and (3) the Si^{29} NMR lineshape is inhomogeneous and is determined by electron-nuclear dipole interactions between the electron and a surrounding uniform distribution of Si^{29} nuclei. In this picture a nuclear spin packet, shifted Δ_j from the center frequency, corresponds to nuclei in a particular shell at a distance $r_{ij} \sim [3\hbar\gamma_e\gamma_n(1-3\cos^2\theta)/4\Delta_j]^{1/3}$ from the ith electron where γ_e and γ_n are the gyromagnetic ratios of the electron and Si^{29}, respectively, and θ is the angle between r_{ij} and the external field. The computer calculations of the local fields produced by shells of nuclei which lie from 2.5 to 150 Å distant from the electron showed that the ratio H_{4i}/H_{1i} was periodic, with a period $1/\tau'$, as the carrier frequency of the applied rf pulses was changed. Presumably, the $1/p$ dependence of the width of the ENDOR response is determined by the Fourier transform of the rf pulse.

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OPTICALLY PUMPED AND MONITORED ELECTRON-NUCLEAR DOUBLE RESONANCE IN ALKALI HALIDES*

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We describe the technique and features of electron-nuclear double-resonance–style resonance measurements in alkali halide F centers using optical pumping and optical monitoring detection of the resonance. Greater sensitivity, ability to see low-field resonances, and greater simplicity in choosing desirable fields and frequencies are the main features of the technique.

This Letter describes the technique and features of optically pumped and optically monitored electron-nuclear double-resonance (ENDOR) experiments in F centers in KBr and KCl. In similarity to conventional ENDOR, two frequencies are applied to the center, one corresponding to electron spin transitions and the other to nuclear hyperfine transitions. In contrast to ENDOR, the change in the electron resonance is monitored not by microwave absorption but by circular dichroism of the sample, which is proportional to the ground-state polarization. The advantages of this method seem to be greater sensitivity in some cases, particularly in the ability to see good signal to noise in only slightly colored samples, and greater simplicity and flexibility in working at very much lower or higher frequencies. The enhancement of polarization by optical pumping also facilitates work at low fields. We suggest the acronym of "OP"-ENDOR or OPENDOR for this technique.

Many of the separate features of this work have already been studied. ENDOR measurements have been made on nearly all the alkali halides.[1-3] Magneto-optical experiments have been done on several F centers to demonstrate optical polarization and dichroism of the centers in response to applied magnetic fields and to stresses.[4-6] Nuclear polarization in solids through optical pumping has also been demonstrated, particularly in doped CaF_2.[7,8] Several methods of optical detection have been applied to EPR in solids.[8,9]

Our technique consists of applying two frequencies in the EPR and NMR ranges to a small sample contained in an optically accessible Dewar and observing the dichroism. Since all that is required is that the frequencies be applied with no necessity to observe rf or microwave absorption, the coil structure may be comparatively rudimentary with a low Q. Appropriate precautions are taken to avoid introducing harmonics of the nuclear transition frequencies.[10]

In one respect there is a fundamental difference between ENDOR and OPENDOR. In conventional ENDOR a "hole" is "burned" in an inhomogeneous line, and the application of a second frequency enhances the EPR signal. In OPENDOR the two frequencies have the same effect, but the dichorism monitors the entire electron line rather than the "burned" portion, and seems to further decrease the signal rather then enhancing it.

The optical apparatus is shown in Fig. 1. The optical phase modulator, which has been described elsewhere,[11,12] produces a monitoring beam whose polarization with respect to a magnetic field along the optical axis changes periodically from σ^+ to σ^- at a frequency of 50 kHz. This kind of modulator utilizes a piece of resonant fused quartz driven at 50 kHz by a matched piece of piezoelectric quartz in such a manner that birefringence is produced where the beam passes through the uniaxial stress at the antinodes of the standing wave. It has the advantage of eliminating varieties of noise present in spinning quarter-wave plates or other mechanical devices. Thus the noise limitation in these experiments comes from other sources: spin-polarization fluctuations due to pumping intensity variations in particular, and sample microphonics in general. When a circularly dichroic sample is placed in the beam, a signal proportional to the dichroism is detected in a phase-sensitive system, which is calibrated either by a circular analyzer or by the Boltzmann polarization of the sample itself. Typical pumping and monitoring levels are 3 mW and 30 μW, respectively; to maximize the flux at the sample, the pumping source is best filtered by interference filters rather than by a monochromator. The largest monitoring and pumping effects typically occur near the half-intensity points of the F-center absorption band.

The samples of Harshaw KCl and KBr were cleaved at $10\times10\times\frac{1}{2}$ to 1 mm and irradiated at room temperature with 145-kV, 20-mA x rays (tungsten target) which were filtered by 0.005 in. of copper. Most measurements were made with samples of 0.25 to 1.0 o.d. at the center of the band at room temperature. Since the samples were lightly colored and since a spot only 1.5 mm in diameter was illuminated by the beams, the number of spins whose resonance was detected was lower than in the previously reported ENDOR measurements.[2,3] For example, the data reported here for KBr were obtained with 1×10^{14} spins; the noise level expressed in the conventional manner is 2×10^9 excess spins/G.

