

On the Electrical Properties of NaNO_3

J. H. FERMOR and A. KJEKSHUS

Kjemisk Institutt A, Universitetet i Oslo, Blindern, Oslo 3, Norway

Zone refined single crystals and polycrystalline samples of sodium nitrate have been subjected to resistivity measurements in the range 25 to 306°C, and to determinations of dielectric constant and dissipation from -65 to 290°C. The low temperature measurements supply evidence of a hitherto undetected, solid state transition at $\sim -30^\circ\text{C}$. The electrical parameters also clearly reflect the second order transformation which occurs in the vicinity of 275°C. The results are discussed in relation to those published previously.

In contrast with the situation in potassium nitrate, where the occurrence of four phases * has been ascertained at atmospheric pressure, the existence of only one structure type has previously been recognized for sodium nitrate. This compound has the calcite type structure,²⁻⁸ and is therefore isostructural with the high temperature phase I of KNO_3 . Calorimetric measurements^{9,10} have shown that NaNO_3 undergoes a second order transformation at 275°C. This transformation has been interpreted as being associated with orientational disorder of the nitrate group by reason of the results of X-ray^{5,6,8} and infrared¹¹ spectroscopic measurements, and by evaluations of the amount of energy involved.^{12,13} The occurrence of the transformation has also been reflected in other physical properties of NaNO_3 , e.g. elasticity,¹⁴ thermal expansion,^{15,16} and also detected in its nuclear magnetic resonance¹⁷ and ultraviolet¹⁸ spectra.

The electrical parameters might also be expected to exhibit a dependence on the transformation and previous measurements of dielectric constant¹⁹ do in fact indicate an anomaly in this temperature range. On the other hand, previous resistivity data,²⁰⁻²⁴ which contain large internal discrepancies, fail to show effects which may be correlated with the transformation. It was therefore considered of interest to redetermine the electrical resistivity of NaNO_3 using zone refined single crystal samples of a high degree of purity, and the improved measuring equipment which is available at this Institute. The measurements have also been extended to low temperatures since comparatively little information has previously been made available on the physical

* *i.e.* those designated I, II, III, and VIII; see Ref. 1.

properties of the compound below room temperature, where *e.g.* the available calorimetric data⁹ show no evidence of phase transformations.

Measurements to determine transport numbers explicitly in NaNO_3 are hindered especially at low temperatures by high resistivity values, but the electrical conduction process has been determined^{24,25} to be of an ionic character, and the majority carriers have been identified²³ as interstitial sodium ions by means of an application of the Wagner effect. (In the latter experiments, a divalent cation impurity (Ba) was introduced substitutionally into the crystal lattice as a means of controlling the density of cation vacancies and hence the density of mobile charge carriers.) These results are in accordance with what may be expected from a consideration of ionic sizes in relation to the structural parameters.

EXPERIMENTAL

Single crystal ingots of sodium nitrate having the approximate dimensions $30 \times 10 \times 10$ mm were grown using zone melting equipment of a conventional design²⁶ which incorporates zone and background heaters. An initial problem of premature fracture of the crystals was solved by raising the background temperature to $\sim 200^\circ\text{C}$, while the melted zone was maintained at as low a temperature as possible in order to avoid decomposition of the compound.

The *p.a.* grade NaNO_3 (Riedel de Haën) carried the analysis (in ppm): Mg (1), K (5), Ca (2) Mn (0.5), Fe (0.25), Pb (0.5), NH_4 (2), Cl (5), NO_2 (0.05), PO_4 (0.25), SO_4 (3).

