for these and other antiferromagnetic salts will be presented in more complete form elsewhere.

We are indebted to Professor J. C. Phillips and Dr. L. L. Lohr for valuable discussions, and to Mr. S. A. Reed for experimental help.

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OBSERVATION OF ELECTRON SPIN RESONANCE IN RUBIDIUM AND CESIUM*

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We have observed electron spin resonance[1] (ESR) in bulk samples of rubidium (1.5-17°K) and cesium (1.5-7°K) at a frequency of 9400 Mc/sec by utilizing the "selective transmission" technique.[2-6] The results we report here complete the ESR g values for the entire alkali-metal series and are of sufficient accuracy to allow meaningful comparisons with theoretical values. For rubidium we know of no previous measurements reported in the literature. For cesium a result has been previously reported,[7] but we believe it to be in error. The values we have obtained are

$$\text{rubidium:}\quad g = 1.999 \pm 0.001$$

$$\text{or}\quad \Delta g = (-0.33 \pm 0.1) \times 10^{-2},$$

$$\text{cesium:}\quad g = 2.013 \pm 0.002$$

$$\text{or}\quad \Delta g = (1.07 \pm 0.2) \times 10^{-2},$$

where Δg, the "g shift," is defined as the difference of the experimental g value and the g of the free electron (2.0023). (The quoted errors represent one standard deviation.) In Fig. 1, the experimental g values of all the alkalis are presented, and also the results of the most extensive calculations.[8] It is seen that, contrary to the conclusion of Bienenstock and Brooks (which was influenced by the lack of reliable data), it is possible that their "core-polarization correction" to the potential is valid for the heavier alkali metals. Thus it may be that only refinements in the computations are needed to produce satisfactory agreement with the experimental values.

The history of ESR in metals has been such that many spurious resonances have been reported in the literature. In addition, we claim that with respect to cesium the previously reported value is in error. Hence, we feel obligated to discuss the method and the specific tests we were able to perform to rule out spurious effects.

Method.—The selective transmission technique utilizes a dc magnetic field and a perpendicular rf magnetic field applied in the usual manner with the sample in the form of a thin foil, but, with the rf field applied to only one surface. The conduction electrons absorb power from the rf field during the time they are in the skin depth. If the spin-relaxation time is long compared to the time required for the electrons to diffuse to the other surface, then the moments of those electrons that have not relaxed will constitute a net transverse magnetization, precessing at the Larmor frequency. This precessing magnetization will radiate power. It is this "transmitted" power (or field) that is measured as a function of frequency (or dc magnetic field). Under suitable experimental conditions, this power can be made comparable or even larger than the power transmitted via skin-effect damping and spurious leakages; hence, its presence can be a very sensitive unambiguous test for ESR in metals.

Tests.—(1) There appears to be some general misunderstanding concerning the relative sensitivities of the usual reflection versus the transmission system. We wish to assert that in principle, the sensitivity of the reflection system is greater than, or equal to, that of the transmission system, for equal parameters such as sample size, cavity Q_0, etc.[9] Consequently, utilizing transmission technique per se is not a criteria for enhancing the reliability of observing ESR in metals. The transmission system can be used effectively to discriminate against paramagnetic absorptions provided the leakage power can be kept sufficiently small. The identification of a "signal" that varies with magnetic field as due to transmission increases in validity as the ratio of the detected power on resonance to power off resonance increases. For our signals to be due to paramagnetic spins in the cavity would require fractional power absorptions of the order of 10%. No such easily seen signals were observed in reflection.

(2) At low temperatures, as mentioned in Ref. 6, it is possible to have field-dependent transmitted power which is not related to the spins, the so-called "geometric cyclotron resonances." There was some broad variation of the base line at the lowest temperatures in the case of rubidium, and very little for cesium. In all cases, the ESR signal was independent of the angle between the magnetic field and the normal to the sample, which is a sensitive discriminatory test.

