ter," and

$$\varphi(z)=\int_0^z \frac{y\,dy}{e^y-1}.$$

We can express Θ_M in terms of d. If the boundaries of the particles are rigidly fixed, they act as nodes and we would expect $\Theta_M = hc/2kd$. On the other hand, if the boundaries are free, Love[5] has shown that $\Theta_M = 3.66hc/2kd$. For microcrystals 60 Å in diameter, we would expect to find $\Theta_M = 7.8°K$ for spherical crystals with fixed boundaries and $\Theta_M = 28.7°K$ for spherical crystals whose boundaries are free. When the data are analyzed by a least-squares computer program, we find $\Theta_M = 23°K$. Likewise for microcrystals 200 Å in diameter we would expect to find $\Theta_M = 2.3°K$ for spherical crystals with fixed boundaries and $\Theta_M = 8.6°K$ for crystals with free boundaries, while the data yield $\Theta_M = 8°K$. These data indicate that the gold microcrystals embedded in gelatin are loosely bound to the gelatin, so that their surfaces are free, but since the recoil-free fraction is not a strong function of Θ_M at low temperatures, these values of Θ_M could be in error by as much as 25%. The experimentally determined values of Θ_D for the 200-Å and the 60-Å samples are 163 and 173°K, respectively.

The measurements described here are the results of three data runs on the same set of microcrystal absorbers. More extensive measurements of this type covering a wider range of crystal size as well as other crystalline materials are planned.

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ULTRAHIGH RESOLUTION $\Delta F = 0, \pm 1$ $(He^3)^+$ HFS SPECTRA BY AN ION-STORAGE COLLISION TECHNIQUE*

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We have studied the hfs spectra of ground-state $(He^3)^+$ ions contained in a quadrupole rf ion trap. Linewidths as narrow as 10 Hz have been obtained thus far, demonstrating the long phase-memory times of the internal precession realizable in our technique.

The hfs levels of $(He^3)^+$ in a magnetic field are split according to the Breit-Rabi formula [Fig. 1(a)] and the following transitions between the sublevels are possible:

$$a\text{: } 00 \leftrightarrow 11 \text{ at } \nu_a = \Delta\nu - \nu_z + \delta,$$

$$b\text{: } 00 \leftrightarrow 10 \text{ at } \nu_b = \Delta\nu + 2\delta,$$

$$c\text{: } 00 \leftrightarrow 1\,{-1} \text{ at } \nu_c = \Delta\nu + \nu_z + \delta,$$

$$d\text{: } 11 \leftrightarrow 10 \text{ at } \nu_d = \nu_z + \delta,$$

$$e\text{: } 11 \leftrightarrow 1\,{-1} \text{ at } \nu_e = \nu_z \text{ (double quantum)},$$

$$f\text{: } 10 \leftrightarrow 1\,{-1} \text{ at } \nu_f = \nu_z - \delta.$$

Here $\Delta\nu \approx 8665.649$ MHz is the absolute value of the zero-field hfs separation, ν_z is defined by $2h\nu_z = -(g_I + g_J)\mu_0 H$, and δ may be expressed as $\delta = \nu_f(\nu_f/\Delta\nu)[1-(4g_I/g_J)+(2\nu_f/\Delta\nu)]$. We have observed all listed transitions in a magnetic field H corresponding to $\nu_f = 10 \times (1 \pm 5 \times 10^{-5})$ MHz (about 7.23 G) and $\delta = 11\,512$ Hz which was stabilized by a potassium optical pumping magnetometer. While the field-dependent transitions showed linewidths $\delta\nu$ of about 2 kHz, due to residual field inhomogeneities and hum, it was possible to reduce that of the only weakly field-dependent b transition to as low as 10 Hz.