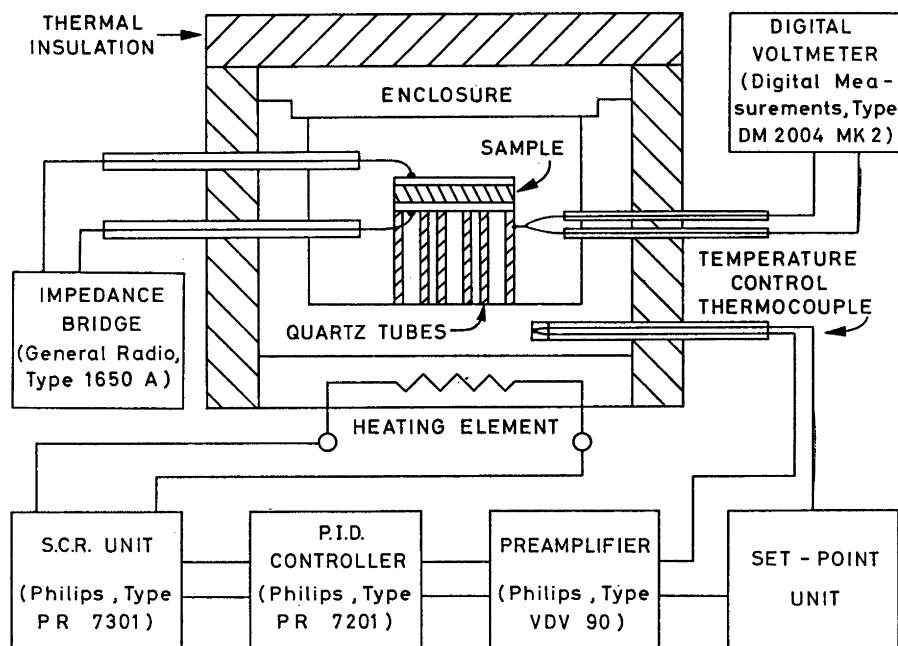


Fig. 1. Sample holder having low electrical capacitance, for use above room temperature, together with temperature control equipment.

and IO_3 (0.5). Mass spectrographic analyses yielded the following impurities (in ppm): Li (35), Mg (<1), Si (7.5), P (1.5), Cl (3.5), K (5), and Ca (2) for the starting material, and Li (8), Mg (1), Si (6), P (<1), Cl (4), K (3), and Ca (1.5) for the zone refined samples. (Other impurities were only present in concentrations less than 1 ppm.) The process of zone refinement thus reduced the content of the lithium impurity by a factor of approximately four and nearly halved the impurity contents of potassium and calcium.

Prismatic samples of rectangular cross section were cut from the single crystal ingots and four electrodes in the form of 0.2 mm diameter silver wires were welded in position by electrically heating the wire whilst it was held in spring loaded contact with the surface of the crystal. This technique results in the formation of stable electrical contacts but occasionally causes thermal fracture of the crystal sample.

The sample was mounted in what is virtually a temperature gradient-free holder²⁷ and its temperature automatically controlled by means of electronic equipment;²⁷ measurement of resistance values being performed at constant sample temperatures using an electrometer bridge circuit.²⁸

Samples which were suitable for the determination of dielectric constant, dissipation and resistivity at low frequencies over the complete temperature range, were formed by solidifying a layer of the compound between pairs of silver plates of area $30 \times 30 \text{ mm}^2$ at a separation of 0.3 mm, and by solidifying a thin film of the compound onto a silver plate and applying the second electrode in the form of conducting silver paint (Leitsilber 200, Degussa). For measurements at low temperatures, the samples were mounted within a liquid nitrogen cryostat,¹ while the results above room temperature were obtained

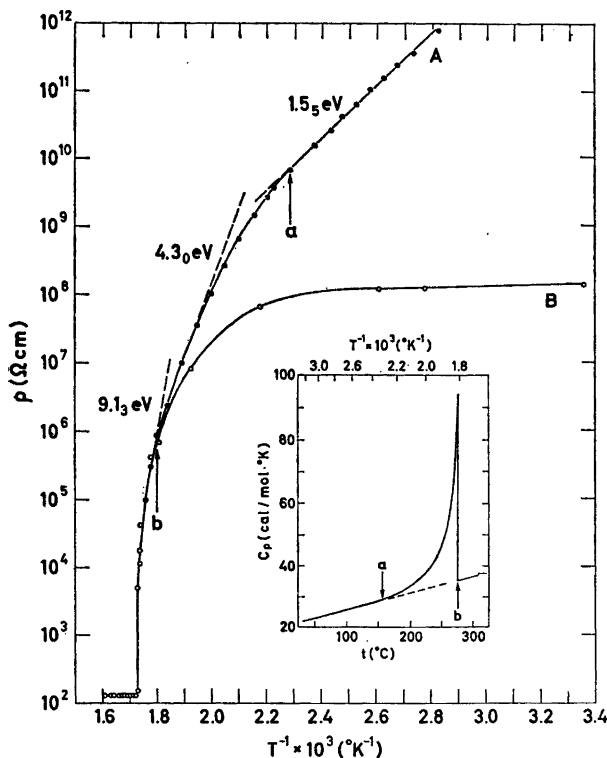


Fig. 2. Log ρ versus T^{-1} for zone refined single crystals (\bullet) and for polycrystalline NaNO_3 (\circ). The specific heat curve of Mustajoki¹⁰ is shown as an inset.

using a specially designed sample holder with low capacitance to ground, and electronic temperature control equipment.

