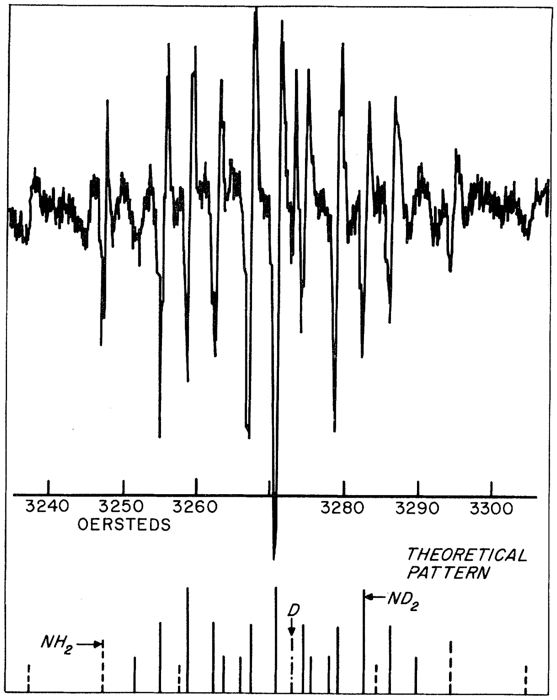

FIG. 2. Electron spin resonance spectrum of ND_2 in an argon matrix at 4.2°K. Also present are spectra of D and NH_2 and weak traces of NHD.

coupling constants were evaluated, as discussed later, and the complete spectrum calculated. The predicted positions of the spectral lines are indicated in the bottom of the figure. Eleven of the lines are clearly recognized in the recording. The others are too close to other lines to be resolved. In addition, one sees the center deuterium atom line, slight traces of NHD, and several lines from NH_2 arising from some remanent NH_3 in the system. The lines of NH_2 and ND_2 were recorded individually on expanded sweeps to determine their field positions with high precision.

If one solves the spin Hamiltonian for the magnetic energy, W, to the first order approximation, one obtains

$$W = M_J g_J \mu_0 H + A M_J \sum_i m_i + B M_J M_I(\mathrm{N}) + \mu_0 H \left[g_I \sum_i m_i + g_I(\mathrm{N}) M_I(\mathrm{N}) \right] \quad (1)$$

where m_i is the nuclear magnetic quantum number of hydrogen (± 1/2) in the case of NH_2 or of deuterium (1, 0, -1) in the case of ND_2, and the other symbols have their usual significance. The hyperfine coupling constants A and B and the electronic g-factor, g_J, can be calculated from the data. The results are given in Table I.

Table I. Electron spin resonance results for NH_2 and ND_2

Radical	A (Mc/sec)	B (Mc/sec)	g_J
NH_2	67.03(20)	28.90(20)	2.00481 (8)
ND_2	10.27(20)	33.28(20)	2.00466 (8)

The ratio of the hydrogenic coupling constants, $A_H/A_D = 6.526$, is in excellent agreement with the predicted ratio, $g_I(\mathrm{H})/g_I(\mathrm{D}) = 6.514$. The difference between the values for the nitrogen coupling constants is unexpected, indicating that the electronic wave functions for the two radicals are somewhat different. It is clear that the inclusion of higher-order terms in the solution of the spin Hamiltonian would not bring the B values into closer agreement. Apparently, the hyperfine interaction with the nitrogen atom is rather sensitive to some small perturbation in the electronic state. Thus far, we have been unable to account for the discrepancy by considering zero-point vibration and the differences in the rotational states of these molecules.

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* This work supported by Bureau of Ordnance, Department of the Navy.

[1] Jen, Foner, Cochran, and Bowers, Phys. Rev. **104**, 846 (1956).

[2] Foner, Jen, Cochran, and Bowers, J. Chem. Phys. **28**, 351 (1958).

[3] Jen, Foner, Cochran, and Bowers, (to be published).

SPIN EXCHANGE IN SUPERCONDUCTORS

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The only known superconductor among the rare earth elements is lanthanum. The elements following lanthanum in the periodic system are either strongly paramagnetic or ferromagnetic, with magnetic moments which are due to their $4f$ electrons. In lutetium, 14 electrons have filled this $4f$ shell entirely and the element does not show pronounced paramagnetism. Lutetium, however, is not superconducting above 1.02°K because its metallic radius has become much smaller and at the same time it is much heavier than lanthanum.