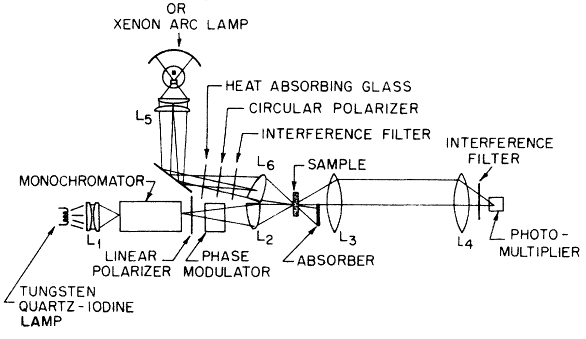

FIG. 1. Optics for a two-beam pumping and monitoring system.

Observations on the optically monitored thermal polarization and on the optically enhanced polarization, shown in Fig. 2, are in general agreement with the results of Karlev, Margerie, and Merle d'Aubigne.[4] Curves a and b show the dichroism signal as a function of magnetic field with continuous monitoring and no optical pumping. At fields greater than 75 G the relaxation time of the sample exceeds the relaxation time caused by the monitoring light, but curve c taken with intermittent monitoring light overcomes this difficulty and shows that a dichroism signal proportional to the field is indeed obtained. Curves d and e show the polarization produced by optically pumping with σ^+ and σ^- light with continuous monitoring. The size of the partial absorption coefficients deduced from the thermal polarization signal indicates that the maximum obtainable optically pumped electron polarization should be about 14%. The difference between the predicted and observed polarizations

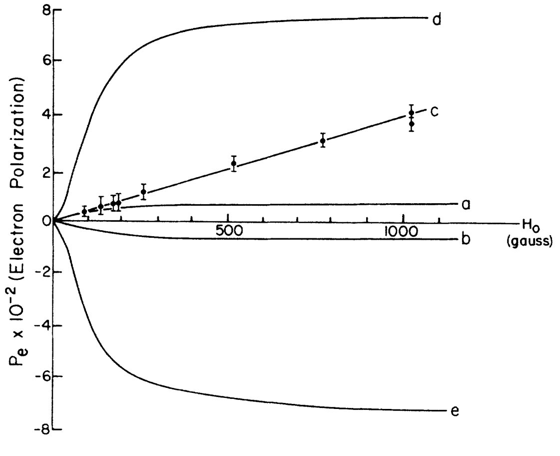

FIG. 2. Field dependence of Boltzmann polarization (a,b,c) and optically induced polarization (d,e). Noise is larger on curve c because of long-term (hours) drift in system sensitivity. Curves a, b, d, and e were recorded in several minutes. Number of spins monitored was 3×10^{14} at 1.7°K.

can be accounted for by the fact that the pumping beam was somewhat elliptically polarized due to imperfections in the Polaroid materials.

Because of the enhancement of polarization by optical pumping and because there is no requirement to make EPR absorption measurements as part of the technique, it is quite simple to carry out resonance in the low-field region where hyperfine decoupling analogous to the Bach-Goudsmit effect is not complete. The application of the EPR frequency results in a dip in the optical-pumping polarization curve centered at the resonant field for $g = 1.99 \pm 0.01$ with a full width at half-maximum which is consistent with that reported near 3000 G.[2]

The application of the nuclear transition frequency results in a further decrease in the polarization signal. Figure 3, scans *a* and *b*, shows the OPENDOR polarization signals which were obtained for KCl and KBr at 460 G when the rf field was swept through the range where ENDOR lines were predicted for the first and second shells. Lines were observed in the predicted positions; their unusual width can be accounted for by the fact that the local fields were comparable with the external field. Since the EPR halfwidths $H_{1/2}$ for KCl and KBr are 50 and 145 G, respectively, the resolution of the 460-G OPENDOR lines is better for KCl than for KBr. More specifically, in the coupled region the usual ENDOR analysis is inadequate; we have carried out computations similar to Deigen's[13] in which the transition-frequency spectrum is given by considering all possible spin couplings for each nuclear shell in a Breit-Rabi type of calculation. These calculations show that the decrease in resolution with decreasing $H_0/H_{1/2}$ may be ascribed to the curvature of the energy levels in the low-field region.

Figure 3, scan *c*, shows the polarization signal at 85 G which was observed with only a nuclear resonance field (no electron resonating field); this unique feature of OPENDOR appears only for H_0 comparable with or less than $H_{1/2}$. The theoretical analysis predicts a signal near 10 MHz from K_{I} and a signal extending from 10 to 25 MHz from Br_{II}. Therefore although the observed 10-MHz resonance could be attributed to K_{I}, the origin of the 20-MHz resonance is not clear. It may be due to "forbidden" transitions in which an electron and two nuclei flip simultaneously in the first shell, a process which was found to be important by Moran.[14] Since the calculated Br_{II} transitions with selected negative spin projections give a resonance spectrum exclusively in the 20-MHz region, it may also be possible that the OPENDOR technique as used here at low fields is sensitive to only a portion of the possible second-shell transitions.