The sample holder is shown in Fig. 1, where it is seen that quartz tubes support the sample at the centre of a heavy brass chamber which is in contact with an 800 W heating element. Coaxially screened leads from the sample are supported by alumina insulation, as also is a thermocouple used for measuring the sample temperature. A second thermocouple inserted into the base of the chamber comprises a part of the automatic control circuitry, which is also shown in Fig. 1. This equipment incorporates a set-point unit, preamplifier, amplifier with differentiating and integrating functions, and a silicon controlled rectifier unit.

Alternating current measurements were performed using an impedance bridge (General Radio, type 1650-A) at frequencies of 1 and 10 kHz, the signal voltage being provided in the latter case by an RC oscillator (Oltronix RCO-6K).

RESULTS

The resistivities of four zone refined single crystal specimens were determined along [001] between 80 and 300°C, the lower temperature being determined by limitations in the measuring equipment, and the upper by the melting point of the compound (306.8°C¹²). The four sets of results were in good agreement, and the data for one of them is presented as curve A in Fig. 2, where the logarithm of the resistivity is plotted as a function of the reciprocal of the absolute temperature. With increasing temperature, this curve shows a linear portion (80–160°C), followed by a curved section (160–240°C) preceding a second linear portion (240–275°C), which is itself interrupted by a third section which is practically linear from 275°C to close to the melting point. The dimensions of the zone refined ingots and their pronounced cleavage

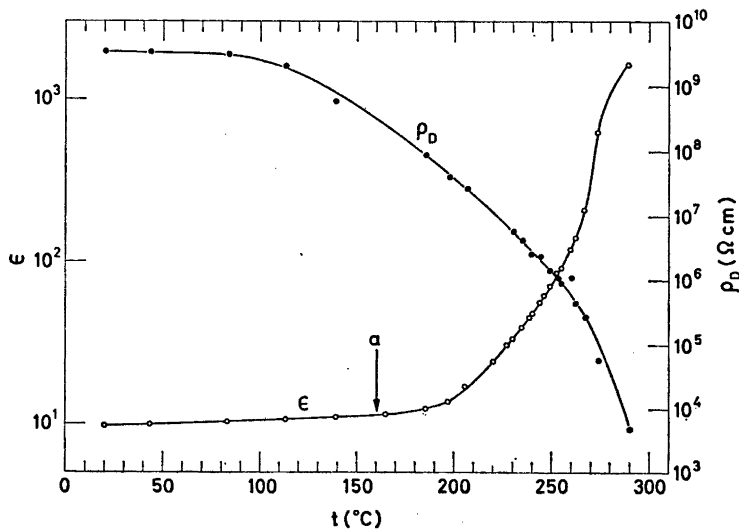


Fig. 3. Temperature variation of dielectric constant ϵ and ρ_D above room temperature for NaNO_3 .

properties prevented the formation of samples suitable for measurements perpendicular to [001].

Although the measuring equipment excludes the effects of polarization potentials, their values may also be observed and were found to be negligible at the higher temperatures. This is in agreement with the observations of Hochberg and Joffé²⁴ who noted an absence of polarization above $\sim 150^\circ\text{C}$.

The temperature dependence of the a.c. resistivity of a layer of NaNO_3 between silver plates, in the liquid and polycrystalline solid states is depicted as curve B in Fig. 2. These data, which were obtained on cooling the sample from 350°C (selected in order to avoid decomposition) match well onto the curve A near the melting point, depart appreciably from it below $\sim 275^\circ\text{C}$, and become almost temperature independent between 150°C and room temperature, where the resistivity level ($\sim 10^8 \Omega \text{ cm}$) is several orders of magnitude below that of curve A.

