Wigner spin rule.

We wish to acknowledge the very capable assistance of F. D. Sinclair.

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DIRECT DISTORTION OF ELECTRONIC CLOUDS OF RARE-GAS ATOMS IN INTENSE ELECTRIC FIELDS

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Self-phase modulation originating from a direct distortion of the atomic electronic charge density has been observed in liquid argon and liquid and solid krypton.

Self-phase modulation (SPM) and small-scale filaments originating from a direct electronic distortion of rare-gas atoms have been observed in liquid argon and liquid and solid krypton. This experimentally demonstrates that significant changes in the atomic shape take place under the action of the radiation pressure from the intense electric fields of picosecond light pulses.

Self-phase modulation was first observed[1] in liquid CS_2 and attributed to the orientational Kerr effect of CS_2 molecules and later to a rocking mechanism.[2] Molecular electronic distortion[3] has been shown to lead to self-trapping in centrosymmetric molecules. Recently SPM was observed in crystals and glasses[4] due to either direct distortion of electronic clouds around nuclei or one of several coupled electronic mechanisms: librational distortion where electronic structure is distorted as the molecule rocks, electron-lattice distortion where the electron cloud distorts as the lattice vibrates, and molecular redistribution where electronic shells are altered as the nuclei redistribute spatially.

Rare-gas liquids are composed of atoms possessing spherical symmetry. Thus there are no orientational, librational, or electron-lattice contributions to the nonlinear refractive index coefficient n_2. Contributions to the nonlinear refractive index might be expected from electrostriction, molecular redistribution, and a direct distortion of the electron clouds. Electrostriction is ruled out because picosecond exciting pulses are too short. Molecular redistribution[5] arises from fluctuations in the local positional arrangement of molecules and can contribute significantly to n_2. However, we estimate[6] n_2 due to all mechanisms except electronic to be 1×10^{-14} esu for liquid argon from depolarized inelastic-scattering data.[7] Electronic distortion ($n_2 = 0.6 \times 10^{-13}$ esu) dominates all nonlinear index contributions. Furthermore, the depolarized inelastic light scattering wing vanishes in solid xenon,[8] implying that the molecular redistribution contribution to n_2 vanishes in rare-gas solids. Observation of self-focusing and SPM in rare-gas liquids and solids appears to provide a direct proof that atomic electronic shells are distorted from their spherical symmetry under the action of the applied field.

Experimentally a Nd glass mode-locked laser is used to generate picosecond light pulses which are then converted in a potassium dihydrogen phosphate crystal to second harmonic pulses at 5300 Å. Second harmonic pulses of power ~$(2.5$-$8) \times 10^8$ W are focused with a 25-cm focal length lens into 12-cm-long samples of argon and krypton. The beam intensity in the liquids is ~4×10^{11} W/cm^2 over a beam waist length of ~7 cm. The beam diameter is photographically measured to be 300 μm at the focal point and 400 μm at 3.5 cm to both sides from the focal distance. A collimated beam of diameter 1.1 mm could not pro-

duce SPM. Filaments are imaged onto a $\frac{3}{4}$-m Jarrell-Ash spectrograph where the spectra are recorded on Polaroid type 57 film. A glass beam splitter deflects a portion of the beam onto a camera where the filaments are simultaneously photographed.

Liquid argon is condensed from Linde research grade gas into an optical Dewar. Liquid krypton is condensed similarly, and solid krypton is grown by slowly lowering the temperature below the freezing point of krypton. All samples appear perfectly clear to the eye. No visible imperfections are observed in krypton solids. The solid is probably composed of large single crystals of size ~1 mm since the growth technique is similar to that of Bolz, Broida, and Peiser.[9]

Spectra showing frequency broadening and SPM from liquid argon and solid krypton are shown in Fig. 1. Sweeps of 1000-6000 cm^{-1} are observed to both the red and blue sides of 5300 Å in liquid argon. Similar spectral sweeps are observed in liquid and solid krypton. A most important point is that the threshold for observing SPM in liquid krypton is 0.64 ± 0.12 that of liquid argon; also the SPM threshold ratio of solid to liquid krypton is 0.86 ± 0.15. In liquid argon, SPM spectra appear at a threshold power of ~0.5 GW focused in a 12-cm sample. At threshold the SPM pulse train consists of a few pulses occurring prior to the most intense pulses in the laser train. This may be because pulses in the laser train broaden in frequency[10] and lengthen in time through the train.[11] Normally one to three small-scale filaments of 5-20 μm in diameter are observed. Sometimes filaments are accompanied by concentric rings progressively weaker in intensity[12] of typical diameters of ~200 and ~350 μm. No large change in shape of the laser pulse train appears upon passage through the sample as displayed on a 0.5-nsec resolution Tektronix 519 scope. The swept light is also collimated, polarized, and modulated. These observations rule out dielectric breakdown.