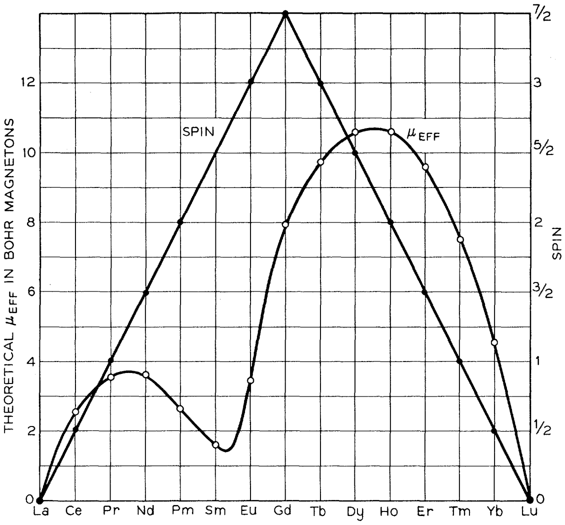

FIG. 1. Effective magnetic moments and spins of the rare earth elements (see reference 2).

The effective magnetic moments of the rare earth elements follow Van Vleck's well-known curve,[1] Fig. 1. These moments, which originate in the low-lying $4f$ shell, are usually assumed to remain undisturbed in almost all chemical compounds which include these elements. It was therefore our hope that by dissolving small amounts of the magnetic rare earth elements in lanthanum, the superconducting transition would be affected by the dipole field from the moment of the rare earth atoms. In Fig. 2 we show the superconducting transitions of lanthanum samples in which 1 at.% of various rare earth elements has been dissolved. It is immediately apparent from these data that the simple assumption that an increase in effective moment should go hand in hand with a decrease of the superconducting transition temperature does not work at all. Instead, the depression of the superconductivity seems to be correlated only with the <u>spin</u> of the solute atoms. (The anomalous behavior of cerium is probably caused by the rather easy shift of part of the $4f$ electron into the $5d$ band; this occurs in the pure metal at low temperature or under pressure.)

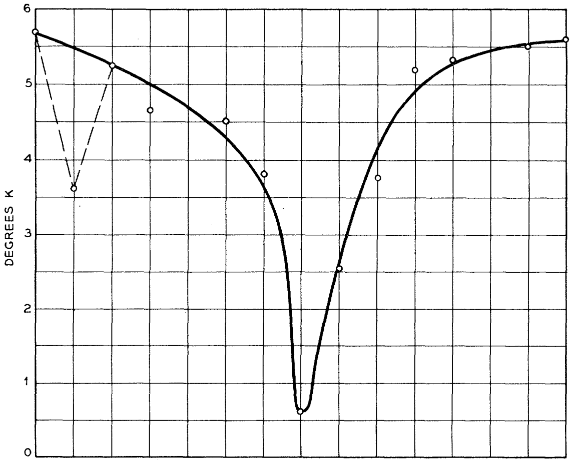

FIG. 2. Superconducting transition temperatures of 1 at.% rare earth solid solutions in lanthanum.

The change in the superconducting transition temperature of lanthanum caused by varying the dissolved amounts of gadolinium was investigated in more detail and the results are shown in Fig. 3. The superconducting transition temperature seems to be a strictly linear function of the amounts of dissolved gadolinium. 2.5 at.% or more of gadolinium in lanthanum causes this solid solution to become ferromagnetic above 1°K. The Curie points within this range are an approximately linear function of the percentage of gadolinium. This suggests the presence of a coupling which aligns the moments spontaneously in these materials and which is different from overlap exchange forces usually considered since the coupling extends over several lattice spacings and is proportional in magnitude to the amount of gadolinium added. By dissolving gadolinium in yttrium, a nonsuperconducting metal, only moderate paramagnetism was observed and solid solutions with even as much as 10 at.% gadolinium did not show any ferromagnetism. On the other hand, solid solutions of gadolinium in thorium, another superconductor, were again ferromagnetic.

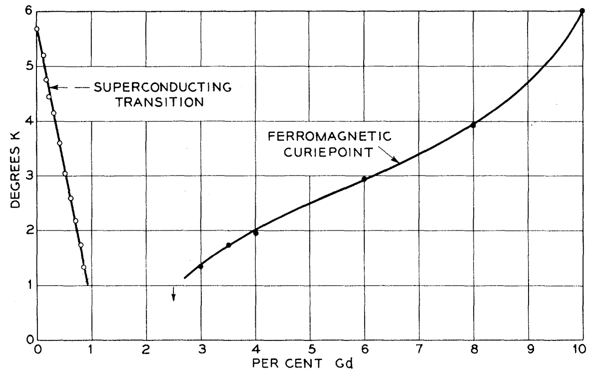

FIG. 3. Ferromagnetic and superconducting transition temperatures of solid solutions of gadolinium in lanthanum.

