

PARAMAGNETIC RESONANCE

PROCEEDINGS OF THE FIRST INTERNATIONAL
CONFERENCE HELD IN JERUSALEM, JULY 16-20, 1962

Edited by

W. LOW

Department of Physics

The Hebrew University of Jerusalem, Israel

Volume II

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P R E F A C E

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This volume contains a collection of papers of the First International Conference on Paramagnetic Resonance held at the Hebrew University of Jerusalem, Israel on July 16-20, 1962. The conference was sponsored by the Hebrew University of Jerusalem, Israel, the International Union of Pure and Applied Physics, and the Israel Academy of Sciences and Humanities.

This conference summarized the advances which have taken place during the last 16 years since the discovery of electron spin resonance by Zavoisky. It also indicated the areas of major interests in this particular field. The topics in this conference were restricted essentially to solids. The major sections of these papers dealt with the electron spin resonance in the iron group and the rare earth groups, the theory related to these spectra, the effects of electric fields, pressure and temperature on these spectra. It discussed the advances in our knowledge of the relaxation phenomena which seem to be now reasonably well understood. Review papers on electron spin resonance in semi-conductors and in biological materials summarizes the results of the last few years in this field. Finally, there were a few selected papers on spin resonance of F centers, organic materials and in glasses.

About 180 scientists from 16 countries participated in this conference. The organizing committee wishes to express its gratitude to all the institutions which have generously assisted in making this conference possible. In addition to the three sponsoring bodies, valuable assistance has been extended by the Charles F. Kettering Foundation, the Office of Naval Research and the Israel National Council for Research and Development. We are also indebted to the National Science Foundation, the Royal Society and other national organizations for the travel support given to many of the scientists.

It is a pleasure to acknowledge the efforts of the Local Arrangements Committee, the Department of Physics of the Hebrew University, and in particular of Mrs. H. Lehrer in planning and running a smoothly conducted conference and in providing an interesting series of social events.

W. Low

Jerusalem, December, 1962

בעיה עיה-ק. ירושלים, תשכ"ג

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**PARAMAGNETIC RELAXATION
LINE WIDTH AND EXCHANGE PHENOMENA**

A.

Spin-Lattice Relaxation in Some Rare Earth Salts*

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ABSTRACT

Measurements of the spin-lattice (i.e. spin-phonon) relaxation rate T_1^{-1} are described for the trivalent rare earth ions Ce, Nd, Pr and Sm in the double nitrate $[\text{La}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}]$ and for Ce and Nd in the ethyl sulfate $[\text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3\cdot 9\text{H}_2\text{O}]$ in the temperature range $1.4 \leq T \leq 5^\circ \text{K}$. The measurements are made by observing the transient recovery of the microwave paramagnetic resonance signal after a saturating pulse. The frequencies used are $\nu \approx 9.3 \text{ kMc/sec}$ and $\nu \approx 34 \text{ kMc/sec}$. By varying such parameters as the paramagnetic ion concentration, the isotopic abundance, the crystal size and orientation, and the pulse width, and by noting the shape of the recovery signal, we are able to establish that the observed relaxation rate corresponds in most cases to the true spin-lattice relaxation rate, except for instances of phonon heating, as discussed in the following paper.

We observe the direct process, $T_1^{-1} \propto T$; the Orbach process, $T_1^{-1} \propto e^{-\Delta/kT}$; and the Raman process $T_1^{-1} \propto T^7$ for non-Kramers doublets and $T_1^{-1} \propto T^9$ for Kramers doublets. Using Orbach's phenomenological approach, we make theoretical estimates of the relaxation rates and find, in most cases, surprisingly good agreement with the measurements. For example, for 1% Nd in the ethyl sulfate with $z \perp H$ at $\nu = 9.3 \text{ kMc/sec}$, we measure $T_1^{-1} = 1.7T + 3.6 \times 10^{-4}T^9 \text{ sec}^{-1}$, to be compared with the theoretical estimate $T_1^{-1} = 1.4T + 1.3 \times 10^{-4}T^9 \text{ sec}^{-1}$. The data, together with similar measurements by others, lead to the overall conclusion that spin-lattice relaxation in the rare earths at helium temperatures is reasonably well understood.

By observing the transient recovery of the microwave paramagnetic resonance signal following the application of a saturating pulse, we have measured the spin-lattice (i.e., spin-phonon) relaxation time T_1 for the trivalent rare earth ions Ce, Nd, Pr, and Sm in the double nitrate $[\text{La}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}]$, hereafter called LaMN] and for Ce and Nd in the ethyl sulfate $[\text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3\cdot 9\text{H}_2\text{O}]$, hereafter called LaES] in the temperature range $1.4 \leq T \leq 5.0^\circ \text{K}$. The measurements reported here were made using an X-band paramagnetic resonance spectrometer operating at a frequency $\nu \approx 9.5 \text{ kMc/sec}$.

Generally we measure the spin-lattice relaxation time T_1 vs. the temperature T , and, except for instances of phonon heating (discussed in the

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