

to see if any experimental relations exist between the susceptibilities and superconducting transition temperatures such as those suggested by Eqs. (III.21) and (III.22). We have, in fact, evidence¹ which shows that χ for the intermetallic compounds V_3Si and V_3Ga , and the metal vanadium, is less than $\chi_{sp,ht.}$ in approximately the degree predicted by Eq. (III.22) and the observed transition temperatures. In the case of Pt metal discussed in this paper for which we find $\chi > \chi_{sp,ht.}$, we conclude that $N(E_f)V$ is negative. According to Eq. (III.20), no energy gap would then exist at absolute zero and we would conclude that Pt would not be a superconductor at any temperature. Thus if superconductivity exists it must arise from considerations not included in the simple BCS theory.⁴⁴

CONCLUSIONS

It has been shown that a consistent interpretation of the Knight shift and susceptibility in platinum metal may be given and that the contributions to each from spin and orbit may be separated. The dominant contribution to K is that of core polarization resulting from the spins of d -band electrons. Both the orbital and s -electron paramagnetism are small as a result of the small number of s electrons and d holes. To construct our K versus χ diagram (Fig. 2) we have used a free-electron estimate for the s -electron susceptibility neglecting s - s and s - d interactions. Since both χ_{VV} and

χ_P^* are positive, our graphical procedure puts an upper bound on both, from which we conclude that neither one can be increased by more than a factor of 2 from the values given. The relative value of orbital and spin contributions in platinum as compared with those in vanadium is clearly consistent with the position of the Fermi level in the d band in each case.

Spin-orbit coupling, which might be thought to be important for the heavy transition metals, has been seen to have a minor effect on the band parameters determined from an analysis of the susceptibility and electronic specific heat.

In Sec. II we have given a formal treatment of the orbital and dipolar hyperfine fields in transition metals including the effects of spin-orbit coupling. The result is obtained in a form particularly suitable for calculations in the tight binding approximation which should be adequate for the d electrons in these metals.

The last section shows that the quantity $N(E_f)V$, which determines the energy gap and transition temperature in the BCS theory, also determines, in the random phase approximation the relation between the measured density of states $N(E_f)$, and the measured spin paramagnetism. Within these approximations, for V positive, a finite energy gap exists and $\chi < \chi_{sp,ht.}$, whereas, for V negative, no energy gap exists and $\chi > \chi_{sp,ht.}$. Since, for Pt $\chi \sim 2\chi_{sp,ht.}$ our theory predicts it not to be superconducting.

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⁴⁴ L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958), [English transl.: Soviet Physics—JETP **7**, 505 (1958)]. G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **38**, 966 (1960), [English transl.: Soviet Physics—JETP **11**, 696 (1960)]. P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

Faraday Rotations of Divalent Rare-Earth Ions in Fluorides. III*

Y. R. SHEN

Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts

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A large rotatory power for Eu^{2+} in cubic fluoride lattices has been observed in the visible range. At frequencies sufficiently removed from the absorption bands, the rotation is proportional to the magnetization. This suggests that the upper levels in the allowed optical transitions are of the P_J character. Measurements on CaF_2 and SrF_2 crystals doped with very low concentrations of Eu ($\sim 0.005\%$) also suggest some possible structure for the strong, sharp characteristic line of Eu^{2+} near 4000 Å. The rotatory powers of several other divalent rare-earth ions in fluorides have also been measured.

IN a previous paper,¹ we reported results of rotation measurements on several rare-earth ions in CaF_2 . In particular, we found that the divalent europium ion (Eu^{2+}) in CaF_2 has enormous rotatory power, which appears proportional to the magnetization at frequencies sufficiently removed from the absorption bands.

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¹ Y. R. Shen and N. Bloembergen, Phys. Rev. **133**, A515 (1964).

These facts are well explained theoretically.² Van Vleck and Penney³ first suggested that for S -state ions in a cubic field, both S_J and $P_{J'}$ levels in the allowed $S_J \rightarrow P_{J'}$ transitions are only slightly perturbed, and hence the rotation should be proportional to the magnetization.

² Y. R. Shen, Phys. Rev. **133**, A511 (1964).

³ J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).