These data suggest that an exchange over conduction electrons[2] leading to ferromagnetism is easy to bring about in an element which by itself is a superconductor.[3]

In an earlier paper,[4] the question was raised whether an electronic configuration favorable to superconductivity might also be favorable to ferromagnetism. The experimental data by which we tried to illustrate this question started with the demonstration that while the germanides of most of the rare earths were either ferromagnetic or superconducting, all investigated silicides with the exception of $PrSi_2$, were neither ferromagnetic nor superconducting. We have now found that this dualism can also be illustrated by forming the AB_2 Laves phase compounds. If B is ruthenium then for A=Sc, Y, La, Ce we find superconductivity and for A=Pr•••Gd•••we have ferromagnets. In Table I the corresponding transition temperatures are listed.

Table I. Transition temperatures of ruthenides.

Compound	Behavior	T_c
$ScRu_2$	superconducting	1.67°
YRu_2	superconducting	1.52°
$LaRu_2$	superconducting	1.63°
$CeRu_2$	superconducting	4.9°
$PrRu_2$	ferromagnetic	40°
$NdRu_2$	ferromagnetic	35°
$ErRu_2$	ferromagnetic	13°

It appears rather remarkable that the compound $CeRu_2$, containing an element with a $4f$ electron, should be superconducting. However, the lattice constant reveals that in this compound at least 25% of the $4f$ electron has been squeezed into the outer shells.[5] In this way, the magnetic moment is reduced, and the number of valence electrons (hence the superconducting transition temperature) is raised considerably.

In summary, we wish to point out that there seems to be a correlation between the Curie points in certain alloys and compounds which include the rare earth elements and the superconducting transition temperatures of other closely related alloys and compounds.

Finally, we would like to thank P. W. Anderson and J. K. Galt for many helpful discussions.

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[1] T. H. Van Vleck, Magnetic and Electric Susceptibilities (Oxford University Press, Oxford, 1932), pp. 243, 244.

[2] F. H. Spedding, Progress of Low-Temperature Physics (North-Holland Publishing Company, Amsterdam, C. Zener, Phys. Rev. 81, 440, (1951); S. V. Vonsorsky, J. Exptl. Thearet. Phys. U.S.S.R. Vol. II, p. 391; 981, (1946).

[3] Calculations by C. Herring, to be published in a subsequent paper, make this idea plausible.

[4] Matthias, Corenzwit, and Zachariasen, Phys. Rev. (in press).

[5] We want to thank Professor W. H. Zachariasen for his help and discussion with respect to these matters.

F AND *V* CENTERS THERMOLUMINESCENT RECOMBINATION*

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In the course of experiments on thermoluminescence of alkali halides, to be published in the near future,[1] the writers have found that current theories, all treating the process as a first-order one,[2] do not allow an easy interpretation of all the experimental features. It was decided, therefore, to investigate a particular case of thermoluminescence in which the nature of the electronic traps was known so that the task of setting up a model which could undergo quantitative examination would be greatly facilitated. X-rayed NaCl was chosen, in which F centers can give rise to thermoluminescence, as is well known.

Using an idea previously advanced by Johnson[3] and by Hill and Schwed,[4] a second-order process was considered and a phenomenological theory of F center thermoluminescence was carried out, starting from the equation

$$-dN_i/dt = p_i \exp(-E/kT)\, N_i(N_i - N_{i0} + n_0). \qquad (1)$$

This equation is based on the hypothesis that there are present in the crystal, together with the F centers, also some kinds of "luminophor" centers L_i. The electrons are supposed to be able to escape from the F-center ground level, with a thermal activation energy E, to reach some higher, excited level (perhaps in the conduction band) from which they can undergo a radiative transition to the L_i levels, with probability factors p_i. N_i means the luminophor center concentration, n the F-center concentration, the index 0 identifying the initial values at the beginning of the ith peak of the "glow curve" considered.

This way of reasoning can interpret satisfactorily many experimental features, and, moreover, it contains the following implications:

(a) The analysis of the glow curves must give a unique E value for all the peaks.[5]

(b) The light of each peak must have its own wavelength.