(3) The characteristic line shapes of the signals agreed with our calculations and experimental verifications with the other well-known alkali resonances.

(4) The temperature dependence of the amplitude of the signal is definitely not $1/T$, and more specifically is exponentially attenuated with the appropriate decay constant calculated

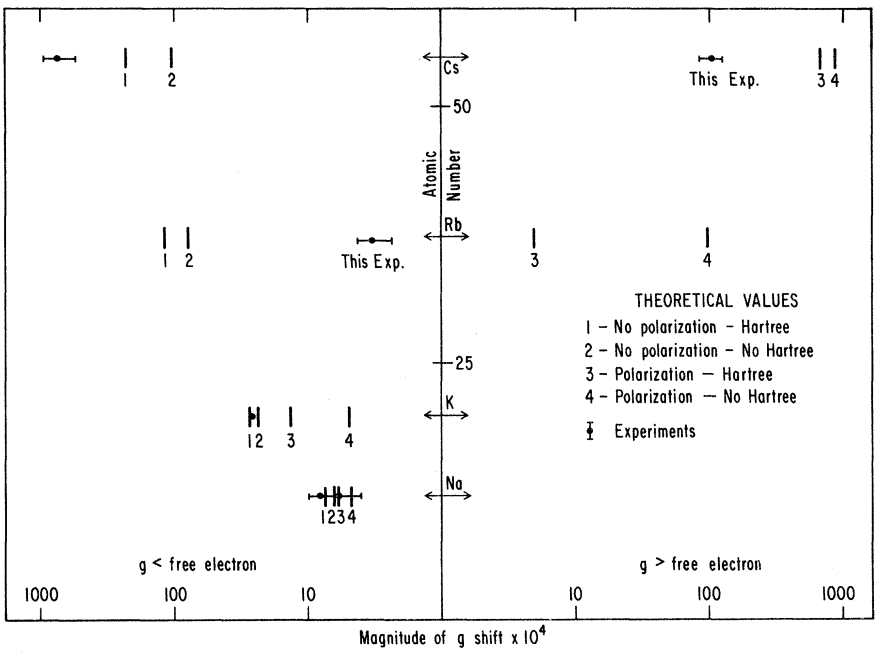

FIG. 1. The log of the magnitude of the g shift for the various alkali metals. The theoretical values were determined utilizing the data presented in Table III of Bienenstock and Brooks (Ref. 8), and interpolated for the appropriate r_s (radius of the Wigner-Seitz sphere). The explanation of the four approximations characterizing the four theoretical values indicated for each metal is explained in that article. (Note: In order to present the data for all the alkalis compactly the above log plot was chosen. To help maintain a proper prospective when comparing the experimental and theoretical values for the individual metals, a linear plot is also helpful.) The experimental g shifts are, for sodium, $(8 \pm 2) \times 10^{-4}$ [G. Feher and A. F. Kip, Phys. Rev. 98, 337 (1955)] and $(6 \pm 2) \times 10^{-4}$ [G. J. King, B. S. Miller, F. F. Carlson, and R. C. McMillan, J. Chem. Phys. 32, 940 (1960)]; for potassium, $(2.6 \pm 0.1) \times 10^{-3}$ [W. M. Walsh, Jr., L. W. Rupp, Jr., and P. H. Schmidt, Bull. Am. Phys. Soc. 10, 450 (1965), Abstract BF3] and $(2.8 \pm 0.6) \times 10^{-3}$ (we have measured the potassium ESR using the transmission technique, with the result indicated; the larger error than that of our 1965 result is due to a much broader line); for rubidium, $(0.33 \pm 0.1) \times 10^{-2}$ (this work); for cesium, $(-1.1 \pm 0.2) \times 10^{-2}$ (this work) and $(7.2 \pm 2) \times 10^{-2}$ (Ref. 7). The g shift for lithium is very small $\{(-2 \pm 2) \times 10^{-6}$ [R. J. Pressley and H. L. Berk, Phys. Rev. 140, A1207 (1965)]$\}$ and the calculated values are expected to be too inaccurate to allow detailed comparison with experiment (Ref. 8).

from the known parameters of the alkali, plus the measured temperature dependence of the resistivity ratio.

