ence on the Fermi Surface (John Wiley & Sons, New York, 1960), p. 100.

[7]This statement is valid even for those field directions in a plane of high symmetry for which open orbits of type A [6] occur, if such an orbit is regarded as the limiting form of a highly extended orbit. It is not true when the field is in the isolated direction of high symmetry which lies at the center of a solid angle of field directions for which open orbits of type B [2,6] occur (for example, the [100], [110], and [111] axes in Au and Cu[1]). In fact the integral in Eq. (2) cannot be defined where orbits of type B occur, and one may envisage the transformation of an electron sheet into a hole sheet as the volume occupied by electrons is expanded to fill more than half the zone by supposing the sheet to pass through intermediate stages for which orbits of type B occur for all field directions.

[8]M. H. Cohen and L. M. Falicov, Phys. Rev. Letters 5, 544 (1960).

[9]L. M. Falicov (to be published); the author is indebted to Dr. L. M. Falicov for communicating the results of his band structure calculations for Mg before publication.

[10]W. L. Gordon, A. S. Joseph, and T. G. Eck, Proceedings of the International Conference on the Fermi Surface (John Wiley & Sons, New York, 1960), p. 84; W. A. Harrison, Phys. Rev. 118, 1190 (1960); see also E. Fawcett, J. Phys. Chem. Solids (to be published).

[11]A. V. Gold, Phil. Trans. Roy. Soc. (London) A251, 85 (1958).

[12]A. R. Mackintosh, Proceedings of the International Conference on the Fermi Surface (John Wiley & Sons, New York, 1960), p. 233.

[13]See, for example, A. V. Gold and M. G. Priestley, Phil. Mag. 5, 1089 (1960), who describe the free-electron model of the Fermi surface of Sn.

RESOLVED ISOTROPIC HYPERFINE STRUCTURE OF THE ELECTRON PARAMAGNETIC RESONANCE ABSORPTION OF F CENTERS IN NaH[†]

W. T. Doyle and W. L. Williams

Physics Department, Dartmouth College, Hanover, New Hampshire

(Received April 21, 1961)

The wide, inhomogeneously broadened electron paramagnetic resonance lines of F centers in alkali halides are due to the hyperfine interactions between the center electron and the surrounding nuclei.[1,2] These lines are commonly structureless and the hyperfine interactions must be studied using the electron nuclear double resonance (ENDOR) method.[3] When the first shell contact interaction predominates, however, and the nuclear spin of the alkali ion is 3/2, one expects a nineteen-line spectrum with relative intensities of the components of 1, 6, 21, 56, 120, 216, 336, 456, 546, and 580, corresponding to total shell nuclear magnetic quantum numbers of $\pm 9, \cdots, 0$, respectively.[1] In a few crystals, viz., LiF and NaF,[4,5] and RbCl,[6] a partially resolved spectrum has been observed. The structure of the LiF line, originally reported to be isotropic,[4,5] is now known to possess many more than the predicted nineteen lines[7] and to be anisotropic.[8] ENDOR studies[9] have shown that the first shell interaction does not predominate in this case, but subsequent calculations[10] have established that the resolved spectrum is consistent with the ENDOR results and with the de Boer model. It seems likely that in RbCl, too, the spectrum is due to more than the first shell nuclei alone,

since the spectrum could not be reconciled with the known isotopic abundances of the alkali ions.[6] In NaF, on the other hand, we believe that the resolved spectrum is due to the first shell interaction as originally reported.[4,5] We have found that the resolution of the NaF spectrum is unimpaired when the sample is in the form of a powder, whereas in LiF the resolution is washed out when the sample is powdered. NaF is thus the only alkali halide in which the hyperfine interaction with the first shell nuclei has been seen directly. However, even in NaF not all of the nineteen lines have been observed, and the signals observed were neither well enough resolved nor strong enough to permit a direct comparison with the predicted relative strengths of the nineteen lines. Since the favorable circumstances in NaF may be traced in part to the relatively large hyperfine interaction constant of sodium, and in part to the low atomic number of fluorine, we were led to examine the spectrum of the very similar crystal NaH, in which it was to be expected that the situation should be even more favorable for the appearance of a resolved first shell structure.

It is known that the hydrides may be colored by radiation and that in LiH the principal product

is colloidal lithium when the irradiation is carried out at room temperature.[11] In contrast with this, x-ray induced F centers in sodium hydride are stable at room temperature, although they are thermally bleached within minutes at temperatures around 100°C. The rate of production of F centers, as well as the optical and thermal bleaching properties, monitored using the electron spin resonance signal, were all found to parallel closely the corresponding properties in the halides.

