the E vector perpendicular to the magnetic field indicating that the transition is electric dipole in nature. The linewidth of the lines is strongly temperature dependent and the lines are not resolved at 77°K. At 1.6°K there is reduced intensity in the long-wavelength line indicating that the energy splitting of 1.5 cm^{-1} occurs in the ground state.

The following model is proposed for these centers. The center consists of a Ca^+ ion in a subsitutional position with associated charge compensation. There are three simple possibilities for this charge compensation:

(a) F^- vacancy in nearest-neighbor position, the center having [111] orientation.

(b) M^+ interstitial, the center having [100] orientation.

(c) M^{3+} ion in nearest positive ion position, the center having [110] orientation.

Model (a) is favored since it does not require a compensating impurity ion and accounts for the ground-state splitting in the following manner. In the free Ca^+ ion the $3d$ levels are about 13 700 cm^{-1} above the $4s$ ground state. In a cubic environment the e orbitals for the $3d$ electron will be lowered in energy relative to both the t_2 orbitals for the $3d$ electron and the $4s$-electron orbital. Hence the ground state may be a ^2E state which is unsplit in first order by either a trigonal field or spin-orbit coupling. The splitting in second order is given by

$$\delta = 2\sqrt{2}\zeta v'/\Delta,$$

where ζ is the spin-orbit coupling constant for a $3d$ electron, 24 cm^{-1} for Ca^+ free ion. The cubic-field splitting parameter Δ for a $3d$ electron is approximately 10 000 cm^{-1}. The above formula would be consistent if the trigonal field parameter v' as defined by Pryce and Runciman[4] has a value of about 220 cm^{-1}. This seems a reasonable value. The ^2E ground state accounts for the similarity of the stress spectra with those previously observed.

The upper state is more doubtful, but an upper $4s$ state would account for there being only a single upper level with a sharp line transition. The t_2 levels of the $3d$ electron will be in this energy region. In addition to the absorption bands reported by Bontinck, there is one observable at 1.0 μ when the sample is at 77°K, but not at room temperature. The presence of this broad obsorption band, possibly due to a t_2 level, close to the sharp lines may help to explain the lack of any sharp-line fluorescence. A $d \rightarrow s$ transition is normally parity forbidden, but the lack of center of symmetry of the proposed center will cause enough mixing of states to permit an electric-dipole transition.

In conclusion, it appears that centers of this type may be found in other systems, and already sharp-line transitions have been found in the visible region for CaF_2 crystals heated in a Sr vapor. The occurrence of these sharp-line transitions enables more detailed studies to be made than is usual in color center research.

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[1] W. Bontinck, Physica 24, 639 (1958).

[2] W. A. Runciman and C. V. Stager, J. Chem. Phys. 37, 196 (1962).

[3] W. A. Runciman and C. V. Stager, J. Chem. Phys. 38, 279 (1963).

[4] M. H. L. Pryce and W. A. Runciman, Discussions Faraday Soc. No. 26, 34 (1958).

MECHANISM FOR SUPERCONDUCTIVITY IN LANTHANUM AND URANIUM*

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We would like to point out that there is experimental evidence indicating that superconductivity in the transition metals[1] is symmetric with respect to the middle of the series, where n, the number of valence electrons, is equal to six; and that Matthias' rule[2] should be modified. This leads us to propose a new mechanism for superconductivity in La and U.

Matthias[2] has proposed an empirical rule for the occurence of superconductivity in the transition elements; namely, that the most favorable values for n are approximately 3, 5, and 7. If we omit the ferromagnetic and antiferromagnetic elements, then an inspection of the data shows that $n = 5$ (V, Nb, Ta) and $n = 7$ (Tc, Re) are indeed favorable. However, for $n = 3$ we have Sc, Y,

Table I. Transition and rare earth elements. The numbers below the symbols are superconducting transition temperatures, 𝒜 means antiferromagnetic, 𝔉 means ferromagnetic, and a blank means it is not superconducting, ferromagnetic, or antiferromagnetic.

