PHYSICAL REVIEW VOLUME 103, NUMBER 6 SEPTEMBER 15, 1956

Knight Shift Measurements for Ba^{135}, Ba^{137}, Cd^{111}, and Cd^{113}

T. J. Rowland
Metals Research Laboratories, Electro Metallurgical Company, Niagara Falls, New York

(Received April 13, 1956)

The shift of the nuclear magnetic resonance frequency caused by the paramagnetism of the conduction electrons has been measured using a nuclear induction spectrometer. The values of the relative isotropic shift are (0.403±0.002)% for barium and (0.415±0.004)% for cadmium. The latter absorption is markedly anisotropic, the shifts perpendicular and parallel to the c axis being (0.401±0.004)% and (0.444±0.004)%, respectively.

THE recent determination[1] of the magnetic moments of Ba^{135} and Ba^{137} has made possible the measurement of the Knight shift[2] in metallic barium. A nuclear induction spectrometer (manufactured by Varian Associates) and an electromagnet having a 12-inch pole diameter and 2.13-inch gap were used. The magnet provided a field having a homogeneity of better than 0.05 gauss over the sample volume and negligible drift during the measurements. The spectrometer frequency was determined using a Signal Corps BC221 frequency meter which was checked against radio station WWV. The stability of the spectrometer oscillator was greater than one part in 250 000.

The reference sample consisted of a saturated, aqueous solution of $BaCl_2$ containing no added paramagnetic impurity. The metallic barium[3] was filed and immediately immersed in benzene to discourage the rapid oxidation of the filings. The particle size was small compared to the skin depth at the frequencies used, and the oxide layer on the particles served to insulate them from each other.

The nuclear magnetic resonance absorption of the barium in solution was compared with the absorption of the same isotope in the metal. The samples were exchanged in the probe without moving the latter, and the magnetic field was changed from one resonance value to the other. Before and after each series of measurements, the magnetic field was checked and the field scanning mechanism calibrated. This was carried out using the easily observed Cl^{35} absorption in a LiCl solution. The somewhat weaker Cl^{35} signal from the $BaCl_2$ solution occurs at a field 11 parts per million lower than that in the LiCl solution. A high radio-frequency field strength and a modulation amplitude of 2.4 gauss, approximately equal to the absorption width, were used to observe the barium resonance. The value of the resonance shift reported is the result of seven or more measurements for each isotope.

For Ba^{137}, the more abundant isotope of the two, the measurements were made by using a frequency of 3.4454 Mc/sec (field about 8260 gauss). The resonance in the metal occurred at a magnetic field (0.403 ±0.002)% lower than that of the same isotope in solution. The Ba^{135} shift, measured using a frequency of 5.0204 Mc/sec (about 11 880 gauss), had the same value within the stated experimental error.

The Knight shift for cadmium was measured in much the same way, a saturated solution of $CdCl_2$ being used for the comparison. The metal which contained less than 0.2% total impurities was filed, and that portion of the filings which passed through a 200-mesh sieve was used for the measurements. This procedure ensured a particle size of less than the skin depth at the frequencies used. The field was calibrated before and after the measurement using the Na^{23} absorption in an aqueous NaCl solution.

The absorption curves of both isotopes in the metal are markedly asymmetric indicating an anisotropy of the Knight shift[4] in this structure. When the external field is parallel to the hexagonal axis, the shift is (0.444±0.004)% but is (0.401±0.004)% when the external field is perpendicular to the hexagonal axis. The anisotropy $(\Delta H_{\parallel}-\Delta H_{\perp})/H_0$ is thus 0.046%. The relative anisotropy $(\Delta H_{\parallel}-\Delta H_{\perp})/\Delta H_{\text{i.s.}}$ is 10.4%. Since the line shape can be explained by assuming axial symmetry of the electron density, the isotropic shift, $\Delta H_{\text{i.s.}}$, can be found as described in reference 4. The result is $\Delta H_{\text{i.s.}}/H_0=(0.415\pm0.004)\%$. The isotropic shift and the anisotropy are the same for both cadmium isotopes. A large part of the stated error is associated with the uncertainty in the exact position of the limits of the region over which the absorption takes place. This is due to the effect of superimposed broadening due to dipolar interaction, and other causes of symmetric broadening. Further work is being done on the accurate interpretation of experimentally obtained line shapes of this type.

Data were obtained at field strengths of 3540, 7100, and 11 870 gauss and the asymmetric broadening was found to be proportional to the applied field, in agreement with the theory. No possibility of confusion with quadrupole effects existed since both isotopes under consideration have a nuclear spin of 1/2. The symmetric

---

[1] H. E. Walchli and T. J. Rowland, Phys. Rev. **102**, 1334 (1956).

[2] W. D. Knight, Phys. Rev. **76**, 1259 (1949); Townes, Herring, and Knight, Phys. Rev. **77**, 852 (1950).