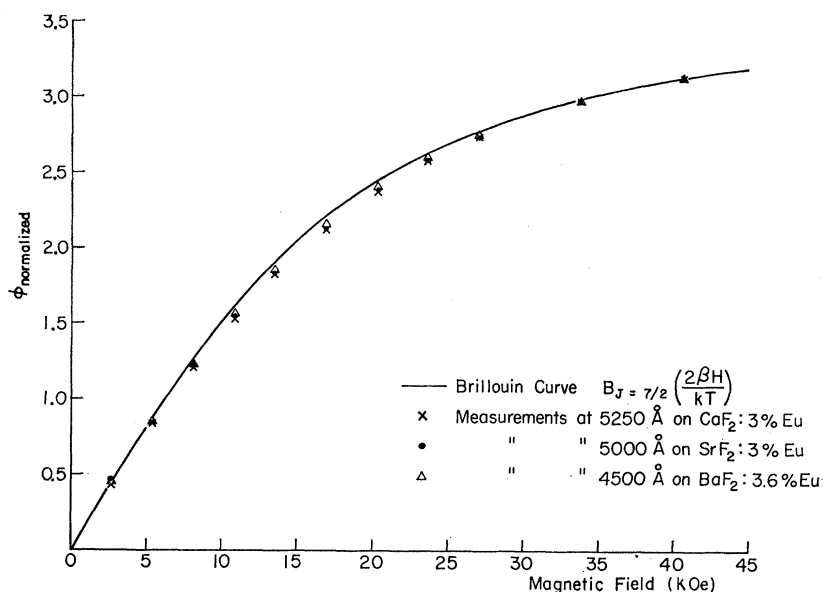


FIG. 1. Measurements of rotation versus magnetic field on CaF₂: 3% Eu, SrF₂: 3% Eu, and BaF₂: 3.6% Eu at 4.2°K. The rotations are normalized by matching to the Brillouin curve at 40.66 kOe. They shift slightly towards the Brillouin curve as the frequency moves towards the absorption band. The samples, 2.5 mm in length, were grown in a hydrogen atmosphere.

In the present note, we would like to report more results of rotation measurements on Eu-doped alkali-earth fluorides, and to show that they agree well with the proposed theory.^{2,3} The large rotatory power of Eu²⁺ also provides the possibility of studying the spectral structure of Eu²⁺ through measurements of rotation on diluted salts. While the structure of the ground octet of Eu²⁺ is fairly well understood,^{4,5} that of the optical excited states still remains unclear, although recently a few experiments have been performed.⁶⁻⁸ Here, the results of rotation measurements enable us to suggest some possible structure for the optical excited states of Eu²⁺. Several other divalent rare-earth impurities in fluorides have also been investigated.

Figure 1 gives the results of rotation measurements on CaF₂, SrF₂, and BaF₂ crystals doped with about 3% of Eu impurities grown in the hydrogen atmosphere by the Stockbarger technique. The rotations are normalized to match the Brillouin curve at the largest field employed. The cross points refer to measurements on CaF₂: Eu at 5250 Å. As the wavelength is gradually reduced to 4500 Å, the normalized rotations shift slightly towards the Brillouin curve. The maximum shift occurs near 15 kOe, and is about 0.02. The same is true for SrF₂: Eu and for BaF₂: Eu, as the wavelength is changed from 5000 to 4300 Å, and from 4500 to 4100 Å, respectively. These results show that at frequencies sufficiently removed from the absorption band,

the rotation is indeed proportional to the magnetization.

This proportionality between rotation and magnetization suggests a well-defined total angular momentum J for the optical excited states in the allowed transitions $(4f)^7 \rightarrow (4f)^6(5d)$, etc. Correspondingly, the crystal field splittings of these states should be small. It is likely that the Russell-Saunders coupling still applies to the excited electronic configurations. Then, the upper level in the allowed transitions should have a 8P_J character.² Moreover, the large rotatory power of Eu²⁺ at visible frequencies (Fig. 2) forbids the over-all splitting of the P multiplet to be less than 1000 cm⁻¹, as the degeneracy of the P multiplet leads to zero paramagnetic rotation.²

The dispersion curves of these samples, in the visible range near absorption, are shown in Fig. 2. We notice that as the host lattice is changed from CaF₂ to SrF₂ to BaF₂, the absorption band edge shifts to the short wavelength side, and the dispersion curves shift correspondingly. For different host lattices, if the light frequencies are at the same distance away from the band edges, the rotatory powers of Eu²⁺ appear nearly the same. This shows that the cubic field does not have large effect on the spectral character of Eu²⁺.