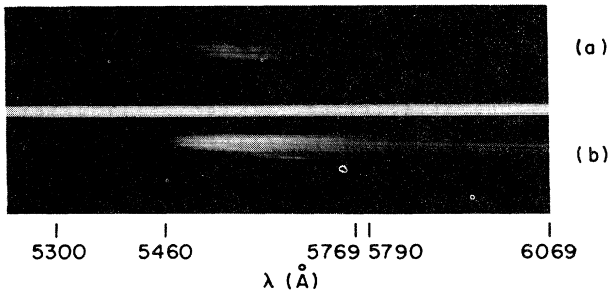

FIG. 1. Self-phase modulation on the Stokes side in (a) liquid argon and (b) solid krypton. Three Corning 3-67 filters absorb the laser light.

To explain these results the following argument is presented which estimates the nonlinear index n_2, self-trapping length, critical self-trapping power, and sweep length. For spherically symmetric atoms the induced dipole moment p may be expressed as a function of the local field E_L in the form[13]

$$p = \alpha_0 E_L + \tfrac{1}{6}\gamma E_L^3 + \cdots, \tag{1}$$

where α_0 is the polarizability and γ is known as the second order hyperpolarizability. The βE_L^2 term vanishes because of inversion symmetry of spherical atoms. The term γ represents electronic distortion which occurs only at intense electric fields. Taking a metallic sphere as a model for a spherical atom, the hyperpolarizability is given by[14]

$$\gamma = \left[\frac{4}{5}\alpha_0 \frac{(a-b)}{R} + \alpha_0 \frac{\Delta V}{V}\right] \frac{2}{E_L^2}, \tag{2}$$

where R is the radius of the undistorted atom, and a and b are the semiaxes of the deformed sphere. The terms in Eq. (2) arise from a change in polarizability due to a change of shape and of volume of the atom. Experimental values of γ are known for He, Ne, Ar, and Kr and are in close agreement with theoretical values.[13, 15, 16] The experimental values[16] of γ for liquid argon and liquid krypton are 5.9×10^{-37} and 14×10^{-37} esu, respectively.

The refractive index[5] in rare-gas liquids is given by $n_\parallel \equiv n_0 + n_2 \langle E^2 \rangle + \cdots$ where $n_\parallel$ is the refractive index parallel to the field, $\langle E^2 \rangle^{1/2}$ is the rms value of the electric field, and $\vec{E} = \frac{1}{2} E_0 \hat{e}_\parallel (e^{i\omega t} + \text{c.c.})$. The electronic nonlinear refractive index in rare gas liquids is given by[17]

$$n_2 = [(n_0^2 + 2)^4 / 81 n_0] \pi N \gamma, \tag{3}$$

where n_0 is the refractive index, and N is the number of atoms per unit volume. The term n_2 is $\simeq 0.6 \times 10^{-13}$ esu in liquid argon and $\simeq 1.36 \times 10^{-13}$ esu in liquid krypton. For liquid argon, liquid krypton, and solid krypton the refractive indices are taken as 1.23, 1.30, and 1.35, respectively.[18]

Intense electric fields distort atoms and produce a birefringence. The anisotropy in refractive index between light traveling with wave vector parallel and perpendicular to the applied electric field is given by[13]

$$\delta n_\parallel - \delta n_\perp = \tfrac{1}{3} n_2 E_0^2, \tag{4}$$

where $\delta n_{\parallel}$ and $\delta n_{\perp}$ are the changes in refractive indices parallel and perpendicular to the field and $\delta n_{\parallel} = 3\delta n_{\perp}$ for electronic processes in spherical atoms.[13,16] The value of this difference is $\sim 5 \times 10^{-5}$ liquid argon at $E_0 \sim 1.5 \times 10^7$ V/cm ($\sim 4 \times 10^{11}$ W/cm^2). This change in index can lead to self-trapping and, because of the high intensity in the filament, SPM.

The critical power for self-focusing[19] and the self-focusing length[20] are given by

$$P_{\mathrm{crit}} \geq (1.22\lambda)^2 c/64 n_2, \tag{5}$$

and

$$l = \frac{a}{2}\left[\frac{2n_0}{n_2}\right]^{1/2} \frac{1}{E_0}. \tag{6}$$

For liquid argon with a, the beam radius, taken to be 150 μm and E_0 as 1.5×10^7 V/cm, the values 3.3 MW and 10 mm are obtained for P_{crit} and l. The self-focusing length is less than the beam waist length in our experiment. This shows that hyperpolarizabilities are clearly large enough at mode-locked laser powers to observe self-focusing caused by the electronic distortion effect.

An estimate of the sweep length[21] $\delta\omega$ in liquid argon is given by

$$\delta\omega \simeq 2\Delta\omega n_2 k E_0^2 l \sim 3 \times 10^4 \ \mathrm{cm}^{-1}, \tag{7}$$

where $\Delta\omega$, the spectral width of the pulse, is taken as 100 cm^{-1}; l, the active sample length, is taken as the beam waist length of ~7 cm; and k, the propagation constant, is 1.46×10^5 cm^{-1}.