(5) The cesium signal did not appear in the rubidium runs and vice versa, although all other equipment, cavities, etc., were the same.

The samples[10] (typically 0.009 to 0.017 cm thick) formed part of the common wall between a pair of TE_{101} cavities tuned to the same frequency. They were protected on both sides from reacting with the atmosphere by 0.003-cm mica windows.[11,12] The microwave power into the "transmitter" cavity was audio modulated and was ≈100 mW. The receiver cavity was coupled to a linear superheterodyne detector incorporating a 60-Mc/sec i.f., using phase-sensitive detection, and having an over-all sensitivity of 10^{-19} W with a one-second time constant. By careful construction and sample mounting (particularly difficult in the case of the more reactive alkalis), leakage power under normal skin-effect conditions was down by ≈160 dB. Additional unmodulated microwave power was fed through a phase shifter and added to the transmitted power so as to allow the detection of that component of the transmitted rf field which is in phase with the reference microwave field. This component is called the signal.

Typical traces of transmission signal versus magnetic field are shown in Fig. 2. The phase of the reference microwave field was adjusted to give a symmetric signal in all cases, and the center of the line is taken as the resonant field as explained in Ref. 5. The linewidths varied slightly from sample to sample but were essentially independent of the temperature and the sample thickness[13] over the ranges measured. Since the resistivity varied appreciably over the temperatures measured, we can assume that the linewidths are due solely to impurity scattering and that further purification of the materials will result in considerably narrower lines. Although the rubidium has a broader line than the cesium, it actually gave stronger transmission signals (mainly due to a greater conductivity) and, as a result of this, plus the accumulation of more statistics, allowed us to assign to its g value a lower over-all error. In view of the fact that the signal is attenuated sharply with increasing temperature, and the lines were broad to start with, it was not practicable at this time to make measurements to determine if there is a g shift with temperature.

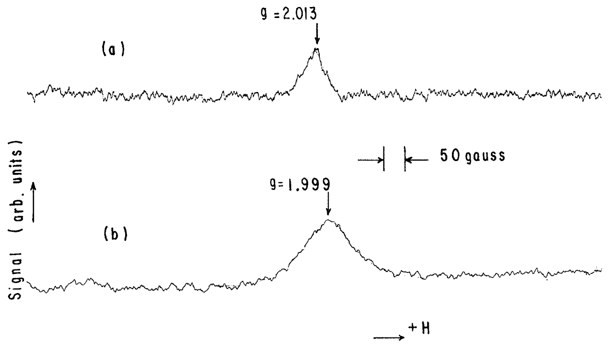

FIG. 2. A photograph of typical transmission signals as a function of the dc magnetic field at $T = 1.5°K$. The data were taken on a twin-track recorder with an nmr signal presented simultaneously with the ESR signal. The nmr probe was calibrated (in reflection) against a reference g marker of P-doped Si located adjacent to the samples. (a) Cesium, $T_2 \cong 1.8\times10^{-9}$ sec. (b) Rubidium, $T_2 \cong 0.9\times10^{-9}$ sec.

In their comparisons of the theoretical results with the limited and erroneous data available at that time, Bienenstock and Brooks noted the (apparent) deficiency of the inclusion of the polarization correction and examined the approximation in detail to see why it caused poorer agreement. They were forced to conclude that they could not see why the discrepancy existed. The rubidium and cesium results now suggest that the correction may indeed be necessary for the heavier alkalis and that further refinements in the calculations are warranted to obtain better agreement with the experimental values.

