sites for sodium ions in the two channels is 2:1. This ratio and also the ratio of the relative weights of the exponential functions found through an analysis of the time evolution of the amplitude of the echo signal suggest that the short relaxation times are associated with nuclei in the pentagonal channel, and the long ones with nuclei in the tetragonal channel. The existence of two independently relaxing nuclear systems is apparently made possible by the fairly long relaxation times T_2 in this compound.

Spin fluctuations in the tungsten $5d$ band are probably the primary channel for spin-lattice relaxation. One might also suggest that fluctuations at neighboring ions are correlated in an antiferromagnetic fashion, because of $d-p$ hybridization effects. The comparatively long times $T_1 \sim 1 \text{ s}$ for the nuclei in the second site can then be explained easily in terms of a mutual cancellation of the $5d$ spin density penetrating into them from the symmetrically arranged tungsten ions. A similar cancellation does not occur for the nuclei in the first site, with the short relaxation times. The fact that the relaxation rate for these nuclei in the sample with $x=0.2$ reaches saturation even at temperatures on the order of 40 K (Fig. 2) implies that most of the spectral weight of the antiferromagnetic fluctuations in the sample with the superconducting composition is at low energies. Incidentally, the temperature dependence of the spin-lattice relaxation rate T_1^{-1} for the sample with $x=0.2$ is reminiscent of that for high- T_c

superconducting systems, e.g., at copper nuclei in a lanthanum–strontium ceramic.⁶ The temperature dependence of T_1^{-1} for the sample with $x=0.4$ also differs from the Korringa law (Fig. 2), although the discrepancy is not as pronounced as in the sample with $x=0.2$. The relaxation rate T_1^{-1} ($x=0.4$) continues to increase with the temperature up to 100 K. In principle, some deviation of the slope dT_1^{-1}/dT from a constant has been observed previously in metals, in particular, in systems with $A-15$ structure.⁷ This result has usually been attributed to the existence of a fine structure in the density of electron states near the Fermi level. The solid line in Fig. 2 shows results calculated on the Korringa relaxation rate with a model density of states with a local dip of width $2\Delta=300$ K near the Fermi level:

$$N(\epsilon) = \begin{cases} N_0, & |\epsilon| > \Delta, \\ N_0/2, & |\epsilon| < \Delta. \end{cases} \quad (1)$$

This calculation, of course, merely illustrates the point that the nonlinearity of $T_1^{-1}(T)$ in the sample with $x=0.4$ could in principle be caused by a variation of the density of states in an energy interval on the order of 0.03 eV. On the other hand, it is obvious that a corresponding fit of the results on $T_1^{-1}(T)$ in the superconducting sample, with $x=0.2$, would be completely devoid of meaning: In this case it would be necessary to assume unrealistic variations of the density of states in a very narrow energy interval, on the order of 10^{-3} eV, in order to describe the saturation of the relaxation rate at only 50 K. Accordingly, the anomalous $T_1^{-1}(T)$ behavior in the sample with $x=0.2$ is probably of a multiparticle correlation nature, as discussed above.

In summary, these results indicate that the Na_xWO_3 sample with the superconducting composition contains low-frequency spin fluctuations of an antiferromagnetic nature, which are apparently a characteristic attribute of oxide superconductors. In this sense, the sodium-tungsten bronzes can be classified as high- T_c superconductors. Since there is no local moment at the tungsten ions, the effective electron–electron repulsion responsible for the strengthening of the antiferromagnetic correlations in this system is apparently of intermediate magnitude in comparison with the gap width. Why the low-frequency spin fluctuations are amplified at a sodium concentration of specifically $x \sim 0.2$ remains an open question. A possible reason is a tendency of the current carriers to localize upon a decrease in the sodium content.⁸ In this case we would naturally expect a strengthening of electron–electron correlations.

¹H. R. Shanks, *Solid State Commun.* **15**, 753 (1974).

²I. A. Garifullin, N. N. Garif'yanov, V. Yu. Maramzin *et al.*, *JETP Lett.* **54**, 380 (1991).

³I. A. Garifullin, N. N. Garif'yanov, V. Yu. Maramzin *et al.*, *Solid State Commun.* **85**, 1001 (1993).

⁴T. A. Ramanarayanan and W. L. Worrell, *J. Electrochem. Soc. Solid State Technol.* **121**, 1530 (1974).

⁵A. Magneli, *Ark. Kem.* **1**, 213 (1949).

⁶Y. Kitaoka *et al.*, *Proc. of the 19-th Intern. Conf. on Low Temperature Physics* (Brighton, UK, 1990).

⁷M. Veger and I. Goldberg, *Solid State Physics* **28**, 2 (1973).

⁸N. F. Mott, *Philos. Mag.* **35**, 111 (1977).

Translated by D. Parsons