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Abstract

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Electron Paramagnetic Resonance in Nb^{4+}

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Electron paramagnetic resonance (EPR) was investigated in a low-temperature ethanolic glass containing the chloride of tetravalent niobium (columbium). $NbCl_4$ was obtained by reducing an ethanolic solution of $NbCl_5$ with zinc and hydrochloric acid. Upon complete reduction, trivalent $NbCl_3$ is formed from $NbCl_5$; the latter, as our experiments have shown, gives no measurable EPR line. This may be connected with a very short spin-lattice relaxation time or with an excessively large initial splitting of the lower spin triplet of the Nb^{3+} ion. Tetravalent niobium chloride arises upon incomplete reduction as a result of the reaction $NbCl_5 + NbCl_3 \rightleftarrows 2NbCl\_4, which does not proceed instantaneously. As a result, the intensity of the EPR effect due to NbCl\_4$ increases with time: after a day it is considerably greater than immediately after reduction. EPR measurements were carried out at a frequency of 9320 Mc/s at 77°K (Fig. 1). Under these conditions, in an ethanolic glass containing 0.1 mole/liter $NbCl_4$, a complex spectrum is observed, consisting of 16 resolved hyperfine-structure (h.f.s.) components, arising from the interaction of the unpaired $4d^1$ electron with the Nb^{93} nucleus (natural niobium contains only this isotope).

The spectrum can be described by the spin Hamiltonian

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

with the values $S = {}^1/2$; $I = {}^9/2$; $g_{\parallel} = 1.82$; $g_{\perp} = 1.80$; $A = 270 \pm 10$ oersted; $B = 146 \pm 10$ oersted.

An example of the recorded spectrum is given in Fig. 1.

In liquid ethanolic solutions of $NbCl_4$ an isotropic spectrum should be observed, consisting of 10 hyperfine components with an averaged h.f.s. constant

$$a = \frac{A + 2B}{3} \simeq 197 \text{ oersted}$$

and with an averaged g-factor;

Fig. 1

Figure 1: Fig. 1

$$g_{\text{eff}} = \frac{g_{\parallel} + 2g_{\perp}}{3} \simeq 1.81.$$

Owing to the very large width of the EPR lines in the liquid ethanolic solution of $NbCl_4$, we were able to observe only h.f.s. components corresponding to the values of the nuclear-spin projections $m = \pm^3/2; \pm^1/2$, with a constant $a \simeq 190$ oersted. Strictly speaking, the EPR data presented are the first for compounds of tetravalent niobium. It is true that in work (1), devoted to the investigation of EPR spectra in single crystals of rutile containing various impurities, information is given on the hyperfine structure of EPR lines due to Nb^{93} nuclei. However, the very small values of the hyperfine-structure constants $A_1 = 2.25$ oersted, $A_2 = 8.56$ oersted, and $A_3 = 1.92$ oersted, their very sharp anisotropy, as well as the considerable anisotropy of the g-factors ($g_1 = 1.948$, $g_2 = 1.981$, $g_3 = 1.973$), show that in this case one is dealing not with an ion in the usual sense, but with a donor $Nb^{5+} + e^-$. The almost two-orders-of-magnitude difference in the values of the h.f.s. constants of Nb^{93} in ethanolic glass and in rutile indicates that the donor

the electron is localized much farther from the Nb^{93} nucleus than the $4d^1$ electron in ordinary compounds of tetravalent niobium.

Let us turn to a discussion of the data we have obtained. In the Nb^{4+} ion, the cubic field of the octahedron formed by six solvent molecules splits the fivefold orbital level of the $4d^1$ electron into an upper doublet and a lower triplet. Fields of low symmetry cause a further splitting of the orbital triplet into a lower singlet and an upper doublet.

Fig. 1

To explain the relaxation mechanism in Nb^{4+} compounds, we may proceed from the theory proposed by Van Vleck for Ti^{3+} salts ([2]). As is known, in this case, according to Van Vleck, the spin-lattice relaxation $T_1 \sim \Delta^6$, where Δ is the splitting of the lower orbital triplet. It follows from our measurements that in ethanol glass at 77°K the spin-lattice relaxation time of Nb^{4+} is of the order of 10^{-8} sec. Therefore the splitting of the orbital triplet must be $\sim 10^3$ cm^{-1}. The values of the g-factors that we determined, far from the pure spin value 2.0023, do not contradict this estimate of Δ.

In liquid ethanolic solutions of niobium chloride, as was indicated above, the lines are so broad that only the lines with $m = \pm 3/2$ and $\pm 1/2$ can be observed with difficulty. Hence it follows that the spin-lattice relaxation time $T_1 \sim 10^{-9}$ sec., i.e., the value of Δ in liquid solutions of $NbCl_4$ is much smaller than in the glassy state. This has a simple explanation. The fields of low symmetry acting

on Nb^{4+} in ethanol glass arise both as a result of distortion of the octahedron itself in the first coordination sphere and owing to particles of the second coordination sphere. In liquid solutions, however, the low-symmetry fields of Nb^{4+} are due only to distortion of the octahedron through the Jahn–Teller effect, whereas the influence of the second coordination sphere is sharply weakened by the averaging action of the Brownian motion of the particles of the liquid.

The situation would be different if we were dealing not with the Nb^{4+} ion, but with the NbO^{2+} ion. Then, as in the case of VO^{2+} ([3]) and MoO^{3+} ([4]), we would observe narrow lines even in liquid solution at room temperature, since in vanadyl and its analogues the strong axial field is created by the bond with oxygen.

In conclusion, it should be noted that, despite the large value of I, the h.f.s. constants of the Nb^{4+} ion are very large in comparison with the observed

in ions of the $3d$ group. This is explained not only by the large nuclear magnetic moment of Nb^{93}, since it does not differ very greatly from the moment of V^{51}, but also by the fact that, in the palladium group, the admixture of the excited $5s$ state to the ground $4d$ state is more significant than the admixture of the $4s$ state for ions of the iron group ([5]).

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Note: Figure translations are in progress. See original paper for figures.