[3] Supplied by Kemet Company, Cleveland, Ohio; major impurities calcium and strontium (about 1%), other impurities total less than 0.5%.

[4] N. Bloembergen and T. J. Rowland, Acta. Metallurgica **1**, 731 (1953).

line broadening can be estimated to be about 0.6 gauss (*half* distance between observed absorption derivative peaks) and may be roughly compared with the square root of the second moment of the absorption calculated using the equation for dipolar broadening alone. The latter value is about 0.22 gauss for polycrystalline cadmium of natural isotopic abundance. The discrepancy of a factor 3 between the observed and calculated symmetric line broadening could be due to an exchange interaction between the nuclear spins of the two isotopes.[5]

The fact that the parallel shift is greater than the perpendicular shift indicates either that the wave function of the conduction electrons near the Fermi level has a greater density in the direction of the hexagonal axis or else that the electron spin-orbit coupling causes the g factor to be larger when the magnetic field is parallel to the hexagonal axis.

The surprising magnitude of the anisotropy is no doubt due to the extreme deviation of the c/a ratio of cadmium (1.886) from that for a close-packed hexagonal array of spheres (1.633).

Preliminary work on cadmium was done with H. E. Walchli using an enriched CdI sample provided by the Stable Isotope Research and Production Division of Oak Ridge National Laboratory.

---

[5] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).

PHYSICAL REVIEW VOLUME 103, NUMBER 6 SEPTEMBER 15, 1956

Effect of Neutral Impurity on the Microwave Conductivity and Dielectric Constant of Germanium at Low Temperatures*

F. A. D'ALTROY† AND H. Y. FAN
Purdue University, Lafayette, Indiana

(Received June 8, 1956)

Conductivity and dielectric constant of germanium at 4.2°K were measured at a frequency of 9200 Mc/sec. The dielectric constant measured for a pure sample is 16.0±0.3. Higher dielectric constants, up to 80, were measured on n- and p-type samples doped with antimony or gallium. The conductivity and the change of dielectric constant are attributed to carriers in the impurity states. A positive contribution, ΔK_b, to the dielectric constant is given by the polarization of neutral impurity atoms and a negative contribution, ΔK_c, is associated with the conduction effect. Using ΔK_b to estimate the ionization energy of the impurity, a value of 0.0099 ev is obtained for a sample containing 1.6×10^{16} cm^{-3} antimony and 0.0084 ev is obtained for a sample containing 3.7×10^{16} cm^{-3} gallium. Samples of higher impurity concentrations showed much higher conductivity and the effect of overlapping of impurity states is shown in the variation of impurity polarizability. The relaxation time and effective mass for the conduction in impurity states are estimated from the dc conductivity and its ratio to the microwave conductivity. Large effective masses, around $1000m$, are obtained for samples of $\sim10^{17}$ cm^{-3} impurity concentration.

I. INTRODUCTION

A SEMICONDUCTOR with small impurity content and very low concentration of free carriers has a dielectric constant characteristic of the pure crystal. Free carriers give rise to conductivity as well as a change in the dielectric constant. On account of the inertia of the carriers, the current in an alternating field has a component out of phase with the field, which contributes to the electric susceptibility. From the conductivity and the change of dielectric constant, the two parameters, relaxation time and effective mass of carriers, can be determined. In order to have an appreciable out-of-phase current, it is necessary to use a sufficiently high frequency which is not too small compared to the collision frequency of the carriers. Conductivity and dielectric constant of germanium have been determined from measurements of microwave transmission through bulk samples by several groups of workers.[1–3] The measurements of Benedict and Shockley and of Goldey and Brown were made at temperatures above 160°K, while our measurements covered the range 20°K to 300°K. The results obtained on the effective masses of electrons and holes are difficult to reconcile with the cyclotron resonance data.[4] No satisfactory explanation for this has yet been found.

The present paper deals with microwave measurements of dielectric constant and conductivity near liquid helium temperature.[5] It will not be concerned with the effect of free carriers. In the samples used, most of the carriers are in the impurity states at this temperature. The samples contain Ga or Sb as im-

---

* Work supported by a Signal Corps Contract.

† Now at Bell Telephone Laboratories, Murray Hill, New Jersey.

[1] F. A. D'Altroy and H. Y. Fan, Proc. Natl. Electronics Conf. **8**, 522 (1952); Phys. Rev. **94**, 1415 and 1405 (1954); **98**, 1561 (1955).

[2] T. S. Benedict and W. Shockley, Phys. Rev. **89**, 1152 (1953); T. S. Benedict, Phys. Rev. **91**, 1565 (1953).

[3] J. M. Goldey and S. C. Brown, Phys. Rev. **98**, 1761 (1955).

[4] H. Y. Fan in *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1.

[5] F. A. D'Altroy and H. Y. Fan, Phys. Rev. **100**, 1260 (1955).