

It was found that the expansion ratio 1.2 is a sharp threshold value. Any expansion below this value produces supersaturated vapor of CO₂ without precipitation. Expansions above 1.2 produce abundant showers of CO₂ crystals. The threshold value increases slightly with lowering of the initial temperature of the chamber. There is an appreciable increase in the number of crystals formed with an increase of the expansion ratio up to 1.4. Above 1.4 the density of showers appears constant. All crystals grow sufficiently to have an appreciable rate of falling. The chamber is clear of all crystals within a maximum of 4 seconds after any expansion. Irradiation of the chamber with x-rays has no effect on the sublimation threshold, nor does it appreciably affect the number of particles formed.

The experiments provide straightforward evidence for the existence of a genuine sublimation process and also for the existence of a definite sublimation threshold. They also indicate that this sublimation threshold is defined primarily in terms of an expansion ratio and not of temperature.

With the same apparatus nitrogen and oxygen were investigated. Expansions were performed in a chamber precooled to the region of the nitrogen triple point and containing saturated vapor of the investigated gas in a helium atmosphere.

Both vapors show very low condensation thresholds. With oxygen even the smallest expansions (in a helium atmosphere free from condensation nuclei) produce dense fog. The threshold expansion ratio for condensation of nitrogen is 1.005. Dense fog produced at this threshold value indicates that the number of active condensation nuclei is of greater order of magnitude than the number of ions in the chamber. The fog has a consistency similar to C. T. R. Wilson's fogs obtained with water vapor, with expansion ratios above his cloud threshold (1.38).

Below their triple points both vapors form homogeneous, stable supercooled droplet clouds. The first crystals of solid nitrogen in nitrogen droplet clouds were observed at an expansion ratio of 5. In oxygen even higher expansion ratios, up to 10, failed to produce crystals.

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² E. M. Fournier d'Albe, *Quart. J. Roy. Met. Soc.* **75**, 1 (1949).

³ A. W. Brewer and H. P. Palmer, *Nature* **161**, 312 (1949).

⁴ C. Salmon and B. M. Cwilong, *New Zealand Sci. Rev.* **8**, 78 (1950).

Photocontrolled Low Frequency Dielectric Dispersion*

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PHOTOCONTROLLED dielectric dispersion has been observed in *F*-centered alkali halide crystals at room temperature. Most of the measurements were carried out on KBr single crystals which had been initially *U*-centered and then colored photochemically with Co⁶⁰-radiation, but the effect has also been verified with additively colored KBr and KI single crystals.

To allow observation of photoeffects, metallic electrodes were either painted or evaporated on opposite crystal faces and incident light directed through the crystal between the electrodes or through one (half-silvered) electrode into the crystal. No significant differences were observed in the behavior of these two types of specimens. Measurements of crystal admittance with or without illumination were carried out over the range from 25 to 10,000 cps and enabled the complex dielectric constant of the crystals to be computed.

In the dark, it was found that crystal dark-currents were purely reactive within the precision of the measurements. The dark dielectric constant of the KBr crystals was found to be about 5,

independent of *F*-center concentration and frequency over the ranges measured. These are expected results; the crystals are good insulators since their ionic conductivity is negligible at room temperature.

On strongly illuminating a crystal with light in its *F* absorption band, it was found that the total crystal current at low frequencies increased by a factor of from 5 to 50 over the dark current and was still largely reactive. This photocurrent depended strongly on *F*-center concentration and light intensity. On determining the real part of the dielectric constant ϵ' and the loss factor ϵ'' , it was found that these quantities exhibited dielectric dispersion behavior, with ϵ' a maximum at zero frequency and ϵ'' a maximum in the low audiofrequencies. No appreciable frequency-independent photoconductivity was observed. Typical results found for a KBr crystal with 1.4×10^{16} *F*-centers per cm³ were a maximum value of ϵ' at zero of 500 and a maximum of ϵ'' of 142 occurring at 85 cps. Applying a theory developed by Fuoss and Kirkwood¹ for large molecules with permanent dipoles having a distribution of relaxation times, it has been found possible to fit experimental ϵ'' and ϵ' curves quite well, whereas equations based on a single relation time will not fit the data at all.