In view of the difficulty of producing single crystals of NaH, the observations reported here were made using commercial sodium hydride powder. This has the advantage of tending to smear out the small anisotropic contribution. This material usually contains an appreciable amount of excess sodium, so the samples used were additively colored at the start. All of the samples exhibited a strong, narrow electron paramagnetic resonance (EPR) line which was identified by its shape, g value, and temperature independence, as conduction electron spin resonance in sodium metal. The narrow resonance was not changed by irradiation and, since it could not be saturated with the microwave power available, it was a simple matter to subtract it from the easily saturated F-center resonance developed by the irradiation.

In Fig. 1 the F-center resonance alone is shown. This curve was obtained by taking the difference between a high- and low-power spectrum. The shape of the spectrum agrees in detail with the predictions of the de Boer model. There are 19 well-resolved lines. The spacing is determined by the first shell hyperfine interaction constant $A(1)$. All of the relative intensities agree with the theoretical distribution to within the experimental error of a few percent, as judged by comparison with computed curves of sums of Gaussian derivatives. It appears from such curves that the ratio of peak separation A to the full
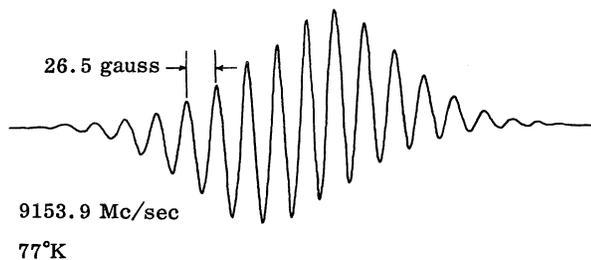
Table I. Experimental results. The g value has been corrected to second order in A/H_0 using the Breit-Rabi equation. The uncertainty quoted for g is the rms deviation from the mean of 15 determinations. The hyperfine interaction energy, A, and the modulus of the wave function at the nucleus, $|\psi|^2$, for the first and second shells were obtained from the peak separation and width, respectively.

$g = 1.9979 \pm 0.0004$	$|\psi(1)|^2 = 4.3 \times 10^{23}$ cm^{-3}
$A(1) = 26.5 \pm 0.2$ gauss	$|\psi(2)|^2 = 0.26 \times 10^{23}$ cm^{-3}
$A(2) = 6.1 \pm 0.3$ gauss	

width, 2σ, between points of maximum and minimum slope (rms width for a Gaussian shape) is about 1.25 ± 0.1. Since the ENDOR studies on LiF have shown that only the first two shells interact strongly with the F-center electron, it is probably safe to assume that the width of the individual peaks is due primarily to the twelve second shell nuclei. When, as in NaH, these have spin 1/2, the relationship of the hyperfine constant to the linewidth is $A = \sigma/\sqrt{3}$.[5] The observed values of A as well as the modulus of the F-center wave function at the nuclei, $|\psi|^2 = 3IA/8\pi\mu$, for the first and second shell are given in Table I. Because they are based upon peak widths rather than resolved spacings, the second shell values are somewhat less reliable. The g value tabulated was corrected to second order in A/H using the Breit-Rabi equation. For this purpose the first shell is treated as a single entity with shell spin $I = 9$.[5] As expected, the g shift is negative and agrees in order of magnitude with the shifts found in the halides.

It appears that sodium hydride is a particularly favorable crystal for viewing the hyperfine interaction of the F-center electron with the first shell nuclei. The validity of the de Boer model is immediately apparent in the resolved spectrum.

26.5 gauss →

9153.9 Mc/sec

77°K

FIG. 1. Derivative of EPR absorption curve for F centers in NaH, showing a well-resolved 19-line spectrum of de Boer shape.

[1]A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, Phys. Rev. 91, 1066 (1953).
[2]A. M. Portis, Phys. Rev. 91, 1071 (1953).
[3]G. Feher, Phys. Rev. 105, 1122 (1957).
[4]N. Lord, Phys. Rev. 105, 756 (1957).
[5]G. J. Wolga and M. W. P. Strandberg, J. Phys. Chem. Solids 9, 309 (1959).
[6]H. C. Wolf and K. H. Hausser, Naturwissenschaften 46, 646 (1959).

[7]Y. W. Kim, R. Kaplan, and P. J. Bray, Bull. Am. Phys. Soc. 3, 178 (1958).