The results of the measurements of the dielectric constant (at 10 kHz, in order to record low values of ρ_D) above room temperature are shown in Fig. 3, where it is seen that an initial linear section is followed at $\sim 160^\circ\text{C}$ by a progressively more rapid increase in value, being at 290°C more than two orders of magnitude above that at room temperature. Also shown in Fig. 3 is the dependence of the quantity ρ_D , calculated from the recorded dissipation $D (=1/(\omega R_p C_p))$ according to the expression

$$\rho_D = S/(\omega C_p D t)$$

where ω is the angular frequency, C_p the recorded parallel capacitance value, t the sample thickness, and S the electrode area. The high values of dissipation recorded near the melting point (where ρ_D is six orders of magnitude lower

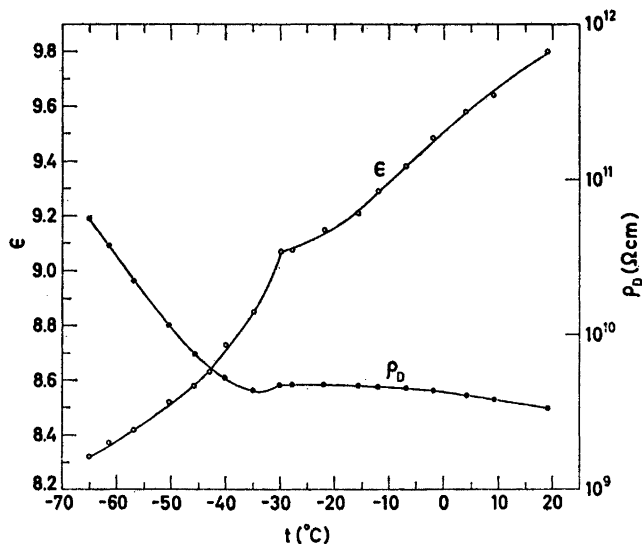


Fig. 4. Dielectric constant ϵ and ρ_D for NaNO_3 below room temperature.

than at room temperature), prevented the extension of these measurements to higher temperatures. In order to investigate the possibility of the high dissipation in this temperature region being associated with ferroelectricity, an X—Y oscilloscope was used to exhibit the charge *versus* voltage characteristic for the sample. No degree of asymmetry could, however, be detected in the oscilloscope trace, which was elliptical.

Similar measurements were also performed on thin polycrystalline films of compound in which the growth axis of the crystallites was clearly parallel to the electrode plate. The temperature dependence of ϵ and ρ_D were of the same form as in Fig. 2, but the relative increase in ϵ was only about 1/7 as great in the latter case.

In view of the high resistivity of NaNO_3 , measurements at low temperatures were restricted to the determination of capacitance value C_p and dissipation D (at 1 kHz). Typical results of such measurements are shown in Fig. 4, where ϵ and ρ_D are plotted as functions of temperature. These curves are markedly anomalous, showing discontinuities of slope at -30°C . Measurements performed on several samples showed that the anomalies are readily reproducible.

DISCUSSION

The temperature dependence of the resistivity of zone refined single crystals of sodium nitrate (curve A, Fig. 2), exhibits three linear sections which, in order of increasing temperature, have the apparent energy gaps 1.5_5 , 4.3_0 , and 9.1_3 eV, respectively. These values, together with those deduced from the literature data at corresponding temperatures, are compiled in Table 1, to facilitate comparison between them.

It is seen that there are substantial variations between the results of different authors, especially between those of Srinivasan²² and the others. These variations may be attributed to differences in impurity content, crystalline form and inhomogeneities of the samples; differences in the accuracy of measurement, and a possible anisotropy of the conduction process. Unfortunately, all too little information is provided by the previous authors to enable the relative importance of these factors to be decided. The present results,

Table 1. Apparent energy gaps at three temperatures for NaNO_3 , taken from previous work and curve A of Fig. 2.

Author (year of publication)	Apparent energy gap (eV)		
	110°C	260°C	295°C
Foussereau ²⁰ (1885)	1.6 ₅	3.4 ₆	4.4 ₂
v. Hevesy ²¹ (1922)	—	5.7 ₆	—
Hochberg and Joffé ²⁴ (1930)	1.5 ₃	—	—
Srinivasan ²² (1963)	~0.5	~4.9	~1.0
Ramasastri and Murti ²³ (1965)	1.8 ₅	2.1 ₂	—
Present work	1.5 ₅	4.3 ₀	9.1 ₃

being obtained by means of an accurate four terminal method of measurement on relatively pure single crystal specimens of good crystalline perfection, should, however, provide an adequate basis for the detailed discussion of electrical conduction in NaNO_3 .

