

is approximately 73% of its value in normal tin. This is consistent with the results of Reif<sup>1</sup> for mercury.

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structure by means of x-rays.

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<sup>1</sup>F. Reif, Phys. Rev. **106**, 208 (1957).

<sup>2</sup>Knight, Androes, and Hammond, Phys. Rev. **104**, 852 (1956).

<sup>3</sup>N. Bloembergen and T. J. Rowland, Acta Met. **1**, 731 (1953).

<sup>4</sup>P. C. Lauterbur (private communication); P. C. Lauterbur and J. J. Burke, Abstracts of papers presented at 133rd meeting of the American Chemical Society 1958, p. 15L.

### EFFECTS OF SPIN-ORBIT COUPLING IN RARE EARTH METALS, AND IN SOLUTIONS OF RARE EARTH METALS

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There are three phenomena of the same general character that occur in rare earth metals or solution thereof:

(1) The reduction of superconducting transition temperature in dilute solutions of the rare earths in lanthanum,<sup>1</sup> or of rare earth compounds in CeRu<sub>2</sub><sup>2</sup> or OsRu<sub>2</sub>.<sup>3</sup>

(2) An extra resistance of the pure metals (and presumably of the alloys<sup>4</sup>) due to spin disorder scattering.

(3) An indirect exchange coupling among the ion spins in analogy with the Ruderman-Kittel mechanism of nuclear spin-spin interaction in metals.<sup>5</sup> This indirect exchange is thought to be responsible for the observed ferromagnetism and/or antiferromagnetism at temperatures of the order of 100°K.<sup>6</sup>

All three effects are supposed to arise from the exchange interaction  $A\vec{S}_{\text{ion}}\cdot\vec{S}_{\text{cond}}$  of the *f*-shell spins with the spins of the conduction electrons. The purpose of this note is to point out the bearing which spin-orbit coupling has on the interaction in the above three cases. Except in the case of europium, discussed separately, we assume the multiplet splitting to be much greater than crystal field splitting. We consider the above three effects in turn.

(1) In a previous note by Herring<sup>7</sup> and in a detailed paper by Suhl and Matthias,<sup>8</sup> it was shown that on the basis of the Bardeen, Cooper, Schrieffer

theory of superconductivity,<sup>9</sup> one expects the exchange interaction to lower the transition temperature of the superconducting state. This depression results from the fact that, partly because of the energy gap, and partly because of the spin-coherence properties of the BCS wave function, the exchange scattering lowers the free energy of the normal state more than that of the superconducting state. It was shown in reference 8 that if spin-orbit coupling is neglected, the reduction is proportional to  $\vec{S}^2 = S(S+1)$ , while when it is included, the reduction is very nearly proportional to the square of the projection of  $\vec{S}$  on the  $\vec{J}$  appropriate to the ground state. The only exception is europium ( $J=0$ ) for which this projection vanishes. In almost all other cases, the agreement with the observed depression of  $T_c$  was substantially improved by using  $\vec{J}(\vec{S}\cdot\vec{J})/J^2$  rather than  $\vec{S}$ . The reason is as follows: The calculation of the depression of free energy is a matter of second order perturbation theory. The operator  $\vec{S}_{\text{ion}}\cdot\vec{S}_{\text{cond}}$  connects the ground state to states with one conduction electron excited and with  $J$  either unchanged or changed by 1. Since in the ground state  $J$  has its maximum or minimum permissible value,<sup>10</sup> only the  $J-J-1$  or the  $J-J+1$  transition need be considered. For definiteness we shall from now on consider only the case  $J-J-1$ . Now the state  $\psi(J-1)$  is removed from the ground state energy by  $\Delta$ , the multiplet

splitting, and  $\Delta$  makes its appearance in the energy denominator, in second order perturbation theory, in addition to the electron excitation energy. Transitions within the ground state of  $J$  involve the latter energy only, which for the important transition is small compared with  $\Delta$ . Therefore, excitation to the state  $\psi(J-1)$  does not contribute appreciably to the energy depression except in europium, where the total effect should come from this excitation. In any case, the fact that only  $J \rightarrow J-1$  transitions are involved, enables us to calculate both the  $\langle J|\vec{S}|J\rangle$  and the  $\langle J|\vec{S}|J-1\rangle$  matrix elements by a simple sum rule. We know that in any representation, in particular in the  $\vec{J}$  representation,  $\vec{S}^2$  must equal  $S(S+1)$ . That is to say,

$$|\langle J|\vec{S}|J\rangle|^2 + |\langle J-1|\vec{S}|J\rangle|^2 = S(S+1).$$

But the first term is  $S(S+1)[\cos^2(\vec{S}, \vec{J})]_{\text{ground state}}$ ; hence the last term on the left-hand side must be  $S(S+1)[\sin^2(\vec{S}, \vec{J})]_{\text{ground state}}$ .

