SOVIET PHYSICS JETP VOLUME 18, NUMBER 5 MAY, 1964

ON HYPERFINE INTERACTION IN Re (VI)

N. S. GARIF'YANOV

Physico-technical Institute, Kazan' Branch, Academy of Sciences U.S.S.R.

Submitted to JETP editor June 14, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) **45**, 1819-1821 (December, 1963)

The anisotropic hyperfine structure of EPR lines from nuclei of Re^{185} and Re^{187} in sulfuric acid and dioxane low temperature glasses containing $ReOCl_4$ is investigated at $\nu = 9320$ Mc and 77°K. An analysis of the hyperfine structure spectra yields the anisotropic hyperfine splitting constants ($A_{\parallel} = 480$ Oe, $A_{\perp} = 400$ Oe) and also the values $g_{\parallel} = 1.90$ and $g_{\perp} = 1.77$.

Low and Llewellyn[1] reported observation in single-crystal $K_2[PtCl_6]$ containing as an impurity tetravalent rhenium ($5d^3$, $S = 3/2$), at $T = 77°K$, of a six-component isotropic hyperfine structure of the EPR lines from Re^{185} and Re^{187}, with constant $A = 109 \pm 0.3$ Oe, and with a spectroscopic splitting factor $g = 2.050 \pm 0.005$. Griffiths et al have previously observed[2] at $T = 20°K$ in the same crystal, also containing Re^{4+}, six weak lines with $g = 1.8$. Finally, Ingram et al[3] observed a single asymmetrical EPR line with $g_{\parallel} = 2.00$ and $g_{\perp} = 1.95$ in an investigation of the hexavalent oxyanion of rhenium ReO_4^{-2} at 20°K.

In the present investigation we studied at $\nu = 9320$ Mc and 77°K the anisotropic hyperfine structure of the EPR lines in low-temperature glasses (supercooled solutions) containing 0.1 mole/liter hexavalent rhenium ($5d^1$, $S = 1/2$).

The low temperature glasses were obtained by rapidly cooling, in liquid nitrogen, solutions of rhenium oxychloride $ReOCl_4$ in concentrated sulfuric acid or in dioxane. A supercooled sulfuric-acid solution of $ReOCl_4$ displays a complicated EPR spectrum, consisting of two overlapping anisotropic hyperfine structures from the isotopes Re^{185} (37.07%) and Re^{187} (62.93%). The centers of these hyperfine structures correspond to values of lines with factors $g_{\parallel}$ and $g_{\perp}$. It must be noted that inasmuch as the nuclear magnetic moments of Re^{185} and Re^{187} are nearly equal ($\mu_{185} = 3.1714\,\mu_{nuc}$ and $\mu_{187} = 3.2039\,\mu_{nuc}$), and the spins are equal to $5/2$, the hyperfine components which have identical projections of the nuclear spin m_I coincide for these isotopes. In supercooled dioxane solution of $ReOCl_4$, like in acid glass, the EPR lines from Re^{185} and Re^{187} have a complicated hyperfine structure. As can be seen from the figure, in dioxane glass the hyperfine components are better resolved at lower intensities of the constant magnetic field H_0, while in acid glass they are better resolved at higher H_0.

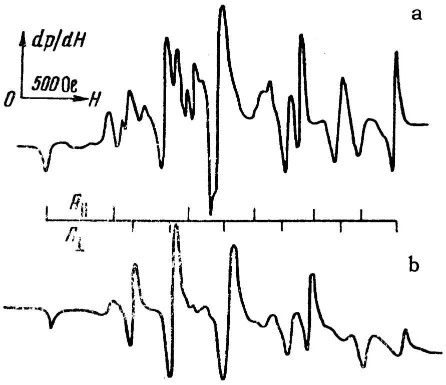
As is well known, the orbital energy levels of Re^{6+} ($5d^1$, $S = 1/2$) are similar to the levels of Ti^{3+} ($3d^1$ $S = 1/2$), that is, the ground state is ^2D. We assume that in low-temperature glasses the Re^{6+} ion is in an octahedral field with a strong axial component along the Re = 0 axis, and the observed spectrum is described by a spin Hamiltonian of the form

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

with $S = 1/2$, $I = 5/2$ for the Re^{185} and Re^{187} nuclei, $g_{\perp} = 1.77 \pm 0.01$, $g_{\parallel} = 1.90 \pm 1.01$, $A_{\perp} = 400 \pm 20$ Oe, and $A_{\parallel} = 480 \pm 20$ Oe. At room temperature the isotropic hfs of liquid solutions of $ReOCl_4$ is not resolved, owing to the short spin-lattice relaxation time.

