

Observation of antiferromagnetic correlations in the Na_xWO_3 system at a low carrier density

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The ESR of Gd^{3+} ions was studied in $\text{Na}_x\text{WO}_3:\text{Gd}$ samples. It was found that strong short-range exchange interactions arise between gadolinium impurities as the sodium concentration in the samples is reduced from $x = 0.90$ to $x = 0.25$. Possible reasons for the formation of exchange clusters are discussed.

The tungsten bronzes with the structural formula M_xWO_3 ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) have been the subject of active research for several decades now (Ref. 1, for example). Analysis of the results shows that the changes caused in the properties of these systems by a variation of the concentration of the alkali metal are strongly reminiscent of the

way in which the properties of metal oxides exhibiting a high- T_c superconductivity evolve as the dopant concentration is varied. One might therefore expect that research on the tungsten bronzes, as model systems, would shed some light on several properties of the high- T_c compounds. Our purpose in the present study was to learn about the evolution of the properties of one member of the family of tungsten bronzes, specifically, sodium-tungsten bronze, Na_xWO_3 , as the sodium concentration was varied.

In this letter we are reporting preliminary results of an ESR study of Na_xWO_3 samples in which $\sim 1\%$ of the sodium ions were replaced by gadolinium. The measurements were carried out on a Bruker BER-418⁸ rf spectrometer over the temperature range 4.2–100 K. The single-crystal samples were prepared by electrolysis of a molten mixture of Na_2WO_4 and WO_3 (Ref. 2). We studied three lots of samples, differing in sodium concentration. The samples with a high sodium concentration ($x \approx 0.9$ and $x \approx 0.5$) had a cubic faceting and were correspondingly yellow or dark red. The faceting of the dark blue samples with $x \approx 0.25$ corresponded to a tetragonal structure. The electrical resistivity of the samples at room temperature, $\rho(300 \text{ K})$, increased with the sodium concentration in the samples, having values of 15, 100, and 1000 $\mu\Omega \cdot \text{cm}$, respectively. The temperature dependence $\rho(T)$ in the samples with $x \approx 0.9$ and $x \approx 0.5$ was of a metallic nature. As the temperature was lowered from room temperature in the tetragonal samples, the resistivity ρ increased slightly to

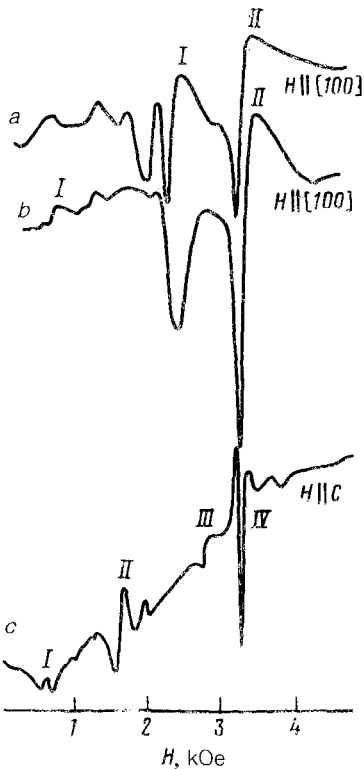


FIG. 1. ESR spectra of Gd^{3+} ions in Na_xWO_3 samples at a temperature of 4.2 K. *a*— $x \approx 0.9$; *b*— $x \approx 0.5$; *c*— $x \approx 0.25$. The curve labels specify the fine-structure component whose parameters are being analyzed.

$T \approx 100$ K, went through a rounded maximum, and then began to decrease.

Figure 1 shows recordings of the ESR spectra of the test samples at a frequency $\nu = 9400$ MHz for one orientation of the crystallographic axes of the crystal with respect to the direction of the external magnetic field. No ESR signal was observed in the samples without a gadolinium impurity.

The Gd^{3+} ion with a spin $S = 7/2$ is in the S state. Nevertheless, in a crystal field the Zeeman splitting for this ion is nonequidistant. The reason is that the ground-state wave function has an admixture of high-lying states with a nonzero orbital angular momentum. This nonequidistant arrangement gives rise to several lines, corresponding to transitions between different spin projections. A sort of "fine structure" arises in the ESR spectrum. We are evidently observing this fine structure in these test samples.

To analyze the temperature dependence of the spectrum, we selected fine-structure components far enough from other lines that mutual effects could be avoided. Figures 2 and 3 show the temperature dependence of the width ΔH and of the total intensity I of these components. Analysis of these results reveals the following.

$Na_{0.9}WO_3 \cdot Gd$. The width of the hyperfine-structure components increases roughly linearly with the temperature, with a slope $d(\Delta H)/dT \approx 2$ Oe/K. The total intensity of these lines, I , which is proportional to the magnetic susceptibility of the spin system responsible for the ESR signal, obeys a Curie law: $I \propto c/T$.

$Na_{0.5}WO_3 \cdot Gd$. The width of the lines does not change with the temperature,

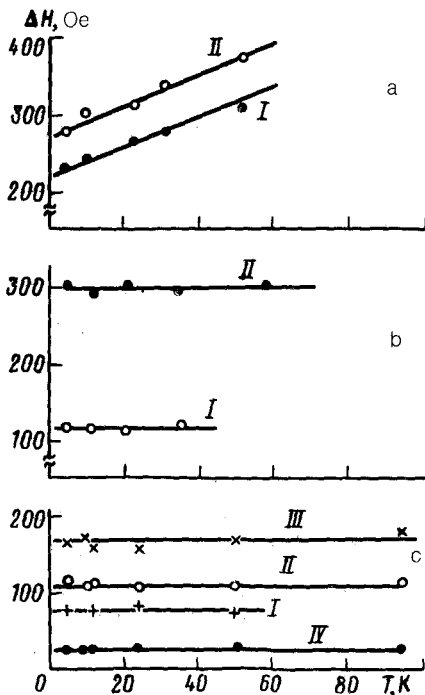


FIG. 2. Temperature dependence of the width of the fine-structure components marked on the spectra in Fig. 1. a— $x \approx 0.9$; b— $x \approx 0.5$; c— $x \approx 0.25$.