$n \equiv$	3	4	5	6	7	8	9	10
3*d*	Sc	Ti 0.39	V 5.03	Cr 𝒜	Mn 𝒜	Fe 𝔉	Co 𝔉	Ni 𝔉
4*d*	Y	Zr 0.55	Nb 9.09	Mo 0.92	Tc 8.22	Ru 0.49	Rh	Pd
5*d*	Lu	Hf 0.165	Ta 4.48	W	Re 1.7	Os 0.65	Ir 0.14	Pt
	La 6.3(α) 4.9(β)	Ce 𝒜	Pr ?	Nd 𝒜	Pm ?	Sm 𝒜	Eu 𝔉	··· ···
	Ac ?	Th 1.37(α)	Pa ?	U 0.7(α)	Np ?	Pu ?	···	···

and Lu not superconducting (nor magnetic) while La is superconducting. Placing La next to Hf in the 5*d* row was merely a convention. If, following Landau and Lifshitz,[3] we put Lu next to Hf, then all transition metals with $n = 3$ are not superconducting (see Table I). The values of n favorable to superconductivity are now 5 and 7 only, and the superconducting transition temperature is therefore a function of n nearly symmetric about $n = 6$. This is consistent with most other properties of the transition elements, for example, the binding energy,[4] the melting points, compressibilities, and the electronic specific heat (near $n = 6$).[5]

Having proposed a change to Matthias' rule in order to bring it into harmony with other properties of the d-shell elements, we now turn to the real reason why La (and U) should be separated from the Sc, Y, and Lu rows of transition elements. In the 4*f* and 5*f* series, La and U occur at the beginning of the series, and in the solid state do not have any occupied 4*f* or, respectively, 5*f* electrons.[6] La, U, and Th are superconducting. As far as is known, all other rare earth elements with partly full *f* shells are antiferromagnetic or ferromagnetic—and not superconducting. Lu, having a filled 4*f* shell, is nonmagnetic and nonsuperconducting like Y. It is understandable that Th ($n = 4$) is superconducting, but superconductivity in La ($n = 3$) and U ($n = 6$) is not consistent with the d-shell transition elements; therefore, a different mechanism is at work.

We propose that this mechanism depends upon the existence of a low-lying virtual *f* level. A model for this interaction in La (or U) might be the following. An incoming electron polarizes a lanthanum ion, i.e., excites the virtual *f* level. Due to the incipient antiferromagnetism of La (the next element Ce is antiferromagnetic), it is energetically favorable for another electron to move in and polarize a neighboring ion with opposite spin direction. Hence we have an attractive interaction between two electrons in a singlet state due to an incipient antiferromagnetism. This is not the virtual spin-wave exchange mechanism discussed by Privorockij[7] for the transition metals. It is possible that our mechanism or something similar to it, such as those proposed by Mottelson[8] or by Cohen,[9] is at work in the 3*d*, 4*d*, and 5*d* superconductors.

Although we expect magnetic impurities to have an adverse effect on superconductivity in La and U, the effect of Ce on La is anomalously large.[10] We feel that this may be due to the proximity of the occupied *f* level in Ce to the Fermi surface.

The presence of a virtual *f* level in La seems to be demonstrated by the heat capacity and paramagnetic susceptibility data for La, Y, and Lu. Whereas the electronic heat capacities are all about the same,[11] La has about 0.5 Bohr magneton, while Sc, Y, and Lu do not have as high a magnetic moment.[12] Finally, La exhibits the $A_{3'}$ crystal structure, a structure which occurs in the magnetic rare earth elements but not in Sc, Y, Lu, or anywhere else.[13]

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[1] "Transition elements" are defined to be those in the first three rows, while La through Yb are called rare earth elements.

[2] B. T. Matthias, Progress in Low-Temperature Physics, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, Chap V, p. 138.

[3] L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Pergamon Press, New York, 1958), p. 245.

[4] L. Brewer, Electronic Structure and Alloy Chemistry of the Transition Elements, edited by Paul A. Beck (Interscience Publishers, Inc., New York, 1963), p. 222.

[5] B. W. Roberts, General Electric Report No.

63-RL-3252M, 1963 (unpublished).

[6] W. H. Zachariasen (private communication).

[7] I. A. Privorockij, Zh. Eksperim. i Teor. Fiz. 43, 2255 (1962) [translation: Soviet Phys.—JETP 16, 1593 (1963)].

[8] Quoted in B. T. Matthias, T. H. Geballe, E. Corenzwit, and O. W. Hull, Phys. Rev. 129, 1025 (1963), footnote 11.

