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HYPERFINE STRUCTURE OF ELECTRON PARAMAGNETIC RESONANCE LINES IN SUPERCOOLED SOLUTIONS OF SALTS OF Ti^{+++}

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The hyperfine structure of the electron paramagnetic resonance lines in supercooled glycerine solutions of $Ti_2(SO_4)_3$, enriched in the isotopes Ti^{47} and Ti^{49}, is investigated at a frequency $\nu = 450$ Mc/sec and a temperature $T = 77°$ K. The nuclear spins obtained are $I = 5/2$ for Ti^{47} and $I = 7/2$ for Ti^{49}. The hyperfine splitting constants $|A|$ and $|B|$ are determined. The hyperfine structure of the electron paramagnetic resonance lines in liquid alcohol solutions of Ti^{49} are not resolved at a frequency of 9430 Mc/sec at $T = 295°$ K.

THE hyperfine structure (hfs) of the electron paramagnetic resonance (e.p.r.) lines of the odd, rare isotopes of titanium in solid solutions of its trivalent compounds has not been studied, due to the great width ΔH of the absorption curves.

In a previous work[1] we reported the existence of narrow symmetric e.p.r. lines in liquid alcohol solutions of Ti^{+++} salts in the frequency range 300 — 9460 Mc/sec. The absorption line is also narrow and symmetric in supercooled alcohol and glycerine solutions of Ti^{+++} at a temperature $T = 77°$ K at a frequency $\nu = 300$ Mc/sec, but becomes broad and asymmetric for $\nu = 9460$ Mc/sec, due to the considerable anisotropy of the g-factor. The g-factors were calculated from an analysis of the curves as: for a supercooled glycerine solution $g_{\|} = 1.99$, $g_{\perp} = 1.93$, and for alcohol $g_{\|} = 2.00$, $g_{\perp} = 1.90$.

We have studied the hfs of the e.p.r. lines in liquid and in supercooled solutions of $Ti_2(SO_4)_3$, enriched in the Ti^{47} and Ti^{49} isotopes to 43.3 and 71.5% respectively. In liquid alcohol and glycerine solutions of Ti^{+++} the measurements were made at $\nu = 9430$ Mc/sec and at $T = 295°$ K, and in supercooled glycerine solutions at frequencies of 450 — 270 Mc/sec and $T = 77°$ K. The concentrations of the solutions were ~ 0.05 mole/liter. The method of measurement has been described earlier[2,3].

As is well known, a double hfs is observed for the e.p.r. lines of supercooled solutions[4] and glasses[5] containing VO^{++} and Cu^{++} under strong field conditions, with hyperfine splitting constants: A for $g_{\|}$ and B for $g_{\perp}$, with $|A| > |B|$. This spectrum is described by a Hamiltonian with axial symmetry, dependent on the spin I, of the form

$$\mathcal{H} = g_{\|}\beta H_z S_z + g_{\perp}\beta (H_x S_x + H_y S_y) + A I_z S_z + B (I_x S_x + I_y S_y).$$

The greater the anisotropy of the g-factor, the stronger the hfs anisotropy. We would expect an analogous picture for the e.p.r. lines in supercooled Ti^{+++} solutions. If the g-factor is isotropic, as in supercooled Mn^{++} solutions,[4] then A = B and the hyperfine structure spectrum is described by an isotropic spin Hamiltonian.

RESULTS OF THE MEASUREMENTS

The hfs of the e.p.r. lines of supercooled glycerine solutions of $^{47}Ti^{+++}$ and $^{49}Ti^{+++}$ are not resolved at a frequency $\nu = 9430$ Mc/sec at 77° K, owing firstly to the large width of the absorption curves, and secondly to the small hyperfine splitting constant. As has been indicated above already, the e.p.r. line width at these frequencies in supercooled Ti^{+++} solutions is determined by the anisotropy of the g-factor. The further experiments were therefore carried out at frequencies 450 — 270 Mc/sec.

We were able to achieve resolution of the hfs of the e.p.r. lines for supercooled $^{47}Ti^{+++}$ and $^{49}Ti^{+++}$ solutions under high field conditions at $\nu = 450$ Mc/sec. Although further narrowing of the e.p.r. line is observed at lower frequencies, the strong field condition is destroyed, and at $\nu = 270$ Mc/sec the hfs for the intermediate field condition is observed.

At a frequency $\nu = 450$ Mc/sec at 77° K the hfs of the e.p.r. lines of supercooled glycerine solutions of $^{47}Ti^{+++}$ consist of five partially resolved peaks (see Fig. 1). We consider that these hfs

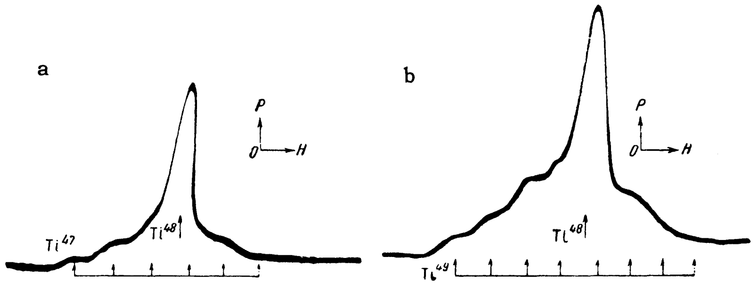

FIG. 1. The hyperfine structure of the e.p.r. lines of supercooled glycerine solution of $\text{Ti}_2(\text{SO}_4)_3$: a – isotope Ti^{47}, b – isotope Ti^{49} (ν = 450 Mc/sec, T = 77°K).