In liquid solutions of Re(VI) there should be observed an isotropic hfs with average constant $A_{av} = 1/3\,|A_{\parallel}| + 2|A_{\perp}|$. Depending on the signs of $A_{\parallel}$ and $A_{\perp}$, A_{av} should equal either 426 or 106 Oe. As was shown earlier[4], in the case of an isotropic hfs, the value of the constant remains unchanged on going from the liquid to the solid state. In addition, the values of the constants A in liquid solutions change insignificantly when a paramagnetic ion[4] goes into a different valence state. Therefore, comparing the values of A_{av} with the value of the isotropic constant $A = 109 \pm 0.3$ Oe, determined by Low and Llewellyn for tetravalent rhenium, we find that the anisotropic constants $A_{\parallel}$ and $A_{\perp}$ have opposite signs.

Finally, it must be noted that we observe in the glasses only the EPR spectrum due to hexavalent rhenium, with an electron spin $S = 1/2$, since no EPR signal can be observed from the lower va-



Spectra of isotropic hfs EPR lines from Re^{185} and Re^{187} in low-temperature glasses containing 0.1 mole per liter of $ReOCl_4$ (ν = 9320 Mc, T = 77°K): a—sulfuric-acid glass, b—dioxane.

lence states of rhenium with $S > 1/2$, owing to the large line width resulting from the unresolved fine structure.

In conclusion, it can be deduced on the basis of many investigations[5-12] devoted to EPR in glasses containing ions of the iron group (n = 3: Ti^{3+}, VO^{2+}, Cr^{5+}, and Cu^{2+}), the palladium group (n = 4: Zr^{3+}, Nb^{4+}, Mo^{5+}, Ag^{2+}), and the platinum group (n = 5: W^{5+}, Re^{6+}), having a ^2D ground state, that with increasing principal quantum number n of the single d-electron in the unfilled shell of the transition-group ions, the hyperfine interaction with the nucleus, which is due in turn to the "S-configuration interaction,"[13] increases. At the same time, we observe in the series n = 3, 4, 5 a shortening in the spin-lattice relaxation time and an increase in the deviation of the g-factor from the pure spin value 2.0023. This is due to the increase in the spin-orbit coupling constant with increasing atomic number of the element.

---

[1] W. Low and P. M. Llewellyn, Phys. Rev. **110**, 842 (1958).

[2] Griffiths, Owen, and Ward, Proc. Roy. Soc. **A219**, 526 (1953).

[3] Corrington, Ingram, Schonland, and Symons, J. Chem. Soc. 4710 (1956).

[4] N. S. Garif'yanov, DAN SSSR **138**, 612 (1961).

[5] N. S. Garif'yanov and E. I. Semenova, JETP **41**, 337 (1961), Soviet Phys. JETP **14**, 243 (1962).

[6] N. S. Garif'yanov, DAN SSSR **103**, 1222 (1955).

[7] N. S. Garif'yanov, FTT **4**, 2450 (1962), Soviet Phys. Solid State **4**, 1795 (1963).

[8] N. S. Garif'yanov and R. S. Yafaev, JETP **43**, 1978 (1962), Soviet Phys. JETP **16**, 1392 (1963).

[9] Fedotov, Garif'yanov, and Kozyrev, DAN SSSR **145**, 1318 (1962).

[10] N. S. Garif'yanov and V. N. Fedotov, JETP **43**, 376 (1962), Soviet Phys. JETP **16**, 269 (1963).

[11] Garif'yanov, Kozyrev, and Semenova, DAN SSSR **147**, 365 (1962).

[12] N. S. Garif'yanov and V. N. Fedotov, FTT **4**, 3538 (1962), Soviet Phys. Solid State **4**, 2589 (1963).

[13] A. A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. **A05**, 135 (1951).

Translated by J. G. Adashko
288