In contrast with earlier data, the results of curve A, Fig. 2, show excellent correlation to exist between the temperature variation of the electrical resistivity and the order-disorder transformation, as, *e.g.*, evidenced by the specific heat data of Mustajoki,¹⁰ which are quoted as an insert to Fig. 2. At 160°C (*i.e.* at the points labeled a in Fig. 2) the onset of the rotational disorder of the nitrate group is clearly reflected in the specific heat curve, and at precisely the same temperature commences the non-linear portion of the curve A. At 275°C (the points b in Fig. 2), where the transformation becomes complete, a discontinuity occurs in the slope of the conductivity curve. The same correlation is exhibited with less precision by curve B* (Fig. 2), for polycrystalline material. The differences from curve A probably result from differences in impurity content, crystalline form and possible frequency dependent effects. Thus the onset and completion of the second order transformation are easily seen in the resistivity results, bringing this parameter into line with the other physical quantities which have been investigated in relation to the transition (see introduction).

A similar situation prevails in the case of the high temperature dielectric constant data (Fig. 3). The onset of the transformation is detectable at the point a (160°C), but the rapid increase of the dissipation value D with increasing temperature prevented extension of the measurements to higher temperatures. Lower values of ϵ were obtained in the case of oriented crystallites, in accordance with the dielectric anisotropy which has been detected earlier.³⁰

The single crystal resistivity data of Fig. 2 may be accounted for on the basis of a conventional model in which three independent conduction mechanisms are present, each being dominant over a restricted span of temperature, and leading to an expression for conductivity ** of the form

$$\sigma = \sum_{i=1}^3 \sigma_{0i} \exp(-W_i/2kT),$$

but this interpretation is considered to be incorrect in view of the correlation with the order-disorder transformation. Additional support for this opinion is provided by nuclear magnetic resonance data.¹⁷ The temperature dependence of the nuclear quadrupole coupling constant shows that above the transition, Na^+ ions migrate very readily through the crystal, a fact which is inconsistent with an interpretation of the high value of apparent energy gap (9.1₃ eV) as relating to the activation and translation of charge carriers in this region. The effect of very low energy barriers associated with facile ionic migration,

* It was convenient to begin the measurements of curve B above the melting point, but the results for this region are to be regarded as purely qualitative compared with, *e.g.*, the definitive measurements of Doucet and Bizouard.²⁹

** It should be noted that in this case, the true energy gaps must be calculated from the apparent values in a manner discussed previously.²⁶ This is particularly important in the case of the slopes intersecting at the point b since there is appreciable overlap in the regions of influence of the two terms concerned.

is reflected in the observation of an elliptical charge *versus* voltage characteristic at temperatures where excessive dissipation occurs (see Fig. 3).

The simple model for ionic conduction in which the activation and translation barrier energies (W_a and W_b , respectively), and hence W ($=W_a+2W_b$) is constant in the expression

$$\rho = \rho_0 \exp(W/2kT)$$

is adequate below the onset of the transition (160°C). The above considerations imply however that a modification of the model is necessary at higher temperatures.

At temperatures up to 160°C, the charge carriers are assumed to be interstitial Na⁺ ions in accordance with the results of Ramasastry and Murti,²³ *i.e.* there appears to be no reason for the conductivity to be regarded as other than intrinsic. The reorientation of nitrate groups above this temperature will, however, have a disruptive effect on the ionic bonds leading to an effective reduction in energy barrier values. In addition, the frequency of reorientation may be expected to exert a controlling influence. It is therefore reasonable to assume that a temperature dependence of W is introduced as a result of the increase in the proportion of disordered nitrate groups (160 to 275°C) and the probable increase in the frequency of reorientation (160 to 306°C) with increasing temperature. If one neglects the possibility of additional complications caused by modifications in the type of carrier mechanism, it may be concluded that the results are consistent with a temperature dependence of either W_a or W_b , or more probably, both of these potential barriers in this region, and that the transitional region between 160 and 275°C corresponds to the properties of an inhomogeneous system, containing an increasing proportion of disordered nitrate groups with temperature. Thus the resistivity curve is thought to differ from the commonly found transition from extrinsic to intrinsic conduction processes with increasing temperature, and to reflect instead the dominant influence of physical changes which are known to occur in the crystal.