The experimental technique used may be considered as an extension of that originated by one of the authors[1] for observing the spin resonance of free electrons, and has been described in greater detail in a previous communication.[2] Briefly, it is based on orienting a sample of $(He^3)^+$ ions, contained in an rf trap,[3] by spin-exchange collisions with a beam of optically pumped Cs atoms and subsequently monitoring changes in the $(He^3)^+$ orientation by their effect on the rate of $(He^3)^+$ neutralization. The latter is due to simultaneous spin-dependent $(He^3)^+$-Cs charge-exchange interactions,[4] and its rate is reflected in the residual number of ions still present at the end of the interaction cycle. The experimental procedure was as follows. The Cs and consequently $(He^3)^+$ polarization was on-off modulated by magnetic resonance disorientation of the Cs atoms. For each on-off pair of observation cycles, the difference of the total residual $(He^3)^+$ charge monitored was formed and the results integrated[5] by charging a capacitor for 30 double cycles with an analog current. By displaying the voltage on the capacitor during the integration period and at its end short-circuiting it, the narrow sawtooth pattern visible in Fig. 1(b) and 1(c) was obtained, the peak heights serving as the desired $(He^3)^+$ polarization signal S. The system was now capable of detecting any transition resulting in a change of the average $(He^3)^+$ electron-spin polarization $p \equiv \langle s_z \rangle / s$. It can be shown that for the states $F = 1$, $M_F = 0, \pm 1$, this average is $p = M_F/F$ and for $F = 0$, one has $p = 0$. Consequently, in order to observe all transitions except b, it was only necessary to apply a cw magnetic rf field of the proper frequency and direction (Fig. 2) and to look for a decrease ΔS in the polarization signal S. For transitions d, e, f, and a one-turn loop around the ion trap containing in its plane both trap axis and magnetic field H was energized from crystal-controlled generators near 10 Mc/sec. The strong ΔS signal resulting from making $p \approx 0$ by equalizing the population of the 11 and 1 −1 levels in transition e at 10 011.5 kHz is shown in Fig. 1(b). To induce the microwave transitions, rf power was fed through a $\lambda/2$ slot antenna in-

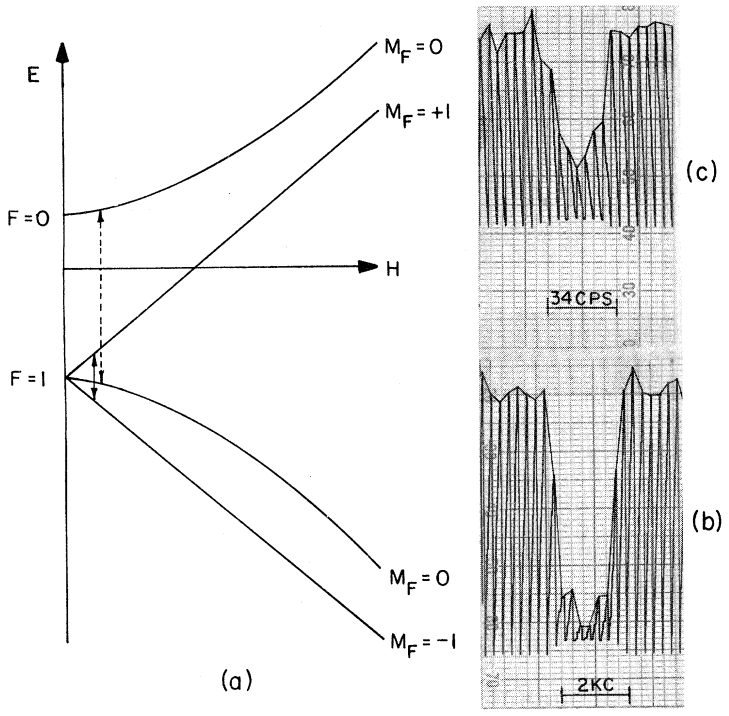

FIG. 1. Hfs levels and transitions of $(He^3)^+$. Corresponding to the full and broken lines in (a), the recorder traces of the ion-polarization signals obtained by sweeping through the $11 \leftrightarrow 1-1$ and $10 \leftrightarrow 00$ transition frequencies at 10.011 5 Mhz and 8665.673 MHz are reproduced in (b) and (c). The peaks of the individual integration spikes have been connected by straight lines.

to the trap structure which now acted as a low-Q TE_{013} cavity. By inclining the trap axis by 45° with respect to the H field, it was possible to induce and observe the a and c transitions at their respective frequencies. The very stable microwave signals necessary were derived (Fig. 2) from a GR 115B secondary frequency standard, which by a low-frequency comparator HP 117A-VLF was constantly compared to WWVB. The GR 115B controlled a HP 5100A frequency synthesizer operating near $\Delta\nu/176 \approx 49.3$ MHz. A Varactor quadrupler followed by a Boonton 230A tuned amplifier served to drive a Dymec 2650A multiplier-klystron stabilizer finally phase-lock-controlling an Z-13B Varian klystron operating near ν_a, ν_c.