In order to study the details of the spectral character, diluted samples must be used. We are particularly interested in the narrow absorption line at 4130 Å for Eu²⁺ in CaF₂, and at 4011.5 Å for Eu²⁺ in SrF₂ [Fig. 3(a),(b)]. This narrow line has large circular dichroism in the presence of magnetic field. Consequently, even for a very small concentration of Eu²⁺ (~0.005%), the rotation in the vicinity of the line is appreciable. It can therefore be used as a means to probe the character of the line.

Figure 4 gives the results of rotation measurements at different wavelengths near the line. The rotations are again normalized by matching to the Brillouin curve at

⁴ C. Rytter, *Helv. Phys. Acta.* **30**, 353 (1957).

⁵ R. Lacroix, *Helv. Phys. Acta.* **30**, 374 (1957).

⁶ A. A. Kaplyanskii and P. P. Feofilov, *Opt. i Spektroskopiya* **13**, 235 (1962) [English transl.: *Opt. Spectry.* (USSR) **13**, 129 (1962)].

⁷ W. A. Runciman and C. V. Stager, *J. Chem. Phys.* **38**, 279 (1963).

⁸ B. P. Zakharchenya and A. Ya Ryskin, *Opt. i Spektroskopiya* **14**, 309 (1963) [English transl.: *Opt. Spectry.* (USSR) **14**, 163 (1963)].

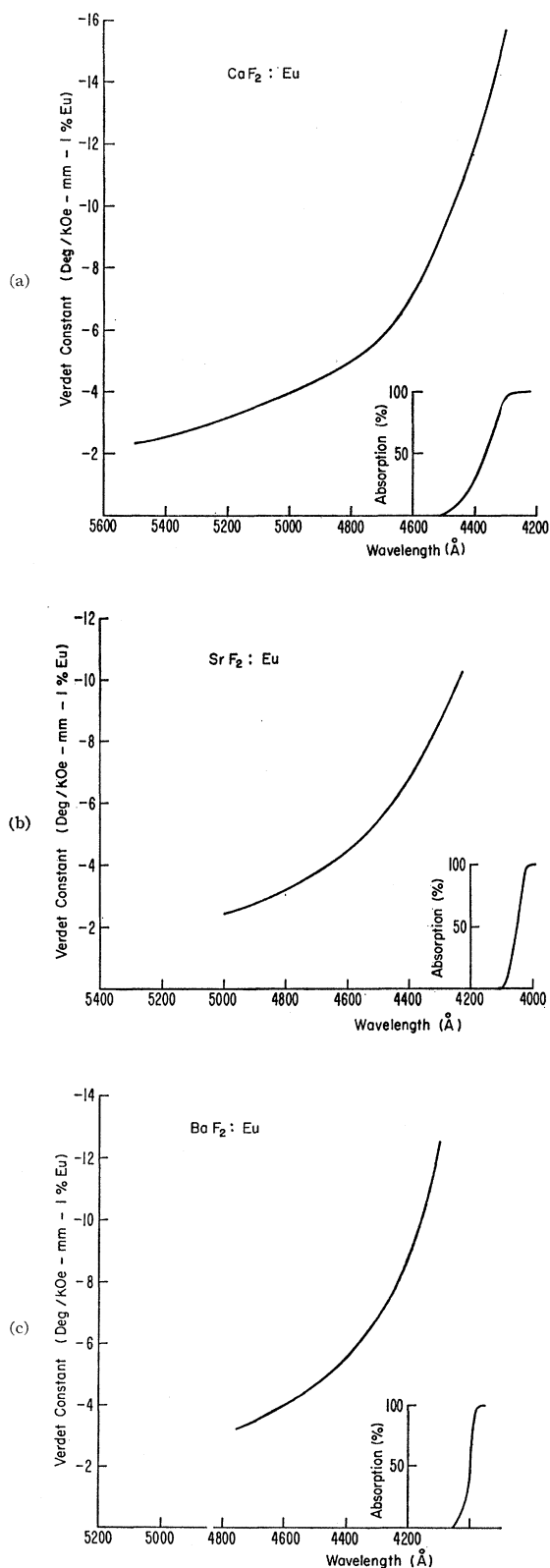


FIG. 2. Rotatory dispersion curves at 4.2°K and 2.71 kOe on (a) CaF₂: 3% Eu; (b) SrF₂: 3% Eu; (c) BaF₂: 3.6% Eu.

