SOVIET PHYSICS JETP VOLUME 17, NUMBER 3 SEPTEMBER, 1963

EPR SPECTRUM AND SPIN-LATTICE RELAXATION OF Cr^{3+} AND Fe^{3+} IN SINGLE CRYSTAL ZINC TUNGSTATE

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Submitted to JETP editor October 19, 1962; resubmitted November 19, 1962

J. Exptl. Theoret. Phys. (U.S.S.R.) **44**, 868–869 (March, 1963)

The EPR of Cr^{3+} and Fe^{3+} ions in $ZnWO_4$ single crystals has been investigated. The spin Hamiltonian parameters for Cr^{3+} have been determined. The spin-lattice relaxation times of Cr^{3+} and Fe^{3+} were determined at helium temperatures.

THE EPR spectra of Fe^{3+} in single crystals of $MgWO_4$, $CdWO_4$, and $ZnWO_4$ have recently been studied.[1,2] We have investigated the EPR of Cr^{3+} and Fe^{3+} in $ZnWO_4$. The single crystals were grown from solution in a flux. The crystallization derived from the oxides ZnO and WO_3, which were dissolved in a Na_2WO_4 flux in equimolar ratio. Small additions of chromium and iron oxides (Cr_2O_3 and Fe_2O_3) were made to the initial mixture. The crystallization took place at temperatures of about 1000 to 1200° C in platinum crucibles. The single crystals obtained were 3 × 3 × 5 mm in size. The chromium and iron ions enter the $ZnWO_4$ lattice isomorphically. Crystals having a concentration of about 0.1% Cr^{3+} were slightly transparent and had a rose color. At a concentration of about 0.3% Fe^{3+} the crystals were completely opaque and black in color. A goniometric investigation showed that the crystals belonged to the monoclinic system, symmetry class L_2PC. The two-fold axis L_2 coincides with the b axis. The symmetry plane P is a cleavage plane and passes through the a and c axes. The growth axis of the crystal lies in the plane P.

The EPR spectrum of chromium was observed in the temperature interval 300 to 1.6° K at frequencies of 9.4 to 45 Gc/sec. The observed spectrum fits the spin Hamiltonian

$$\hat{\mathscr{H}} = g\beta\mathbf{H}\hat{S} + D\left(\hat{S}_z^2 - \tfrac{1}{3}S(S+1)\right) + E\left(\hat{S}_x^2 - \hat{S}_y^2\right) \qquad (1)$$

with constants $D = +25.4 \pm 0.05$ Gc/sec, $E = 2.37 \pm 0.03$ Gc/sec, $g_z = 1.98 \pm 0.01$, $g_y = 1.97 \pm 0.01$, $g_x = 1.96 \pm 0.01$.

The sign of D was determined from the temperature dependence of the line intensities. The magnetic axis x coincides with the b axis, and the y and z axes lie in the cleavage plane with the y axis along the axis of growth.

The spin-lattice relaxation time T_1 was measured at the orientation $\mathbf{H} \parallel z$ by the pulse saturation method at 9.4 Gc/sec for the transition $M = +1/2 \longleftrightarrow -1/2$. At a chromium concentration of 0.1%, which corresponds to 1% by weight in the starting mixture, it was found that $T_1 = 1.1$ msec at 4.2° K and 5.3 msec at 1.6° K. These values of the spin-lattice relaxation time agree with the temperature dependence

$$T_1 = 1.15\left(\exp(\delta/kT) - 1\right)\cdot 10^{-3}\ \text{sec} \qquad (2)$$

with the parameter $\delta/k = 2.8°$ K, which corresponds to a splitting of 58 Gc/sec. This dependence can be explained by direct resonance processes if it is assumed that the relaxation directly between the investigated levels $M = \pm 1/2$ is forbidden and occurs via the upper level $M = 3/2$, which lies a distance δ from the level $M = 1/2$. From spectroscopic data, the splitting between the levels $M = 1/2$ and $M = 3/2$ equals 60.1 Gc/sec, i.e., close to 58 Gc/sec, which confirms the validity of the assumed relaxation mechanism.

Besides Cr^{3+}, the crystals obtained also contained the same amount of Fe^{3+} ions. The magnetic y axis of the Fe^{3+} ion coincides with the x axis for the Cr^{3+} ion, and the x and z axes lie in the ac plane. The angle between the z and c axes equals 47°, as in [2]. The spin-lattice relaxation time for Fe^{3+} was found to be markedly shorter than for Cr^{3+}. At 4.2° K, T_1, as measured by the pulse saturation method at 9.4 Gc/sec, was 75 μsec, which practically agrees with the dependence $T_1 \sim 1/T$ in this temperature interval.

Crystals containing a large amount of iron (~ 0.3%) were also investigated; these did not contain chromium. It was found that at 1.6° K $T_1 = 85 \pm 5\,\mu$sec. It also turned out that there were two unequivalent groups of iron ions in these crystals.

The y axes of the unequivalent ions were the same, and the x and z axes of one group corresponded respectively to the z′ and x′ axes of the other group. In mixed crystals containing Cr^{3+} and Fe^{3+} in small and approximately the same concentrations, the two unequivalent systems of Fe^{3+} ions were not found.

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Translated by L. M. Matarrese
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