[8]Y. W. Kim, R. Kaplan, and P. J. Bray, Phys. Rev. Letters 6, 4 (1961).

[9]W. C. Holton, H. Blum, and C. P. Slichter, Phys. Rev. Letters 5, 197 (1960).

[10]H. Blum and W. C. Holton, Bull. Am. Phys. Soc. 6, 112 (1961).

[11]W. T. Doyle, D. J. E. Ingram, and M. J. A. Smith, Phys. Rev. Letters 2, 497 (1959).

MAGNETIC COOLING WITH PARAMAGNETIC METALS*

R. D. Parks and W. A. Little

Department of Physics, Stanford University, Stanford, California

(Received April 19, 1961)

In this Letter we report on an investigation of the magnetic properties at low temperatures of a series of thorium-erbium alloys. These alloys are unique in that even for high spin densities magnetic ordering occurs only at temperatures well below 1°K. For this reason it is possible to use such alloys as the cooling agents in adiabatic demagnetization experiments.

Conventional paramagnetic salts used for this purpose such as potassium chrome alum and ferric ammonium alum, being dielectric crystals, have a thermal conductivity due to the lattice which varies as T^3. Consequently, at temperatures below 0.1°K this becomes exceedingly small, resulting in very low rates of heat transfer between the paramagnetic salt and the sample being cooled. In a metal, however, the thermal conductivity which is due to the conduction electrons varies linearly with T. For temperatures below 0.1°K this greatly exceeds that of a dielectric crystal. In addition a metal is more durable than conventional cooling salts which decompose on exposure to air or heat. For these reasons we have looked for a paramagnetic alloy which could be used instead of a paramagnetic salt for magnetic cooling. This search led us to the study of thorium—rare earth alloys. As reported earlier,[1] we found some magnetic cooling below 1°K with thorium-dysprosium alloys. We have now investigated the thorium-erbium system and have found excellent cooling properties to temperatures below 0.1°K.

The alloys were prepared by melting thorium and erbium metals together under argon in an arc furnace. This method is described in more detail elsewhere.[1] A series of Th-Er samples were adiabatically demagnetized from initial temperatures of 0.73°K and varying magnetic fields up to 8400 gauss. The cooling curves appear in Fig. 1. When demagnetized from fields of about 8000 gauss, all the samples cooled
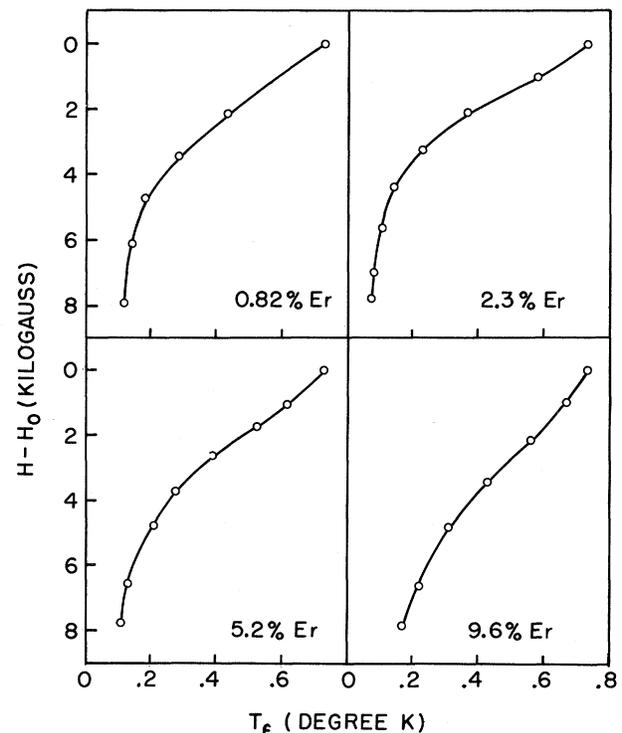

FIG. 1. Magnetic cooling curves of different Th-Er alloys. T_f is the final temperature reached by the samples when demagnetized from an initial temperature of 0.73°K and from a magnetic field of H. A residual field of 500 gauss (H_0) was left on the sample to suppress either superconductivity or antiferromagnetic ordering. The complete removal of H resulted in a small increase in temperature which is characteristic of the onset of either phenomenon.

to temperatures below 0.2°K. The 2.3% Er sample reached a final temperature of 0.07°K. From these curves one should expect that for larger values of H/T_i (T_i = initial temperature) the samples should reach even lower final temperatures. In the most dilute sample (0.82% Er) the electronic entropy is an appreciable fraction