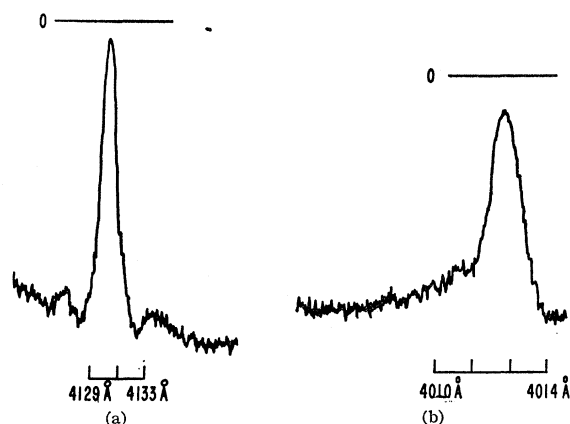


FIG. 3. Narrow spectral lines of Eu²⁺ in CaF₂ and SrF₂ at 4.2°K. The samples, 2.5 mm in length, were grown in a hydrogen atmosphere. (a) CaF₂: 0.005% Eu; (b) SrF₂: 0.007% Eu.

the largest field employed. Comparison with Fig. 1 shows how the rotation deviates from the magnetization curve as the wavelength moves towards the line. It is seen that the proportionality between rotation and magnetization is not badly destroyed at a light frequency 150 cm⁻¹ away from resonance. We therefore have reason to believe the narrow line to arise from $^8S_{J'} \rightarrow ^8P_{J'}$ transitions. From the amount of deviation of rotation from the magnetization curve, it is estimated that the crystal field splitting of the $^8P_{J'}$ level is probably of the order of 10~20 cm⁻¹, as Van Vleck and Penney have predicted.³

Since the multiplet 8P is regular, its lowest level has $J=5/2$ and $g_J=16/7$. This level is split into a doublet and a quartet in the cubic field. Runciman and Stager⁷ have suggested that the sharp line should arise from transitions to a quartet. However, the little bump superimposed to the sharp line at the short wavelength side (Fig. 3) may well be due to transitions to the doublet, judging from its small intensity and large circular dichroism and line shift in the magnetic field. A detailed analysis of the Zeeman pattern of the narrow line and the corresponding circular dichroisms in its components is necessary before we can say anything definite.⁹

The Zeeman components of the narrow line in SrF₂:Eu²⁺ are not as clearly resolved as those in CaF₂:Eu²⁺. The difference in the crystal field strength of the two lattices is possibly the reason. If the group of unresolved Zeeman components of the line in SrF₂:Eu²⁺ is taken as a single broadened line, the rotatory dispersion about it has the usual S-shaped curve.² This is shown in Fig. 5 with the corresponding circular dichroism shown in Fig. 6. From Fig. 3(b), the oscillator strength¹⁰ of the sharp zero-field line is about 1.2×10^{-4} . On the other hand, we can calculate the oscillator strength by assum-

⁹ Dr. B. P. Zakharchenya has noticed that his analytical results on Zeeman splittings of the line do not agree with what Runciman and Stager have found.

¹⁰ The oscillator strength is defined as: $f_{ba}^l = (4m\omega_{ba}/\hbar e^2) |\langle b | e/m\omega(\pi - i\hbar s \times \mathbf{k})_i \exp(-i\mathbf{k} \cdot \mathbf{r}) | a \rangle|^2 \rho_a^0$. See Refs. 1 and 2.

