(North-Holland Publishing Company, Amsterdam, 1961), Vol. III.

<sup>4</sup>R. B. Lewis and T. R. Carver, Phys. Rev. Letters 12, 693 (1964).

 ${}^{5}N$ . S. Vander Ven and R. T. Schumacher, Phys. Rev. Letters 12, 695 (1964).

6Sheldon Schultz and Clancy Latham, Phys. Rev. Letters 15, 148 (1965).

 ${}^{7}R$ . A. Levy, Phys. Rev. 102, 31 (1956).

<sup>8</sup>A. Bienenstock and H. Brooks, Phys. Rev. 136, A784 (1964).

<sup>9</sup>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).

## $g$  VALUES OF RUBIDIUM AND CESIUM CONDUCTION ELECTRONS

%. M. Walsh, Jr., L. W. Rupp, Jr., and P. H. Schmidt

Bell Telephone Laboratories, Murray Hill, New Jersey (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<sup>1</sup>:  $g_{\text{Rb}} = 1.9984 \pm 0.0001$ ,  $g_{\text{Cs}} = 2.005_{\text{s}} \pm 0.001$ . The cesium result differs sharply from an earlier value (1.93) reported by Levy' 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,  $\delta g = g - g_0$ , 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,<sup>3</sup> 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  $(-0.1 \text{ mm})$  sheets rolled out between layers of Parafilm<sup>5</sup> under degassed mineral oil. Rectangular samples eut from these sheets were placed inside a rectangular  $TE_{101}$  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  $\sim1.3\text{ K}$  to minimize line broadening due to phonon-induced spin-lattice relaxation which becomes significant by  $4.2^{\circ}$ K.

The rubidium metal used in our experiments was prepared by reduction of a highly purified chloride followed by vacuum distillation.<sup>6</sup> 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 <sup>a</sup>	2.0023	$(-2 \pm 2) \times 10^{-6}$
Na <sup>b</sup>	2.0015	$(-8 \pm 1) \times 10^{-4}$
$K^{\rm C}$	1.9997	$(-26 \pm 1) \times 10^{-4}$
$Rb^d$	1.9984	$(-39 \pm 1) \times 10^{-4}$
$\mathrm{c}\mathrm{s}^{\mathrm{d}}$	2.005 <sub>5</sub>	$(+32 \pm 10) \times 10^{-4}$

 ${}^{a}$ Ref. 5; R. J. Pressley and H. L. Berk, Phys. Rev. 140, A1207 (1965).

bRef. 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, <sup>940</sup> (1960) measured  $\delta g = -6 \times 10^{-4}$ .

 $c_{\text{Ref. 4.}}$ 

This work.

ture to  $\sim 1.3$ °K. An additional indication of purity was the observed CESR linewidth of  $0.4$  G at low temperature corresponding to a spin-lattice relaxation time  $T_1 > 2 \times 10^{-7}$  sec.<sup>5</sup> The g value was measured relative to that of a lithium metal reference as illustrated in Fig. 1(a).



FIG. 1. {a) The conduction-electron resonance signals of thin plates of lithium and rubidium observed simultaneously at 1.3°K and 11.9155 kMc/sec. {b) Field derivative of the cesium CKSR signal recorded at 1.3'K and 11.8745 kMc/sec. The rolling base line results from a broad paramagnetic resonance of unknown origin present in the "empty" cavity.

We found it necessary to operate at rather low microwave power levels (&1 mW average) in order to avoid partial saturation of the narrow CESR lines with concomitant "day"-shifting of the line positions due to Overhauser polarization of the metal nuclei.<sup> $7,8$ </sup>

Cesium metal was obtained from Mine Safety Appliances, Inc., as well as other sources. The largest decrease in resistivity observed in the commercial material was  $~150$ , again between room temperature and  $\sim 1.3\textdegree K$ . The linewidth of the CESR signal proved to be  $\sim 30$ G  $(T_1 \sim 2.5 \times 10^{-9} \text{ sec})$ , and the resonance could be observed only by recording the field derivative of the cavity loss using 165-cps field modulation and synchronous detection as shown in Fig. 1(b). The g-value determination was made by averaging many such traces with field markers provided by an external proton nmr probe and using the line-shape analysis appropriate to a metal slab in the anomalous skin-effect regime. $5,9$  Microwave and nmr frequencies were accurately determined and the nmr probe readings were corrected for magnetic field inhomogeneity. At best, however, our cesium measurement is marginal since the CESR signal is observed against a field-dependent base line due to a broad paramagnetic resonance present in the empty cavity despite repeated gold plating. It is anticipated that purification of cesium analogous to that described above for rubidium will lead to narrower CESR signals and a significant improvement in the gvalue determination.

In Fig. 2 the observed  $g$  shifts are compared with values computed by Bienenstock and Brooks.' Four theoretical curves are shown for various values of the Wigner-Seitz sphere radii corresponding to inclusion or neglect of a Hartree electron-electron interaction potential  $(H$  or  $NH$ ) and of a core-polarization correction (P or NP) which takes into account distortion of the ion cores by the valence electrons.<sup>10</sup> Though it is clear that numerical agreement is not to be found, it is noteworthy that the experimental values are distinctly less negative than the shifts calculated neglecting core polarization. This fact constitutes the first real evidence that such a contribution to the  $g$  value is physically operative. It is now conceivable that another round of computations of improved self-consistency may yield agreement with the g values which are now experimentally known for the entire alkali-metal series.



FIG. 2. (a) Comparison of the rubidium g shift with values calculated by Bienenstock and Brooks including or neglecting a Hartree electron-electron potential term (H or NH) and a core-polarization correction (P or NP).<sup>3</sup> The abscissa is the Wigner-Seitz sphere radius in units of the Bohr radius. (b) The same comparison for cesium.

We wish to thank G. Adams for providing resistivity ratio measurements. We have benefited from comparison of our results with those of Schultz and Shanabarger obtained concurrently by the spin-resonance transmission technique.  ${}^{2}$ R. A. Levy, Phys. Rev. 102, 31 (1956).

3A. Bienenstock and H. Brooks, Phys. Rev. 136, A 784 (1964).

 $4W$ . M. Walsh, Jr., L. W. Rupp, Jr., and P. H. Schmidt, Phys. Rev. (to be published).

 ${}^{5}$ G. Feher and A. F. Kip. Phys. Rev. 98, 337 (1955).  ${}^6P$ . H. Schmidt, to be published.

 ${}^{7}$ A. W. Overhauser, Phys. Rev. 92, 411 (1953).

<sup>8</sup>M. Gueron and Ch. Ryter, Phys. Rev. Letters 3, 338 (1959).

<sup>9</sup>F. J. Dyson, Phys. Rev. 98, 349 (1955).

 $^{10}$ H. Brooks and F. S. Ham, Phys. Rev. 112, 344 (1958).

These experiments were performed independently of, and essentially simultaneously with, those reported by S. Schultz and M. R. Shanabarger, Phys. Rev. Letters  $16$ , 178 (1965). Their g values differ somewhat from our own but the physical significance of the results is clear.



FIG. 1. (a) The conduction-electron resonance signals of thin plates of lithium and rubidium observed simultaneously at 1.3°K and 11.9155 kMc/sec. (b) Field derivative of the cesium CESR signal recorded at 1.3°K and 11.8745 kMc/sec. The rolling base line results from a broad paramagnetic resonance of unknown origin present in the "empty" cavity.