However, in order to detect the b transition which, of course, was of primary experimental interest, a more complex multiple rf resonance scheme had to be developed. For purposes of explanation, we shall assume all the Cs atoms to be in the state $F = M_F = I + \frac{1}{2}$ corresponding to an electron-spin polarization $P = 1$. Then, due to spin exchange, all $(He^3)^+$ ions will soon be in the state 11 corresponding to $p = P = 1$. If now an ion undergoes d transitions at a rate $f_d \gg f_e$, where f_e is the rate at which it experiences spin-exchange collisions, the average $(He^3)^+$ polarization p and with it S will drop by about one-half, corresponding to equalization of the populations of the participating levels. In addition, an rf field at ν_c and capable of inducing c transitions at a rate $f_c = f_d$ is switched on causing at first no further reduction in S since the 1 −1 level is unoccupied. However, by inducing in addition b transitions at a rate $f_b \approx f_d$, it becomes possible to reduce p to nearly zero since all four participating levels will now tend to be equally populated, causing a sizable additional polarization signal ΔS to be registered. For experimental execution of this scheme, the output from a crystal controlled oscillator at ν_d = 10 023 024 Hz was adjusted to a value just large enough to reduce S by not quite one-half. Again the microwave power, now set at ν_c, was adjusted to a level which in previous experiments with the a transition alone had been found to reduce S by not quite one-half, and was amplitude modulated at ν_f = 10 000 000 Hz derived from the standard to create a weak sideband near ν_b. In order to search for the b transition, it was now only necessary to shift the klystron frequency a few hundred cycles, well within the width of the c and d transitions, and finally to reduce the 10-MHz modulation amplitude and thereby the power in the sideband in order to avoid rf broadening. The H field was modulated by a noise spectrum extending from about 10 to 100 Hz at an amplitude corresponding to a spectral width of the field-dependent lines of about 1 kHz in order to approximate flat spectrum conditions for the c and d transitions which make it possible to in-

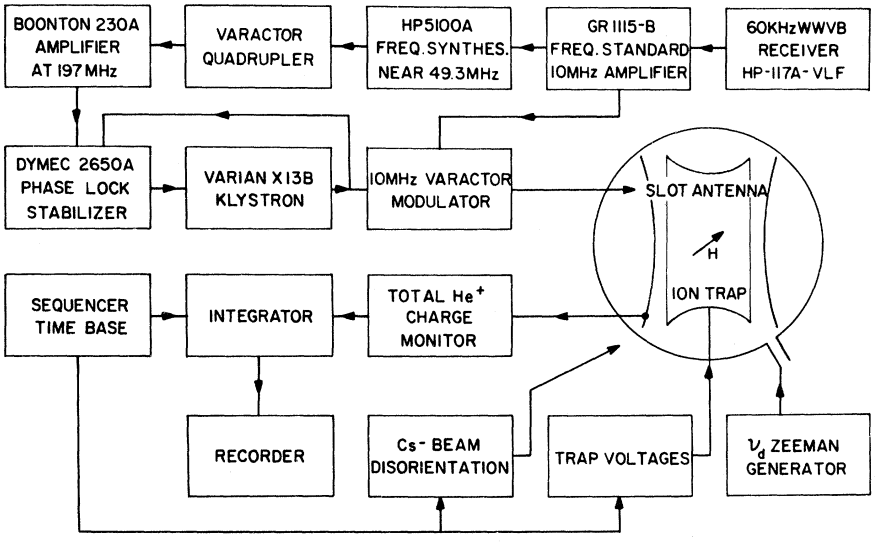

FIG. 2. Block diagram of experimental arrangement employed in measuring $(He^3)^+$ 10 ↔ 00 hfs transition by multiple rf resonance scheme.

duce them with minimum rf broadening of the 00 and 10 levels. A ν_b-resonance signal obtained as described above is shown in Fig. 1(c). Eight b-transition runs were carried out, and by averaging of the visually determined line centers a precise value for ν_b was obtained resulting in the final value

$$\Delta\nu = 8\,665\,649\,905 \pm 50 \text{ Hz}.$$

The large quoted error is to allow for as yet incompletely checked conceivable systematic shifts. No corrections for second-order Doppler effect have been applied. The field-dependent transitions were found consistent with this value to within their uncertainty.

The above value may be compared with the $2s$ hfs separation in $(He^3)^+$ measured by Novick and Commins[6] by means of a beam technique,

$$\Delta\nu_{2s} = 1\,083\,354\,990 \pm 200 \text{ Hz},$$

to yield the ratio

$$(8\Delta\nu_{2s}/\Delta\nu_{1s})_{\text{exp}} = 1 + (137.5 \pm 0.2) \times 10^{-6}.$$

The theoretical value for hydrogenic atoms[7] has been accurately calculated and compares favorably with experiment in the case of hydrogen. For $(He^3)^+$, this calculation yields

$$(8\Delta\nu_{2s}/\Delta\nu_{1s})_{\text{theor}} = 1 + (138.3 \pm 0.04) \times 10^{-6}.$$

There is a small discrepancy which we cannot explain at present.