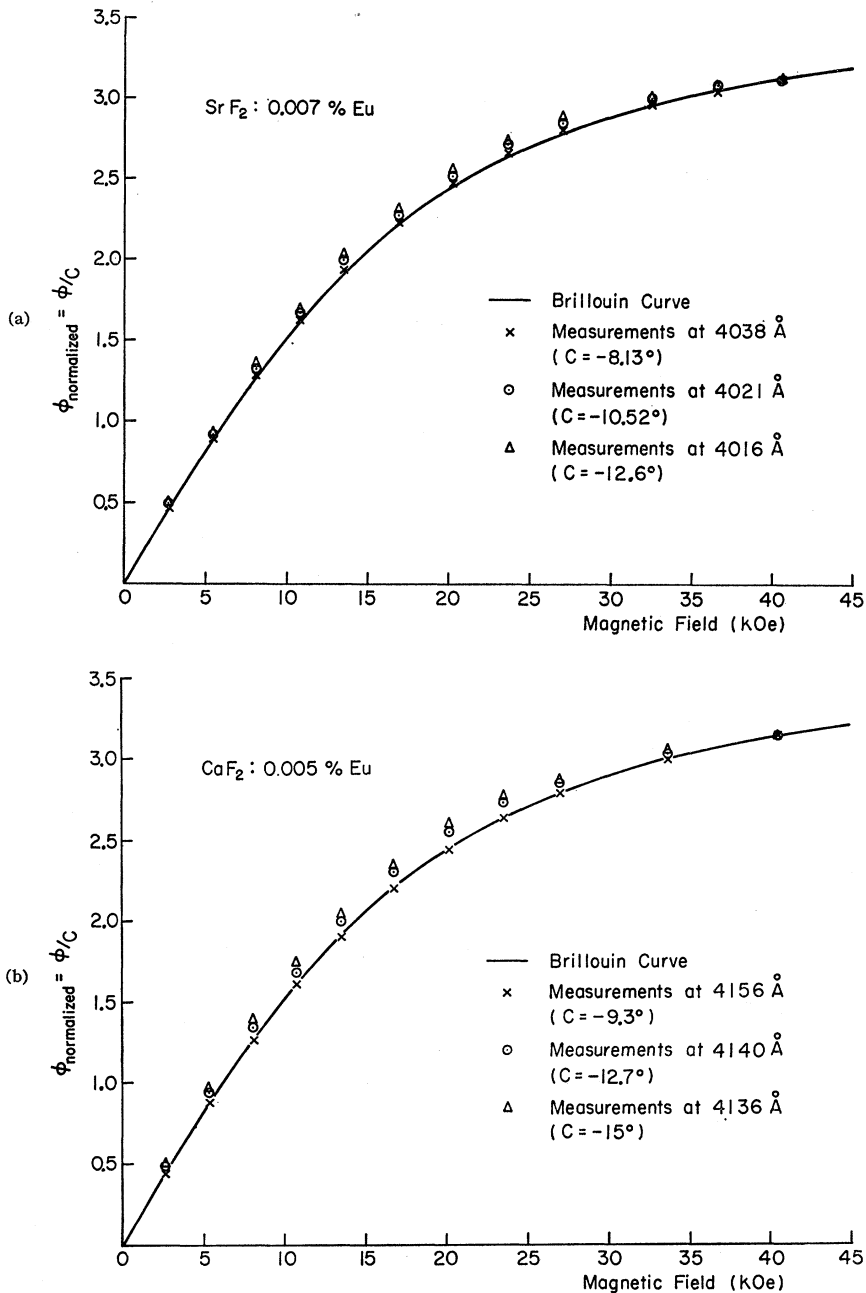


FIG. 4. Measurements of rotation versus magnetic field at 4.2°K at several wavelengths near the narrow spectral line. The rotations are normalized by matching to the Brillouin curve at 40.66 kOe. (a) $\text{CaF}_2: 0.005\% \text{Eu}$; (b) $\text{SrF}_2: 0.007\% \text{Eu}$.

ing that the 8P multiplet is $(4f)^6 \ ^7F(5d) \ ^8P$. If we match the calculated value to the experimental value of the oscillator strength for the zero-field line, we find a value 1.1×10^{-9} cm for the radial integral $\langle 4f | r | 5d \rangle$.¹¹ We can then calculate the circular dichroism and hence the rotation. The results are in close agreement with the experimental values.

Because of the large rotation observable even in

¹¹ This value of radial integral seems rather small in comparison with the values calculated for trivalent rare-earth ions. See B. R. Judd, *Phys. Rev.* **127**, 750 (1963).

dilute crystals, we can also use the combined microwave-optical technique to detect magnetic resonances in the ground states of Eu^{2+} . The hyperfine structure of Eu^{2+} , however, will decrease the sensitivity of detection.

In general, strong absorption bands of divalent rare-earth ions in the visible and near-visible range give rise to a large rotatory power. Figure 7 shows the rotatory dispersion for a sample of $\text{CaF}_2: 0.1\% \text{Tm}$ γ radiated. Before irradiation, the Tm impurities are presumably

¹² It is suggested by Professor N. Bloembergen.