To summarize: For elements other than Eu, only the  $\cos^2$  term need be considered, since the energy denominator of the term involving  $\sin^2$  is of order  $\Delta \sim 1000 \text{ cm}^{-1}$  whereas the important difference in the reductions of free energy of the normal and superconducting states derives from electron excitations of order  $\hbar\omega_{\text{Debye}} \sim 200 \text{ cm}^{-1}$ . In the case of europium, however, only the  $\sin^2$  term survives and equals unity, so that  $\vec{S}^2$  may be replaced by the spin-only value. We have computed the corresponding depression of  $T_c$ . To account for the data<sup>1</sup> we require a value of  $\Delta$  between 0.1 and 0.2 times the Debye energy, i.e., 20 to 40 wave numbers. Even though  $\Delta$  for europium should be moderately small (perhaps 100 to 200 wave numbers) it is not easy to see why it should be as small as this. Perhaps part of the reason is that the  $f$  shell attempts to complete itself at the expense of the outer electrons, leading to a larger depression in  $T_c$  due to the resulting larger value of the spin.

(2) We now turn attention to spin disorder resistance. Anderson and Legvold<sup>2</sup> have calculated the spin disorder resistance in rare earth metals, to the right of Gd inclusive by a subtraction procedure on the raw data correcting for phonon and impurity scattering. For all of these elements  $\Delta \gg 300^\circ\text{K}$  so that real collisions involving a change in  $J$  are negligible (like  $e^{-\Delta/kT}$ ). The only resistance-contributing matrix elements are those diagonal in  $J$ ; hence we expect a dependence like  $S(S+1)\cos^2(\vec{S}, \vec{J}) = [(J+1)/J]S^2$  for elements to the right of Gd. A detailed com-

Table I. Spin disorder resistance of rare earth metals to the right of Gd. Column 2 gives the data referred to Gd, corrected by Anderson and Legvold for phonon and impurity scattering. Column 3 gives the ratio expected on the basis of spin alone (zero spin-orbit coupling). Column 4 gives the ratio expected when spin-orbit effects are included.

Element	"Observed"	Ratio on spin basis alone	Spin-orbit factor included
Gd	1.00	1.00	1.00
Tb	0.76	0.76	0.67
Dy	0.64	0.56	0.45
Ho	0.34	0.38	0.29
Er	0.22	0.24	0.16
Tm	0.09	0.13	0.08
Yb	0.01	0.05	0.02

parison with the estimates of Anderson and Legvold (Table I) shows that accord with experiment is considerably worsened by inclusion of spin-orbit effects. As comparison with the data on suppression of superconductivity was improved by inclusion of spin-orbit effects (and this was comparison with "raw" data), we feel that the estimate of Anderson and Legvold of the spin-disorder resistance is quite likely to be quantitatively unreliable. There is no obvious reason why, in one situation, the orbital moment should be quenched, and not in the other.

We may note that Eu presents an extremely interesting case as here  $\Delta J=0$  is forbidden. Inelastic scattering will give a spin-disorder resistance proportional to  $e^{-\Delta/kT}$ , and crystalline field effects will mix a small amount of  $J=2$  into the ground state to give a small temperature-independent term for a certain range (no spin order). We know of no experimental verification of this prediction.

(3) Finally we point out how the indirect spin-spin exchange is corrected for spin-orbit coupling. We follow reference 5. Then the Fourier transform of the exchange potential is

$$F(q) = A^2 S(S+1) \left[ \cos^2(\vec{S}, \vec{J}) \sum_p \frac{1}{\epsilon(p) - \epsilon(p+q)} + \sin^2(\vec{S}, \vec{J}) \sum_p \frac{1}{\epsilon(p) - \epsilon(p+q) + \Delta} \right].$$

It is thus seen that the short-range part of the potential (high  $q$ ) is unaffected by spin-orbit coupling whereas a portion of the long-range part is damped out at distances of  $O[(\epsilon_F/\Delta)a]$ , where

$a$  is the lattice spacing. Thus a change in shape is brought about. If ferromagnetism arises from delicate balance of the oscillating parts of the Kittel-Ruderman potential, it is quite possible that the above-mentioned change in shape could bring about qualitative changes in magnetic properties. The statistical mechanical consequences are being worked out at present, both for pure samples and for dilute alloys.