The chief interest in our measurement of $\Delta\nu_{1s}$ derives from the more exacting test it provides, in combination with the $\Delta\nu_{2s}$ value of Novick and Commins, of radiative correction models in hydrogenic atoms, which play a role in theoretical calculations[8] of the hydrogen hfs and their bearing on the proton structure. From the purely spectroscopic point of view, our relative linewidth $\delta\nu/\Delta\nu \approx 10^{-9}$ is already comparable to $(T_2\Delta\nu)^{-1}$ values observed for H atoms in hydrocarbon- and fluorocarbon-coated storage bulbs.[9]

Even though the potential of ion-storage techniques for high-resolution rf spectroscopy had been recognized as early as 1956,[10] the present work constitutes the first experimental realization of this potential. In contrast to the atom/coated-storage bulb situation, where the H-Teflon combination appears to be hard to improve upon, our experiment may be considered but the first successful one of a class of future high-resolution experiments which are based on "ion-storage collision" (ISC) techniques.[11] While in the present study a polarized Cs beam was used, linearly polarized photons have also served successfully as the anisotropic projectiles in an analogous $\Delta F = 0$ experiment[12] on H_2^+ based on the photodissociation reaction, and work on ordinary optical pumping of stored ions in under way. Even the presently available limited arsenal of projectiles of proven usefulness should allow similar studies of a large number of ions including heavy and multiply charged ones, being not necessarily in S states, and also bringing $\Delta\nu$ values of many hundreds of gigahertzes within reach. Simultaneous work in this laboratory directed toward thermalization and/or refrigeration of the ions by radiation damping of their oscillatory motion, which we have already experimentally demonstrated for stored electrons, should make it possible to approach closely the ideal of isolated atomic systems forever floating at rest in free space[11] and thereby reduce linewidth and shifts by orders of magnitude. The extremely narrow relative linewidth then to be expected may also make feasible the development of infrared lasers whose frequency is primarily determined by the molecular oscillators, as in the hydrogen maser,[9] and not by the dimensions of the resonator cavity, as in all present lasers. All this should lead to a variety of ultimate atomic clocks, bringing within reach accurate tests not only of the usual relativistic effects, but also of the possible variation in time of the fine-structure constant α and other dimensionless constants. Fractional changes of α as large as 1 part in 10^{12} per year may be envisioned on the basis of Mach's ideas as a consequence of the expansion of the universe,[13] which proceeds at a rate of about 1 part in 10^{10} per year. This might be tested by, for example, comparing nuclear and rotational hfs frequencies in H_2^+ over an extended period, since their ratio is proportional to α^2.

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THOMSON AND RAMAN SCATTERING BY MOBILE ELECTRONS IN CRYSTALS

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In this Letter we discuss the scattering of light by mobile electrons (or holes) in semiconducting crystals. Two processes will be considered: elastic (Thomson) scattering, and Raman scattering by electrons in a magnetic field. The elastic scattering has previously been treated[1,2] within the framework of the effective-mass theory (which is valid at low frequencies). We will show that, at higher frequencies, it is possible to achieve large enhancements of the cross section. This result may be of some importance since incoherent scattering experiments in solids are presently made difficult by the smallness of the cross section.

The Raman process we treat is one in which the electron changes its Landau-level quantum number by $\Delta n = 2$, and the outgoing radiation is shifted in frequency by twice the cyclotron frequency. For free, nonrelativistic electrons, it is easy to see that the matrix element for such a transition vanishes. However, if the electrons are relativistic (or the band structure nonparabolic) the cross section is finite and, in appropriate materials, can attain quite reasonable values.

Consider first the elastic scattering. Interest in this process has been aroused by recent papers[1,2] in which it is shown that a study of such scattering gives detailed information concerning the plasma properties of electrons in semiconductors. The multivalley semiconductor is of particular interest since it can support an acoustic mode (the so-called plasma sound wave) whose existence and dispersion relation one hopes to infer from the spectrum of the scattered light. In both the analyses referred to above, the electrons are described in the effective-mass approximation, and an individual electron is assumed to scatter with cross section

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{m_0 c^2}\right)^2 (\vec{\epsilon}_0 \cdot \alpha \cdot \vec{\epsilon}_1)^2, \tag{1}$$

where $\vec{\epsilon}_0$, $\vec{\epsilon}_1$ are polarization vectors of the incident and scattered light, and α the (dimensionless) reciprocal effective-mass tensor. The main aim of these calculations was to determine how the intensity and spectrum of scattered light is modified by Coulomb interactions between electrons. Here, on the other hand, we consider the problem of scattering by a single electron in the conduction band of an otherwise intrinsic semiconductor. This system is described by the Hamiltonian

$$H = \frac{[\vec{p} - (e/c)\vec{A}]^2}{2m_0} + V(r), \tag{2}$$