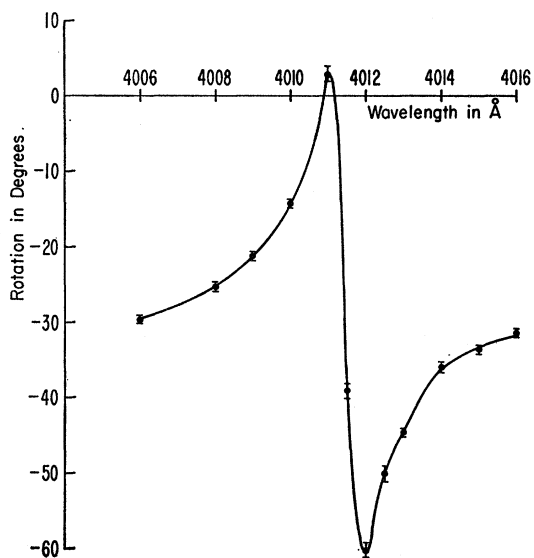


FIG. 5. Rotatory dispersion of SrF₂:0.007% Eu about the 4011.5 Å line of Eu²⁺ at 4.2°K and 21.6 kOe.

all in the trivalent state. Because of the small rotatory power of Tm³⁺, the paramagnetic rotation due to Tm impurities is undetectable. Assume 10% conversion of Tm³⁺ to Tm²⁺ from irradiation. Then, Fig. 7 shows that 1% of Tm²⁺ will have a rotatory power of 10 deg/

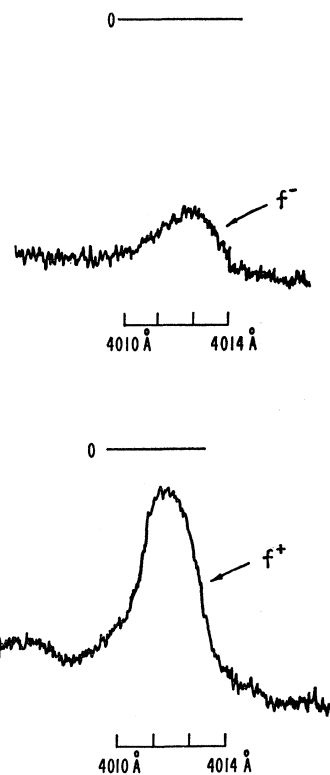


FIG. 6. Circular dichroism of the 4011.5 Å line of Eu²⁺ in SrF₂:0.007% Eu at 4.2°K and 21.6 kOe.

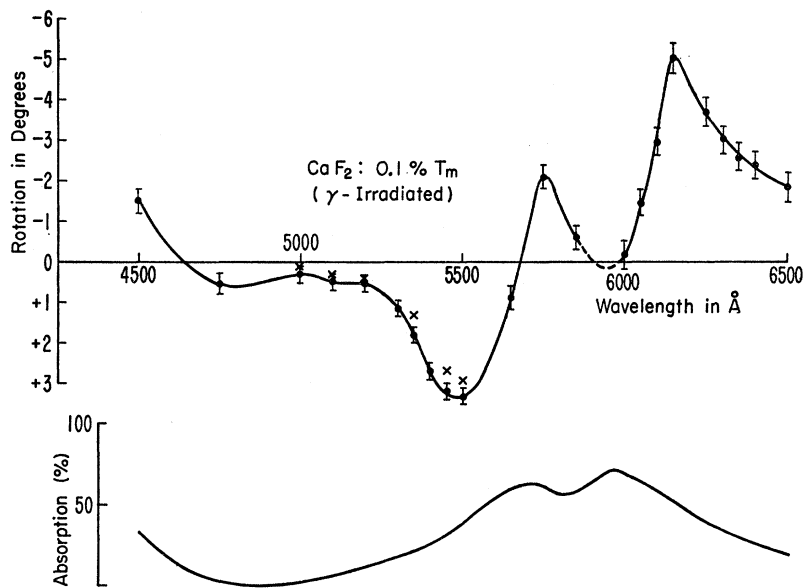


FIG. 7. Rotatory dispersion of CaF₂:0.1% Tm at 4.2°K and 21.6 kOe. The sample, 2.5 mm in length, were γ radiated. \square Measurements made 3 days after γ irradiation. \times Measurements made 24 days after γ irradiation.

kOe-mm at 6150 Å and 21.7 kOe. The rotation measurements can also be used as a sensitive method to detect the relaxation of divalent ions back to trivalent ions. The reconversion of Tm²⁺ to Tm³⁺ is about 10% in a three-week period. We have also measured the rotations due to Sm²⁺ and Yb²⁺. These ions are diamagnetic and consequently no appreciable rotations are detectable.

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