Preliminary measurements of photocurrent as a function of *F*-center concentration and light intensity at a single frequency showed that the photocurrent varied approximately with the square root of these quantities. Further measurements of ϵ' and ϵ'' as functions of frequency have shown, however, that the preceding results were caused by a shift in the frequency at which the maximum of the ϵ'' curve occurred toward higher frequencies with increasing *F*-center concentration or light intensity, without an appreciable change in the maximum values of ϵ' and ϵ'' themselves. These results suggest that the effect may be largely the result of Maxwell-Wagner type losses associated with the photoconductivity of a crystal under illumination. No polarization effects have been observed: the photocurrent obeys Ohm's law up to the maximum field strength applied, 500 volts/cm, and the insertion of a 300-volt dc battery in series with the applied ac voltage has no effect on the results. This work will be more fully discussed in a later paper.

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¹ R. M. Fuoss and J. G. Kirkwood, *J. Am. Chem. Soc.* **63**, 385 (1941).

$L(L+1)$ Correction in the Spectra of the Iron Group

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IT was recently pointed out by Trees¹ that the agreement between the theoretical formulas and the experimental data in the *d*⁵s configuration of Mn II and Fe III is greatly improved by the addition of a correction term of the form $\alpha L(L+1)$. We verified that this correction is also very important in many other spectra of the iron group, and that the values of α obtained by least squares from different spectra are very consistent.

It is the purpose of this letter to show that this effect may be explained by the sole mathematical assumption that the deviations from the theoretical formulas in the *n*-electron configurations are the sum of the deviations of the interaction of each couple from the corresponding formulas. It is, however, not easy to justify this assumption, as the linearity property, which holds for every first-order effect, is not expected to hold for the deviations from Slater's formulas, which are generally considered to be the result of second-order effects.

It is known that the spectra of the configurations *d*² do not fit Slater's formulas very well;² but if we introduce two correction terms $\alpha\varphi_1(L)$ and $\beta\varphi_2(L)$, where φ_1 and φ_2 are any functions of *L*, it will be always possible to represent exactly the five terms of *d*², as we have now five free parameters.

Without any loss of generality we may therefore represent the deviations from Slater's formulas in d^2 by

$$2\alpha(\mathbf{l}_1 \cdot \mathbf{l}_2) + \beta q_{12},$$

where q is the operator, already defined elsewhere,³ which vanishes for $L \neq 0$ and equals 5 for the S -state. Then, according to our assumption, the deviations in the configuration d^n will be represented by

$$\sum_{i < k} [2\alpha(\mathbf{l}_i \cdot \mathbf{l}_k) + \beta q_{ik}] = \alpha[L(L+1) - 6n] + \beta Q.$$

As Q is different from zero only for the higher terms of every configuration and vanishes or has very small expectation values for almost all the terms which are experimentally known, the second correction has no practical importance, and the only important one is the $L(L+1)$ correction.

It may also be pointed out that this correction explains the constancy of the ratio $(^1S-^1D)/(^1D-^3P)$ in the configurations $2p^2$ and $2p^4$ of the first period, and predicts that the ratio $(^2P-^2D)/(^2D-^4S)$ in the configuration $2p^3$ should be $4/9$ of the former ratio, in excellent agreement with the experimental data.⁴

¹ R. E. Trees, Phys. Rev. **83**, 756 (1951).

² E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 203.

³ G. Racah, Phys. Rev. **62**, 438 (1942), Eq. (90), and **63**, 367 (1943), Eq. (35).

⁴ See reference 2, p. 198.

The $L(L+1)$ Correction to the Slater Formulas for the Energy Levels

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IN recent papers^{1,2} it has been pointed out that a correction of form $\alpha L(L+1)$ produces greatly improved agreement between theoretical and experimental term values in the configuration d^5s of Mn II and Fe III. This correction represents a polarization energy, and rigorous treatment of second-order effects is difficult even for the highly simplified wave functions of electrons in a solid.³ No satisfactory simple theory to explain this effect has as yet been found, but the following comments may be helpful.

The fact that the errors in all configurations of type $3d^n$ decrease as L increases has already been noted.² A variation independent of spin and proportional to $L(L+1)$ was, however, felt to be quantitatively justifiable only for the d^5 configuration. In the d^6 configuration of Fe III a correction proportional to $L(L+1)$ reduces the mean deviation only from $\pm 876 \text{ cm}^{-1}$ ⁴ to $\pm 439 \text{ cm}^{-1}$.⁵ This is a relatively small improvement compared to the reduction from $\pm 852 \text{ cm}^{-1}$ to $\pm 105 \text{ cm}^{-1}$ found in the d^5s configuration of Fe III. The value of α in the d^6 configuration, namely 67.4, is consistent with the value 80.7 in the d^5s configuration. This, together with the similarity of the trend in the errors for all $3d^n$ configurations, indicates that the corrections are at least approximately related according to the theory just advanced by Racah⁶ in which the polarization energy is treated linearly. However, as his theory leads essentially to a correction of form $L(L+1)$ for all configurations, it will not realize the full possibilities for accurate prediction of levels to ± 100 – 200 cm^{-1} in the $3d^6$ configuration of Fe III.