Since P_{crit} goes as γ^{-1}, Eq. (5) shows that the self-trapping threshold for liquid krypton should be lower than that of liquid argon. This is experimentally observed. Since self-trapping thresholds differ slightly in liquid and solid krypton, direct distortion and not molecular redistribution produce SPM. This result also provides a strong argument that electron-lattice distortion is apparently not playing much of a role in SPM from solid krypton. Rather, the reason that solid krypton has a slightly lower SPM threshold than liquid krypton can probably be attributed to its higher density (16%) and higher refractive index contribution (10%). The physical reason for γ in krypton being ~2.4 times larger than for argon is that the outer electron shell for rare-gas atoms is less tightly bound, and hence, more distortable as Z increases.

To summarize, SPM and self-focusing in liquid argon arise from the nonlinear refractive index of which the electronic contribution dominates.

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KNIGHT SHIFT AND ZERO-FIELD SPLITTING IN RHENIUM DETERMINED BY NUCLEAR ACOUSTIC RESONANCE

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Nuclear acoustic resonance signals have been observed in a single crystal of rhenium metal. From measurements of the resonance fields at different frequencies, values for the Knight shift and zero-field splitting at 4.2°K are obtained. The Knight shift, referred to aqueous $NaReO_4$, is found to be $(1.02 \pm 0.06)\%$. The zero-field splitting, $3e^2qQ/20h$, is found to be 40.6 ± 0.35 MHz for Re^{185} and 38.35 ± 0.2 MHz for Re^{187}.

Effects which arise from a noncubic lattice structure are most easily studied in a single crystal. In this Letter, we report the first observation of nuclear acoustic resonance (NAR) in a noncubic metal. We have observed NAR in a single crystal of rhenium, which has the hexagonal close-packed structure, and we have determined the Knight shift and zero-field splitting.

In a noncubic crystal, there is a static electric field gradient (EFG) at the nuclear position. This EFG interacts with the nuclear electric quadrupole moment, eQ, to produce a splitting of the nuclear levels in the absence of a magnetic field. If eQ and the EFG are significant, as in rhenium metal, this splitting may be quite large. Rhenium has two naturally abundant isotopes, Re^{185} and Re^{187}, with electric quadrupole moments of 2.9 and 2.7 b, respectively. For each isotope, $I = \frac{5}{2}$ and the Hamiltonian in the presence of a magnetic field is given by[1]

$$\mathcal{H} = h\nu_E[(3I_{z'}^2 - I^2) - y(1+K)I_z], \quad (1)$$

where the z' axis is parallel to the crystalline c axis and the z axis is oriented along the dc magnetic field, $\vec{H}_0$. In this expression, $h\nu_E$ is equal to $e^2qQ/4I(2I-1)$ and eq is the $z'z'$ component of the EFG tensor, K is the Knight shift, and y is equal to $\gamma H_0/2\pi\nu_E$, where γ is the nuclear gyromagnetic ratio. For rhenium metal, an average value of ν_E has been determined by calorimetric measurements,[2-4] but there has been no nuclear magnetic resonance measurement of K or ν_E. This is probably because of the severe line broadening caused by quadrupole effects in a powder, and the small rf skin depth in a single crystal. In an NAR experiment, however, the nuclear spins absorb energy from a sound wave propagating within a single crystal, and there is no rf skin depth problem. Therefore, NAR is an especially appropriate tool for the investigation of noncubic metals.

There are two reported NAR interaction mechanisms in metals. In aluminum metal,[5] the dominant coupling is between the oscillating magnetic field induced by the sound wave in the presence of a large magnetic field and the magnetic dipole moment of the nucleus. In tantalum metal,[6] the dominant coupling is between the oscillating EFG created by the sound wave and the electric quadrupole moment of the nucleus. We have calculated the acoustic absorption coefficient due to magnetic dipolar coupling and found it to be smaller than our noise level at the frequencies used in this experiment. The dominant interac-

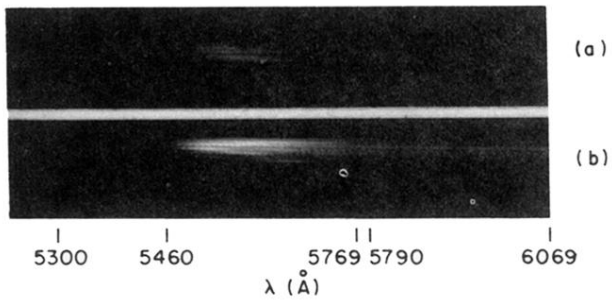

FIG. 1. Self-phase modulation on the Stokes side in (a) liquid argon and (b) solid krypton. Three Corning 3-67 filters absorb the laser light.