[9] M. H. Cohen, in abstracts of the Conference on the Science of Superconductivity, Colgate University, 26-29 August 1963 (unpublished).

[10] H. Suhl and B. T. Matthias, Phys. Rev. 114, 977 (1963).

[11] L. D. Jennings *et al.*, J. Chem. Phys. 33, 1849 (1960).

[12] K. A. Gschneidner and B. T. Matthias, *Rare Earth Research*, edited by E. V. Kleber (MacMillan and Company, Ltd., London, England, 1961), p. 158.

[13] K. A. Gschneidner, *Rare Earth Alloys* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1961), p. 13.

INTENSITY-INDUCED OPTICAL ABSORPTION CROSS SECTION IN CS_2

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This Letter reports the direct observation of intense radiation-induced absorption in liquid carbon disulfide and in several other "highly transparent" materials. This effect was first observed during an attempt to stimulate Raman laser emission[1,2] in CS_2. The induced absorption produced a strong cavity loading which apparently precluded Raman laser emission. To study this effect, we have made direct absorption measurements at 6943 Å. For CS_2 we find a total absorption cross section σ linear in incident photon flux F, $\sigma=\sigma_0+\sigma_1 F$, with $\sigma_1=(5\pm4)\times10^{-51}$ cm^4 sec.

Absorption measurements were made using the external beam of a Q-switched[3] ruby laser. The parallel, linearly polarized beam had the following characteristics: peak power, 1.0×10^6 watts; pulse duration, 40 nsec; spectral width of emission at 6943 Å, 2 cm^{-1}; and angular diameter at half-intensity, 0.24°.

To enhance the nonlinear absorption, the beam was focused within the sample by a lens having a 4.83-cm focal length in air. Portions of the incident and transmitted beams were reflected by 45° glass plates onto diffusely scattering white surfaces viewed through a distant lens by matched 925 phototubes provided with 6940 ± 100Å interference filters. The phototube signals were displayed on a dual-beam oscilloscope having a 12-nsec rise time.

Incident beam intensity was varied over a 20-dB range by appropriate reflecting attenuators; the laser power level was held fixed to avoid any systematic variation of the complex intensity distribution near the focus. Similarly, possible gain-bandpass errors were minimized by holding the detector signals approximately constant through the use of calibrated attenuating filters in front of the detector lens.

Figure 1(a) shows the dependence of transmitted peak power, P_t, on indicent peak power, P_0, observed for spectroscopic grade CS_2 at room temperature. The probable error is estimated to be ±30% in the absolute P_0 scale, and ±20% in the P_0/P_t scale. The data were taken over a five-week period and showed no systematic trend

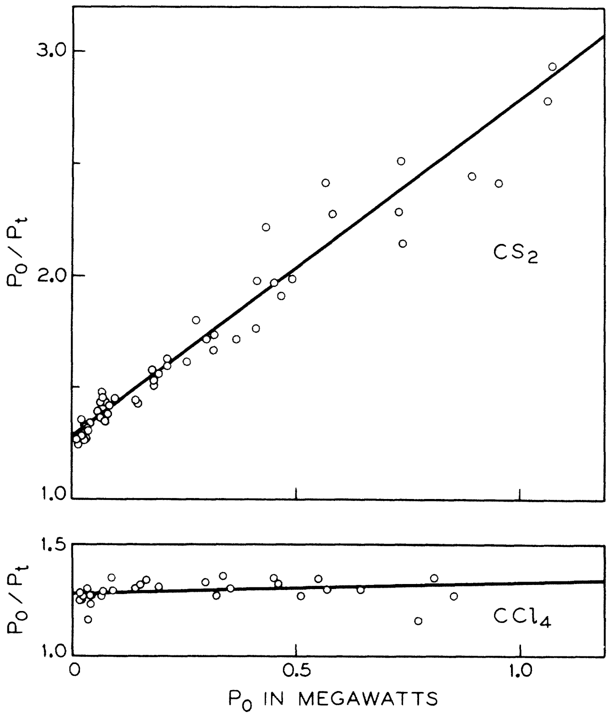

FIG. 1. Ratio of incident power P_0 to transmitted power P_t as a function of P_0.