The deduced reduction in energy barrier values with increasing temperature, may have implications in relation to the melting process in NaNO₃.

Below room temperature, dielectric constant data (Fig. 4) have a discontinuity of slope at -30°C, which is accompanied by a marked anomaly in ρ_D , indicating the occurrence of a structural alteration in the vicinity of this temperature. Since only minor differences are observed between the X-ray diffractograms obtained at room and liquid nitrogen temperatures, it is clear that only a minor change in structure is involved, probably other than a geometrical change within the nitrate group.

Acknowledgements. This work was made possible by the kind provision of laboratory facilities by Professor H. Haraldsen and the financial support of *Norges almenvitenskapelige forskningsråd*.

REFERENCES

1. Fermor, J. H. and Kjekshus, A. *Acta Chem. Scand.* **22** (1968) 836.
2. Bragg, W. L. *Proc. Roy. Soc. (London)* **A 89** (1914) 468.
3. Wyckoff, R. W. G. *Phys. Rev.* **16** (1920) 149.
4. Kracek, F. C., Posnjak, E. and Hendrieks, S. B. *J. Am. Chem. Soc.* **53** (1931) 3339.
5. Tahvonen, P. E. *Ann. Acad. Sci. Fennicæ Ser. A I* **1947** No. 42.
6. Siegel, L. A. *J. Chem. Phys.* **17** (1949) 1146.
7. Sass, R. L., Vidale, R. and Donohue, J. *Acta Cryst.* **10** (1957) 567.
8. Shinnaka, Y. *J. Phys. Soc. Japan* **19** (1964) 1281.
9. Sokolov, V. A. and Schmidt, N. E. *Izv. Sektora Fiz.-Khim. Analiza, Inst. Obschch. Neorgan. Khim. Akad. Nauk SSSR* **26** (1955) 123.
10. Mustajoki, A. *Ann. Acad. Sci. Fennicæ Ser. A VI* **1957** No. 5.
11. Hexter, R. M. *Spectrochim. Acta* **10** (1958) 291.
12. Janz, G. J., Kelly, F. J. and Perano, J. L. *J. Chem. Eng. Data* **9** (1964) 133.
13. Newns, D. M. and Stavely, L. A. K. *Chem. Rev.* **66** (1966) 267.
14. Kornfel'd, M. I. and Chubinov, A. A. *Soviet Physics — JETP* **6** (1958) 26.
15. Kracek, F. C. *J. Am. Chem. Soc.* **53** (1931) 2609.
16. Kantola, M. and Vilhonen, E. *Ann. Acad. Sci. Fennicæ A VI* **1960** No. 54.
17. Eades, R. G., Hughes, D. G. and Andrew, E. R. *Proc. Phys. Soc.* **71** (1958) 1019.
18. Cleaver, B., Rhodes, E. and Ubbelohde, A. R. *Proc. Roy. Soc. (London)* **A 276** (1963) 453.
19. Korotaev, N. N. and Korotaev, K. A. *Tr. Permsk. Gos. Sel'skokhoz. Inst.* **25** (1964) 93.
20. Foussereau, M. G. *Ann. Chim. Phys.* **5** (1885) 317.
21. v. Hevesy, G. *Z. Physik* **10** (1922) 80.
22. Srinivasan, S. *Phil. Mag.* **8** (1963) 1601.
23. Ramasastry, C. and Murti, Y. V. G. S. *Indian J. Pure Appl. Phys.* **3** (1965) 265.
24. Hochberg, B. and Joffé, V. *Z. Physik* **66** (1930) 172.
25. Hochberg, B. and Joffé, V. *Phys. Z. Sowjetunion* **1** (1932) 237.
26. Fermor, J. H. and Kjekshus, A. *Acta Chem. Scand.* **21** (1967) 1267.
27. Fermor, J. H. and Kjekshus, A. *Tidsskr. Kjemi, Bergvesen Met.* **27** (1967) 28.
28. Fermor, J. H. and Kjekshus, A. *Rev. Sci. Instr.* **36** (1965) 763.
29. Doucet, Y. and Bizouard, M. *Bull. Soc. Chim. France* **1959** 1570.
30. Hochberg, B. *Phys. Z. Sowjetunion* **5** (1934) 253.

Received September 14, 1967.