peaks belong to the e.p.r. line produced by the term with $g_{\parallel}$ and the constant A. The more intense e.p.r. line from $^{48}\text{Ti}^{+++}$ lies between the third and fourth hfs peaks. These peaks are therefore badly resolved. On the other hand, the e.p.r. line from $^{48}\text{Ti}^{+++}$ at the given frequency should lie practically in the center of the spectrum and the total number of hfs peaks from $^{47}\text{Ti}^{+++}$ should be six. The last, sixth, peak is not observed because of its great width.

As a result, the hfs spectrum of the e.p.r. line from the $^{47}\text{Ti}^{+++}$ ion is explained if the spin of the Ti^{47} isotope is given by the value $I = 5/2$. The hyperfine splitting constant A is of the order of 30 oe: it was determined from the resolved hfs peaks. Besides this hfs there is a second, unresolved, hfs of the line, determined by the terms with $g_{\perp}$ and the constant B. This unresolved hfs is superimposed on the e.p.r. line from Ti^{48}, so that the difference between the resonance values of the field H* for the lines corresponding to the factors $g_{\parallel}$ and $g_{\perp}$ amounts to less than 4 oe.

From a graphical analysis of the width of the combined curve, consisting of the unresolved hfs components and the e.p.r. line from $^{48}\text{Ti}^{+++}$, the value of $|B|$ was calculated as ~ 2 oe.

At a frequency $\nu = 450$ Mc/sec the hfs spectrum of the e.p.r. lines of supercooled glycerine solutions of $^{49}\text{Ti}^{+++}$ at T = 77° K has seven partially resolved peaks (see Fig. 1). The intense e.p.r. line from $^{48}\text{Ti}^{+++}$ lies between the fourth and fifth hfs peaks. In addition, the absorption line from $^{48}\text{Ti}^{+++}$ at this frequency should lie practically in the center of the hfs spectrum. The total number of peaks of the hfs spectrum of $^{49}\text{Ti}^{+++}$ for the line related to $g_{\parallel}$ should therefore equal eight. Due to the anisotropy of the hfs, the sixth and seventh peaks are broadened and merge into one broad peak, while the eighth peak is not observed at all. The spectrum of the e.p.r. line from $^{49}\text{Ti}^{+++}$ is thus produced by a nuclear spin of the isotope $^{49}\text{Ti}^{+++}$ equal to $I = 7/2$. $|A|$ is of the order of 30 oe.

The unresolved hfs lines, determined by the terms with $g_{\perp}$ in the Hamiltonian are superimposed on the absorption line of $^{48}\text{Ti}^{+++}$. A graphical analysis of this total curve gives $|B| = 2$ oe.

At a frequency $\nu = 9430$ Mc/sec at T = 295° K, the hfs of the e.p.r. line of an alcohol solution of $\text{Ti}_2(\text{SO}_4)_3$, enriched in the isotope Ti^{49}, is not resolved. The e.p.r. line consists of two parts, a broad base and a narrow peak.

The broad curve is produced as a result of the superposition of unresolved hfs peaks from $^{49}\text{Ti}^{+++}$, and the peak is from the e.p.r. line from $^{48}\text{Ti}^{+++}$. The hyperfine splitting constant was determined from a graphical analysis of the broad curve as $|a| \approx 12$ oe. As is well known, in liquid solutions an averaged hfs is observed with $|a| = (A+2B)/3$. Substituting the values of A and B determined for the hfs of the e.p.r. line in supercooled $^{49}\text{Ti}^{+++}$ solutions, we obtain $|a| \approx 11$ oe.

We did not study the hfs of the e.p.r. line of liquid alcohol solutions of $^{47}\text{Ti}^{+++}$, as Ti^{+++} in alcohol solutions rapidly oxidizes to Ti^{++++}.

DISCUSSION OF THE RESULTS

As was shown above, the hfs components of the e.p.r. lines of supercooled Ti^{+++} solutions, enriched in the Ti^{47} and Ti^{49} isotopes, are not fully resolved. The values of the nuclear spins, $I = 5/2$ for the isotope Ti^{47} and $I = 7/2$ for Ti^{49} were therefore obtained not by means of a simple count of the total number of hfs components, but only from the number of those components which lie in the resolved half of the spectrum.

The values obtained for the spins of the isotopes Ti^{47} and Ti^{49} can also be calculated from the ratio of the hyperfine splitting constants, since the nuclear magnetic moments for these isotopes were determined accurately by the method of nuclear paramagnetic resonance.[6]

We have thus been able by the e.p.r. method to confirm the values of the nuclear spins of Ti^{47} and Ti^{49} obtained earlier indirectly from measurements of nuclear paramagnetic resonance in these titanium isotopes.[6,7]

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