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Studies of the Internal Fields Acting on Nuclei in Ferrimagnetic and Paramagnetic Solids, Using Recoil-Free Resonance Absorption (Mössbauer Effect)*

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Recoil-free gamma ray absorption spectra have been observed in ferrimagnetic and paramagnetic solids containing nuclei of Fe^{57} and Dy^{161}, using radioactive sources of Co^{57} and Tb^{161}. The hyperfine Zeeman splittings in ferrimagnetic materials permit a determination of the effective magnetic field (H_{eff}) at the nuclei. H_{eff} at Fe^{57} nuclei in yttrium iron garnet, dysprosium iron garnet and in some spinel ferrites have been measured at 300°K and 85°K. Measurements on Fe_3O_4 confirm Verwey's hypothesis of a fast exchange between ferrous and ferric ions in the octahedral sites above the transition temperature. H_{eff} at Dy^{161} in dysprosium iron garnet has been found to be 3.5×10^6 oe at 85°K and 7.5×10^5 oe at 300°K and is proportional to the Dy sub-lattice spontaneous magnetization. A large temperature dependent quadrupole interaction in DIG has been observed, which is ascribed to an effective electric field gradient at the Dy nuclei produced by the partially aligned orbitals of the $4f$ electrons, and thus correlated with the spontaneous magnetization.

The shape of the recoil-free absorption spectrum obtained in iron garnet absorbers has been investigated, using as a source, a Co^{57} source embedded in stainless steel. The results confirm the existence of two iron sub-lattices each showing a Zeeman structure characterized by different parameters. No significant differences have been detected between the Zeeman structure in yttrium iron garnet and dysprosium iron garnet. The values obtained for the effective magnetic field at the Fe^{57} unclei at room temperature are 3.90×10^5 oe and 4.85×10^5 oe for the "d" and "a" iron lattice sites respectively. At liquid air temperature the corresponding fields are 4.6×10^5 oe and 5.4×10^5 oe respectively. The mean value of the chemical shift for the "d" sites relative to stainless steel is about 0.04 ± 0.005 cm/sec and about 0.06 ± 0.005 cm/sec for the "a" sites.

A study has also been made of the internal fields acting on Fe^{57} nuclei in some spinel ferrites, with particular reference to the low temperature order-disorder transition in magnetite, using the techniques of Mössbauer absorption. For the Fe^{3+} ions at both the octahedral sites in nickel ferrite ($NiFe_2O_4$) at 300°K, γFe_2O_3 at 85°K and 300°K, and magnetite (Fe_3O_4) at 85°K, the effective magnetic field at the Fe^{57} nuclei is the same and equal to about 5.1×10^5 oe. In magnetite, the value of H_{eff} in the Fe^{2+} ions is about 4.5×10^5 oe at 85°K. Measurements on Fe_3O_4 at room temperatures provide a microscopic confirmation of Verwey's hypothesis that above the transition temperature in magnetite there is a fast exchange between the ferrous and ferric ions in the octahedral sites. The average value obtained for the chemical shift (relative to stainless steel) for the Fe^{3+} ions in the various cases investigated was about .045 cm/sec; the value for the Fe^{2+} ions in Fe_3O_4 at 85°K was about 0.115 cm/sec.

The hyperfine Zeeman splittings in the recoil-free absorption spectrum of the 26 kev γ-rays from Dy^{161m} ($\tau_{1/2}\sim3\times10^{-8}$ sec) in Dy^{161} situated in dysprosium iron garnet (DIG) have been observed. This is possible since in the rare earth iron garnets ($5Fe_2O_3\cdot3M_2O_3$) the sublattice of the rare earth ions below the Curie temperature (~560°K) shows a temperature dependent spontaneous magnetization. Nearly all the rare earth elements can be incorporated in iron garnets and since an appreciable recoil-free efficiency is expected at liquid air temperature for the γ transition from the first excited state of many rare

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earth nuclei, the method is of general application. Values for the effective magnetic field at the nucleus (H_{eff}) and the magnetic and quadrupole moments of the ground state and first excited state of Dy^{161} are derived. A strongly temperature dependent nuclear quadrupole interaction has been observed.

The recoil-free absorption spectrum of polycrystalline DIG, isotopically enriched in Dy^{161}, was measured using a source of 6.7 day Tb^{161} diffused into copper. At 85°K, the magnetic hyperfine interactions ($g\mu_n H_{eff}$) of the ground state and first excited state of Dy^{161} are (-400 ± 40)Mcs/sec and $(+455\pm40)$ Mcs/sec respectively. The electric quadrupole interactions ($eqQ/4$) at this temperature are (120 ± 30)Mcs/sec and (90 ± 30)Mcs/sec respectively. At 300°K H_{eff} is 4.6 times smaller, and illustrates the proportionality between H_{eff} and spontaneous magnetization of the dysprosium sublattice. Assuming Park's value of (-0.37 ± 0.05) nm for the Dy^{161} ground state magnetic moment, we obtain $H_{eff}(85°K)=3.5\times10^6$ oe, and $(+0.42\pm0.08)$ nm for the magnetic moment of the first excited state. At 300°K a relatively much smaller quadrupole interaction obtains (<20 Mcs/sec). The strongly temperature dependent quadrupole interaction is interpreted as being largely due to an effective electric field gradient (q_{eff}) produced at the nucleus by the $4f$ electrons which should be partially aligned below the Curie temperature. q_{eff} should have an axis of symmetry parallel to H_{eff}. A theory for this quadrupole interaction has been developed based on a modified Brillouin function, correlating q_{eff} with the spontaneous magnetization and H_{eff}.

Recoil-free absorption spectra have been measured in paramagnetic Dy_2O_3 over a temperature range from 85°K to 630°K. The spectra show definite structure at low temperatures, but the structure gradually disappears and the spectrum narrows with increasing temperature. The results can be interpreted in terms of temperature dependent quadrupole interactions and paramagnetic interactions. The possibility of short range ferrimagnetic order, however, cannot be excluded as an explanation of the structure at low temperatures.

References

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DISCUSSION

R. J. ELLIOTT: The crystalline electric field splitting of the energy levels will also give rise to a temperature dependent quadrupole splitting if the spin relaxation time is short. Such an effect has been observed by Mössbauer in rare earth salts. I wonder if it might not be important in your case.

S. G. COHEN: We have not taken into account the influence of the crystalline field on the quadrupole interaction because the Dy environment is nearly cubic and also since the Stark level splittings are small compared with kT, the temperature dependence would be rather small. Moreover, Hall, Bunbury and Boyle's recent measurement on antiferromagnetic Dy metal confirms the picture of a quadrupole interaction correlated with the spontaneous magnetization.