A basis for the favored position of the d^5 configuration relative to the d^6 configuration exists in the fact that in the former case most of the term values are rational functions of the Slater integrals (i.e., the eigenfunctions are characterized by a single seniority number,⁷ whereas most of the d^6 eigenfunctions are linear combinations of states with two seniority numbers). The one term with an irrational theoretical value in the $3d^5 4s$ configuration of Fe III for which an unperturbed experimental value is available is the $3d^5(a^2D)4s, c^3D$. For this term the error was $+442 \text{ cm}^{-1}$

while for all other levels the absolute value of the errors was less than 200 cm^{-1} . It seems likely from this that the correction of form $\alpha L(L+1)$ applies only to terms that are rational functions of the Slater parameters.

This conclusion can be checked very nicely in the $3d^6$ configuration of Fe III against the 6 rational levels for which experimental values are available. A correction proportional to $L(L+1)$ need not be applied to the usual Slater formulas, as such a correction can be absorbed in the values of the parameters A, B, C .⁸ These 6 levels can be fitted with a mean deviation of $\pm 150 \text{ cm}^{-1}$, and no deviation exceeds 200 cm^{-1} in absolute value.⁹ This is to be compared with the deviation of $\pm 876 \text{ cm}^{-1}$ in fitting all levels.

The correction to be applied when the term value is not a rational function of the Slater parameters, so that agreement of equal accuracy will be obtained, has not yet been found. However, if the eigenfunction is

$$C_1\psi(d^n v_1 SL) + C_2\psi(d^n v_2 SL),$$

a correction of form

$$(1 + 2C_1C_2)\alpha L(L+1)$$

will produce close agreement in the $3d^5(a^2D)4s, c^3D$ term discussed previously. A check of the validity of this correction in the d^6 configuration has not yet been made. In any event, it does not seem likely that the extra refinement needed to get a correction for levels with irrational term values can be derived theoretically by treating the polarization energy linearly.

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¹ R. E. Trees, Phys. Rev. **83**, 756 (1951).

² R. E. Trees, Phys. Rev. **84**, 1089 (1951).

³ E. Wigner, Phys. Rev. **46**, 1002 (1934); W. Macke, Z. Naturforsch. **5a**, No. 4, 192 (1950).

⁴ R. E. Trees, Phys. Rev. **82**, 683 (1951).

⁵ Values of the parameters are $A=19,969, B=953, C=3652, \alpha=67$.

⁶ G. Racah, Phys. Rev. **85**, 381 (1951).

⁷ The seniority number is introduced by G. Racah, Phys. Rev. **63**, 367 (1943).

⁸ For instance, a $d^6 3H$ term has the energy $(A-17B+4C)$; with an $\alpha L(L+1)$ correction this becomes

$$A-17B+4C+30\alpha = (A-36\alpha) - 17(B-2\alpha) + 4(C+8\alpha).$$

The four parameters A, B, C, α are thus replaced by the three parameters $A-36\alpha, B-2\alpha, C+8\alpha$. This same substitution applies in all six levels.

⁹ Values of the parameters are $A=18,400, B=853, C=4116$.

The Magnetic Threshold Field Curve of a Superconductor

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A NUMBER of authors¹ have considered the relation between the shape of the critical field vs temperature curve of a superconductor and the temperature dependence of the specific heat in both normal and superconducting states, from somewhat different points of view. In general, however, use is made of the Gorter-Casimir thermodynamic formulas² together with the assumption of a parabolic shape for the H_c vs T curve to obtain the familiar expression

$$\gamma = VH_0^2/2\pi T_0^2, \quad (1)$$

where γ is the "Sommerfeld term" (for the normal state), H_0 is the value of H_c at the absolute zero, V is the atomic volume, and T_0 is the zero-field transition temperature.

The complete expression one obtains is

$$\Delta C = C_s - C_n = -(VH_0^2/2\pi T_0^2)T + (3VH_0^2/2\pi T_0^4)T^3 \quad (2)$$

and on the assumption that C_n contains only a lattice term plus the Sommerfeld term, while C_s contains the same lattice term plus a T^2 -term for the electron assembly, one derives relation (1) above; i.e., the linear term in (2) is identified with $-\gamma T$. We then have

$$\Delta C = -\gamma T + (3\gamma/T_0^2)T^3. \quad (3)$$