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<sup>1</sup>Matthias, Suhl, and Corenzwit, Phys. Rev. Lett. 1, 92 (1958).

<sup>2</sup>Matthias, Suhl, and Corenzwit, Phys. Rev. Lett. 1,

449 (1958).

<sup>3</sup>Suhl, Matthias, and Corenzwit, J. Phys. Chem. Solids (to be published).

<sup>4</sup>G. S. Anderson and S. Legvold, Phys. Rev. Lett. 1, 322 (1958).

<sup>5</sup>M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).

<sup>6</sup>For example: Thoburn, Legvold, and Spedding, Phys. Rev. 110, 1298 (1958).

<sup>7</sup>C. Herring, Proceedings of the Kamerlingh-Onnes Memorial Conference on Low-Temperature Physics, Leiden, Holland, 1958 (unpublished).

<sup>8</sup>H. Suhl and B. T. Matthias, Phys. Rev. (to be published).

<sup>9</sup>Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957).

<sup>10</sup>Depending on whether the element is to the right or left of Gd.

## POLARIZATION OF PHOTOCONDUCTIVITY EXCITATION BANDS IN CdS SINGLE CRYSTALS

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The wavelength of light required to excite the maximum photoconductivity in CdS crystals has been found to vary with its plane of polarization in respect to crystal orientation.<sup>1</sup> Gobrecht and Bartschat<sup>2</sup> have previously observed this effect. The crystals we used were obtained by vapor phase growth in a  $H_2 - H_2S$  atmosphere. These samples were ribbon-type single crystals 5 to 10 mm long, 1 mm wide, 10 to 100  $\mu$  thick with the  $c$  axis in the plane of the ribbon and usually inclined at some angle to the long, straight edges of the crystal. Ohmic contacts were made to the crystal by evaporating indium onto its ends.

The photoconductivity was excited by monochromatic light from a Beckman DU spectrophotometer provided with a polarizer over the exit slit and with the plane of the crystal perpendicular to the incident light. The photocurrent was measured with a Keithley 200B electrometer with 45 or 90 volts applied across the crystal. In these experiments, the photocurrent was measured as a function of wavelength, with the polarizer set at a given angle. The relation of the monochromator polarizer to the  $c$  crystal axis was then determined with a polarizing eyepiece crossed with respect to polarizer. The pair of crossed polarizers was rotated to determine the extinction angles and thus the  $c$  axis.

Spectral response of photocurrent for these crystals was typical of CdS, i.e., beginning with

a short-wavelength tail, rising to a peak, and falling off rapidly at first and then more slowly toward the long wavelengths.<sup>2</sup> Figure 1 gives the change in wavelength at the photocurrent maximum,  $\Delta\lambda(\max)$ , as a function of the angle of polarization of incident light with respect to the  $c$  axis for a typical crystal. In all, 27 crystals from 14 separately grown batches were examined and  $\Delta\lambda(\max)$  was found to be  $39 \pm 5$  A or approximately 0.019 ev. When the electric vector  $\vec{E}$  was parallel to the  $c$  axis, the wavelength of exciting light was a minimum ( $\lambda_{\parallel} = 5069$  A; and when perpendicular, a maximum ( $\lambda_{\perp} = 5108$  A).

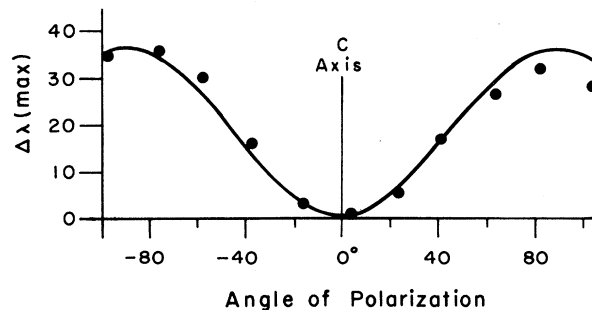


FIG. 1. Change in wavelength for photoconductivity maximum  $\Delta\lambda(\max)$  as a function of angle between incident plane polarized light and  $c$  axis of crystal. In the crystal shown,  $\lambda_0$  is the wavelength of maximum photocurrent for excitation with light parallel to the  $c$  axis. The average  $\Delta\lambda = 39 \pm 5$  A.