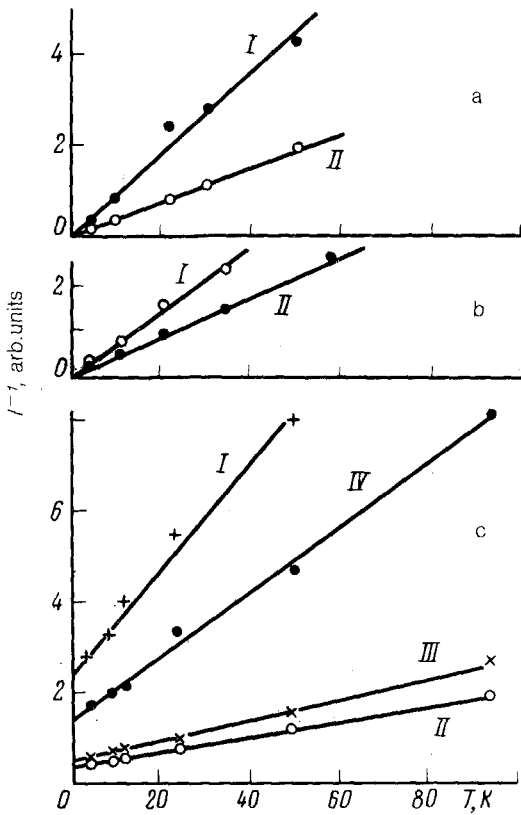


FIG. 3. Total intensity of the fine-structure components versus the temperature. The notation is the same as in Fig. 2. The scale for component I(\circ) in Fig. 3b has been reduced by a factor of 10.

within the experimental errors. The total intensity of the hyperfine-structure components obeys a Curie law, as in the yellow sample.

$\text{Na}_{0.25}\text{WO}_3:\text{Gd}$. No temperature dependence of ΔH is found. The samples of this composition have a distinctive feature: The total intensity of the hyperfine-structure components obeys a Curie-Weiss law $I \propto c/(T - \vartheta)$ with $\vartheta \simeq -20$ K.

Let us discuss these results briefly. We know that in metallic samples a major component of the ESR linewidth of localized magnetic moments is the Korringa component, which stems from thermal fluctuations of the exchange interactions between localized moments and conduction electrons:

$$\Delta H_{\text{corr}} = \frac{\pi}{g\mu_B} [J\rho(\epsilon_f)]^2 |k_B T.$$

Here J is the integral of the exchange interaction between the localized moments and the conduction electrons, while $\rho(\epsilon_f)$ is the density of states of the conduction electrons at the Fermi level. Since the current carriers in this system appear to be primarily of a d and p nature,³ we would expect the exchange interaction of the f electrons of Gd^{3+} with carriers to be slight. The comparatively small value of the Korringa slope in the sample with $x \simeq 0.9$ is therefore not surprising, nor is the decrease (or disappear-

ance) of this slope with increasing carrier density in the samples with a lower sodium content.

The most interesting aspect of these results is the sharp change in the behavior of the total intensity of the hyperfine components as we go from the metallic samples ($x \approx 0.9$ and $x \approx 0.5$) to the samples with $x \approx 0.25$, which are superconductors according to the data of Ref. 4. The Curie law observed in the samples with the high sodium content is evidence that the exchange interactions between Gd^{3+} ions are weak. In a tetragonal sample, in contrast, the $I(T)$ behavior clearly indicates a strong antiferromagnetic exchange between Gd^{3+} ions. On the other hand, the very fact that we observe a fine structure and the fact that there are no indications of the appearance of a magnetically ordered state at low temperatures in the ESR spectrum of the Gd^{3+} ions indicate that we are dealing with a short-range exchange, which does not extend to intermediate distances between the magnetic impurities.

One might suppose that the primary mechanism for exchange between Gd^{3+} ions in this system is an indirect interaction through hybridized d - p bands. The strengthening of this interaction with decreasing sodium content implies that a role is being played by a nonlocal spin susceptibility $\chi(q=0)$ of the d - p band. In view of the experimental fact that the homogeneous static susceptibility $\chi(q=0)$ decreases in this case,⁴ we conclude that some fairly strong antiferromagnetic correlations arise in the d band with decreasing dopant content. These correlations increase the spin susceptibility $\chi(q)$ at large wave vectors, $q \approx \pi a^{-1}$ (a is the lattice constant). This effect should strengthen the indirect exchange at the shortest distances between Gd^{3+} ions. The ESR method thus makes it possible to detect the appearance of strong antiferromagnetic correlations in the Na_xWO_3 d band at compositions corresponding to superconductivity. One might expect that detailed studies of samples with various sodium and gadolinium concentrations would make it possible to determine how the spin susceptibility $\chi(q)$ depends on the carrier density and the wave vector.

There appears to be an analogy with the properties of high- T_c superconducting systems. In the latter systems, antiferromagnetic spin correlations in the d - p band of the CuO_2 planes lead (on the one hand) to an indirect interaction between the spins of copper nuclei⁵ and (on the other) to an increase in the rate of their spin-lattice relaxation.⁶

In conclusion we should point out that the interpretation offered here is valid only if the gadolinium impurity is distributed randomly over the sample. We cannot completely rule out the possibility that in the tetragonal phase the gadolinium ions become distributed in a nonuniform way over the sample for some reason or other, forming small structural clusters.

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