

responding experiment has not yet been carried out.

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ELECTRON SPIN RESONANCE OF ACCEPTOR STATES IN DIAMOND

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Previous work^{1,2} reporting electron spin resonance in diamond has been concerned exclusively with paramagnetic centers produced by irradiation with fast neutrons. Using standard resonance techniques we have recently detected at room temperature a family of weak, narrow ($\Delta H \approx \frac{1}{3}$ oersted) resonance lines near $g=2$ in natural unirradiated diamonds. There are between 14 and 30 or more lines in the spectrum, depending on the orientation of the dc magnetic field with respect to the crystallographic axes; and these are contained in a total magnetic field spread of approximately 30 oersteds. The resonances are easily saturated, full resolution of the spectrum being obtained only when the input power to the resonant cavity ($Q_L \approx 5000$) is limited to a few microwatts. The diamonds, supplied by the Rough Diamond Company, New York City, displayed a yellowish coloration whose intensity varied from sample to sample.

It is proposed that the observed spectrum is due to bound aluminum acceptors. This interpretation is based on the following arguments: The results of previous spectrographic studies³

of the naturally occurring impurities in diamond indicate that aluminum is one of the most frequently found elements in diamonds. It is furthermore likely⁴ that aluminum with three outer electrons would enter the diamond lattice substitutionally and that a large fraction of the resulting number of "holes" would be bound to their acceptor atoms even at room temperature because of the large ionization energy of diamond as compared to germanium and silicon. One can account qualitatively for the observed spectrum by considering the spin resonance of an unpaired electron localized along one of the four tetrahedral bonds joining an aluminum atom with its nearest neighbor carbon atoms. A small amount of *s*-character at the aluminum nucleus of the wave function of the unpaired electron will give rise to six ($J_{Al} = \frac{5}{2}$) hyperfine lines ($\Delta M_I = 0$). The interaction of the quadrupole moment of the aluminum nucleus with the field gradient of the unpaired electron will add so-called "forbidden" resonances (eight transitions $\Delta M_I = \pm 1$, eight transitions $\Delta M_I = \pm 2$) to the spectrum. The lines for which $\Delta M_I = \pm 2$ are generally pronounced only when the angle θ between the dc field H_0 and the symmetry axis for the axially symmetric electric field (the Al-C bond direction) is approximately 90° . As there are four equally probable bond directions along which the "hole" can be oriented, there will be four dissimilar but overlapping sets of lines for an arbitrary orientation of the dc field with respect to the crystal axes. In such a case the spectrum is complex and difficult to analyze. If the crystal is oriented so that the dc field H_0 is parallel to a [100] direction of the crystal, thus making an equal angle ($\theta \approx 55^\circ$) with each of the tetrahedral bonds, the four sets of lines should coincide. Experimentally this is the case (Fig. 1), and the 14 distinct lines observed in this orientation are probably the transitions $\Delta M_I = 0$, $\Delta M_I = \pm 1$.

Application of perturbation theory to reconstruct the spectrum theoretically is difficult in

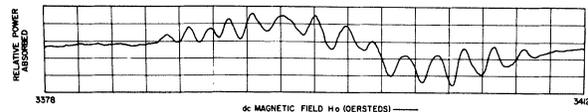


FIG. 1. Electron spin resonance spectrum of aluminum in diamond at 9478 Mc/sec (temp. = 295°K). The dc magnetic field is parallel to a [100] direction of the sample. (Note that for this orientation the line widths are greater than the $\frac{1}{3}$ -oersted value stated in the text because of the superposition of several sets of lines).

this case because the hyperfine, quadrupole, and even nuclear magnetic energies are all of the same order of magnitude. The above model accounts for most of the features of the spectrum and is quite similar to the model proposed by Griffiths *et al.*¹ and by O'Brien and Pryce² to explain the resonances observed in irradiated (smoky) quartz where the effects were ultimately due to the presence of naturally occurring aluminum impurities.

The assumption in the above model that each hole is oriented along a definite tetrahedral bond direction may imply that in the diamond-Al system the spin precession frequency in a field of approximately 3 kilogauss is large compared to a molecular resonance frequency governing the rate at which the hole flips from one tetrahedral bond direction into another. A more detailed analysis of the observed resonances is in progress.

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OSCILLATORY ETTINGHAUSEN-NERNST EFFECT*

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A number of metals which exhibit the de Haas-van Alphen effect show a similar oscillatory field dependence in their galvanomagnetic and thermomagnetic properties. Oscillations which are periodic in H^{-1} have been observed, in the case of one or more metals, in the magnetoresistance, thermal conductivity, Hall effect, and thermoelectric power.¹ Reported here are observations at liquid helium temperatures of such oscillations in the Ettinghausen-Nernst effect.

The sample was a single crystal of zinc in the form of a rectangular parallelepiped of dimensions 26.58×8.00×0.345 mm. With the crystal mounted vertically, the hexagonal axis lay in the

horizontal plane at an angle of 44° with the normal to the large face. An electric current of one ampere passed between two pressure contacts at one end of the crystal, thus heating that end. With a heat current passing down the length of the crystal, the electric potential was measured between probes placed transverse to this current. This potential was amplified and fed to a recording potentiometer, as the magnetic field was increased at a uniform rate. A photograph of one recorder trace is seen in Fig. 1. The horizontal pips are not noise but signals superimposed on the recorder trace to indicate pres-

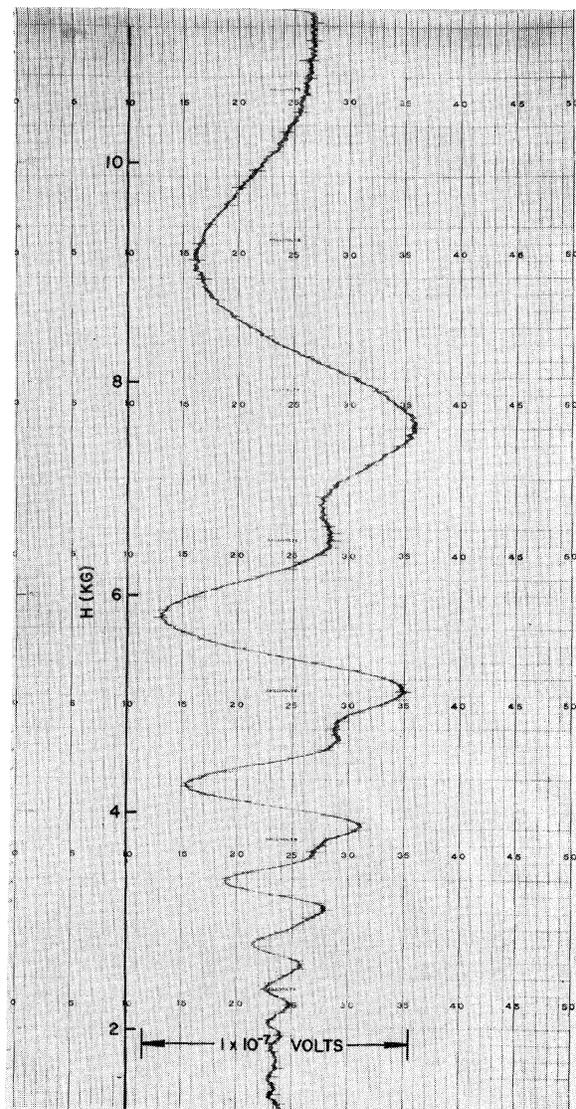


FIG. 1. A typical recording of the Ettinghausen-Nernst potential for uniformly increasing magnetic field.