We would like to thank Mr. Clancy Latham for his help in developing the techniques necessary for preparing the alkali samples. We wish to thank the authors of the paper[1] immediately following this paper for communicating to us their results in advance of publication.

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[9] The proof of this statement will be published in a separate paper.

[10] All our materials were obtained from the MSA Research Corporation, Callery, Pennsylvania, whose material had a typical resistance ratio R.T./4°K of 400 for rubidium and 250 for cesium.

[11] A separate paper is being prepared to discuss the techniques developed to prepare and handle the alkali samples.

[12] We have found mica to be one of the better materials to use in protecting all the alkali metals. It is true that it generally has a variety of broad paramagnetic absorptions but these (and any others) are specifically discriminated against as discussed in the text.

[13] There is a slight narrowing of the line with change in thickness to be expected due to the nature of the transmission line shape. However, we are concerned with larger changes such as would indicate the presence of surface relaxation as seen in copper (Ref. 5).

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g VALUES OF RUBIDIUM AND CESIUM CONDUCTION ELECTRONS

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(Received 20 December 1965)

We wish to report observation of conduction electron spin resonance (CESR) in bulk samples of metallic rubidium and cesium. The resonance linewidths are sufficiently narrow to permit *g*-value determinations for the two heaviest alkali metals[1]: $g_{\rm Rb} = 1.9984 \pm 0.0001$, $g_{\rm Cs} = 2.005_5 \pm 0.001$. The cesium result differs sharply from an earlier value (1.93) reported by Levy[2] who examined cesium particles precipitated from a frozen metal-ammonia solution. We have not observed any indication of resonance corresponding to such a gyromagnetic ratio.

The observed *g* values are remarkably close to that of the free electron $g = 2.0023$, when the progression of *g* shifts, $\delta g \equiv g - g_0$, for the lighter alkali metals is considered (Table I). In particular, the positive shift for cesium is surprising. These new results suggest that core-polarization contributions to the *g* shifts as calculated by Bienenstock and Brooks,[3] which did not appear to be significant for the light alkalis,[3,4] do play an important role in the case of rubidium and cesium.

Both metals were examined in the form of thin (~0.1 mm) sheets rolled out between layers of Parafilm[5] under degassed mineral oil. Rectangular samples cut from these sheets were placed inside a rectangular $\rm TE_{101}$ cavity resonant near 12 kMc/sec. The cavity loss, largely determined by the specimen surface resistance, was monitored in reflection using a conventional homodyne spectrometer. The magnetic field was applied in the sample plane and could be rotated relative to the linearly polarized microwave currents on the sample in order to verify the magnetic dipole character of the signals being examined. The cavity and sample were usually held near ~1.3°K to minimize line broadening due to phonon-induced spin-lattice relaxation which becomes significant by 4.2°K.

The rubidium metal used in our experiments was prepared by reduction of a highly purified chloride followed by vacuum distillation.[6] The resistivity of the distilled metal decreased by a factor ~3000 upon cooling from room tempera-

Table I. *g* values and *g* shifts of the alkali metals.

Metal	g	δg
Li[a]	2.0023	$(-2 \pm 2) \times 10^{-6}$
Na[b]	2.0015	$(-8 \pm 1) \times 10^{-4}$
K[c]	1.9997	$(-26 \pm 1) \times 10^{-4}$
Rb[d]	1.9984	$(-39 \pm 1) \times 10^{-4}$
Cs[d]	2.005_5	$(+32 \pm 10) \times 10^{-4}$

[a] Ref. 5; R. J. Pressley and H. L. Berk, Phys. Rev. 140, A1207 (1965).

[b] Ref. 5; Ch. Ryter, Phys. Letters 4, 69 (1963); G. J. King, B. S. Miller, F. F. Carlson, and R. C. McMillan, J. Chem. Phys. 32, 940 (1960) measured $\delta g = -6 \times 10^{-4}$.

[c] Ref. 4.

[d] This work.