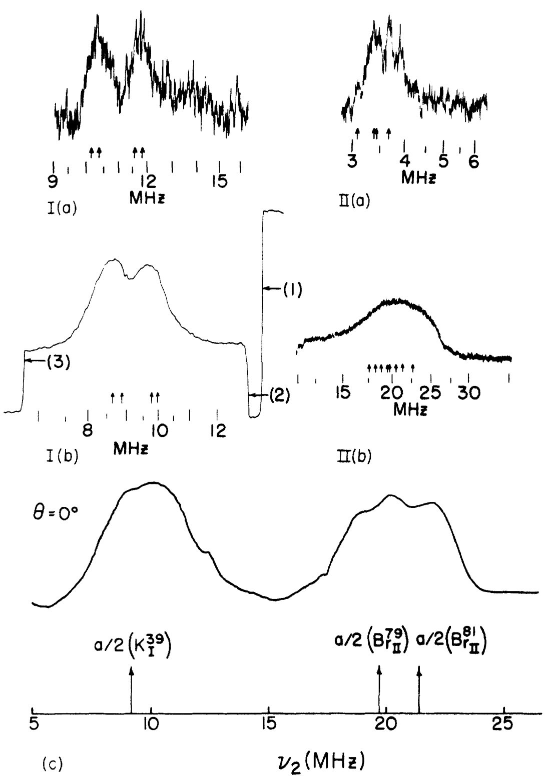

FIG. 3. Observed OPENDOR first- (I) and second-shell (II) resonances for KCl (a) and KBr (b) at 460 G. Arrows indicate predicted ENDOR lines using Eq. (2) of Ref. 1. In drawing I(b), looking from right to left, the arrow labeled (1) shows the effect of turning on the optical-pumping beam, (2) shows the effect of turning on the electron-resonating field, and (3) shows the effect of turning off the electron-resonating field. The nuclear-resonating field was on at constant strength from the 12- to the 7-MHz markers. Lock-in amplifier time constants were 3 sec for I(a) and II(a), 1 sec for I(b), and 0.01 sec for II(b). Scan (c) shows observed resonances in KBr at 85 G with no electron-resonating field. Arrows indicate $a/2$ for the first and second shells. Time constant was 1 sec. θ is the angle between H_0 and the [100] direction.

In addition to these low-field experiments, which are somewhat difficult to interpret, it should be pointed out that the greater sensitivity and flexibility of the optical-monitoring technique should aid in the study of double resonance at much higher fields where the resolution of the ENDOR lines is greater. For instance in the 50-

kG region, the construction of a paramagnetic resonance spectrometer at 140 GHz is difficult and expensive, but the application of this frequency by harmonic generation, with optical detection of the resonance by dichroism monitoring, is considerably simpler. It would also be interesting to study whether resonance modulation of the light will be present either in direct resonance of the F-center electron or in the hyperfine structure.[15,16]

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CHARGE-STATE POPULATIONS OF 5- TO 36-MeV CHANNELED OXYGEN AND CARBON IONS

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Equilibrium and nonequilibrium charge-state distributions have been obtained for high-energy ions emerging from crystals. In a major channeling direction in silicon, the slower ions and those incident in low charge states emerge nearly at equilibrium, with a mean charge close to that in a random direction. High-energy channeled oxygen 8^+ ions emerge far from equilibrium, indicating a capture cross section of less than 2×10^{-19} cm^2.

The fraction of particles in each state of ionization has been measured for beams of ions emerging from thin crystal foils in the direction of a major crystal axis at velocities near 10^9 cm/sec. Previous measurements have shown a decrease in the mean charge when a beam of 40-MeV iodine ions is aligned with a major axis.[1] The present results indicate a slight increase for C and O ions, together with an extremely small electron-capture cross section.

The apparatus used is the same as that for studies of electron-capture and -loss cross sections in collisions with gas atoms.[2] In brief, oxygen ions are accelerated in the 7-MV tandem Van de Graaff of the Niels Bohr Institute in Copenhagen and stripped to high charges in a thin carbon foil following the energy-analyzing magnet. Ions of a single charge are selected by a beam-switching magnet and are directed onto the thin crystal foil through a collimating system with a half-angle of acceptance 0.03°. The ions emerging from the foil pass through an aperture of half-angle ~0.1° at a scattering angle of 0 ± 0.02 and are then deflected in proportion to their charges by a third magnet. A position-sensitive detector[3] and a two-dimensional pulse-height analyzer are used to obtain the number N_i of ions in each charge state i. Peak-to-valley ratios are typically greater than 10^3, and 10^5 total counts are used, leading to a typical statistical error of 0.001 in an individual charge-state fraction Φ_i. No deadtime corrections are needed because a single electronic system is used to determine all N_i.