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We are presently studying the same phenom-
enon in the Hall-effect geometry (previously
referred to as case A), but the signal is quite
small (10^{-11} V cm^2/A) and consequently diffi-
cult to detect.

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[1]F. London, Superfluids (John Wiley & Sons, Inc.,
New York, 1950), Vol. 1, pp. 55, §8.

[2]H. Lewis, Phys. Rev. 92, 1149 (1953), and 100, 641
(1955).

[3]R. Jaggi and R. Sommerhalder, Helv. Phys. Acta 32,
167 (1959).

[4]D. Shoenberg, Superconductivity (Cambridge Univer-
sity Press, New York, 1952), p. 49.

[5]W. A. Zisman, Rev. Sci. Instr. 3, 367 (1932); and
Ralph E. Simon, Phys. Rev. 116, 613 (1959).

ELECTRICAL CONDUCTIVITY OF POTASSIUM CHLORIDE

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The electrical conductivity of potassium chloride is discussed within the framework
of a four-defect model of the crystal. The four defects are mobile anion and cation va-
cancies and immobile divalent cation impurities and divalent cation impurity-cation va-
cancy complexes. The Teltow formulation of the four-defect model fails to describe
precisely the measured electrical conductivity of KCl over the entire intrinsic and ex-
trinsic range.

The electrical conductivity of alkali-halide
crystals has usually been discussed in terms
of a four-defect model of an ionic crystal, the
four defects being anion vacancies, cation va-
cancies, divalent impurity cations, and diva-
lent cation impurity-cation vacancy complex-
es. In the Teltow formulation[1] of the four-de-
fect model the defects are treated as noninter-
acting particles, the divalent cation impurities
and cation vacancies are considered as com-
plexes only when they are on nearest-neighbor
lattice sites, and the mobility of the ions is
given by the product of a jump-attempt frequen-
cy (ν) and a Boltzmann factor. It has been cus-
tomary in the analysis of conductivity data to
extract values for the various parameters,
assumed to be temperature independent in the
Teltow formulation, i.e., the entropy (s) and
enthalpy (h) of Schottky-defect formation, the
entropies ($\Delta s_\pm$) and enthalpies ($\Delta h_\pm$) of vacan-
cy motion, and the binding energy of the com-
plexes. It is our intent to show the limitations
of the Teltow formulas for KCl.

In the intrinsic region where the effect of
the impurity content is negligible, the Teltow
expression for the conductivity reduces to the
sum of two exponentials,

$$\sigma T = \frac{N a^2 e^2 \nu}{k}\left[\exp\left(S_+ - \frac{W_+}{kT}\right) + \exp\left(S_- - \frac{W_-}{kT}\right)\right], \quad (1)$$

where N is the number of cations per unit vol-
ume, a is the lattice parameter, e is the elec-
tronic charge, $S_\pm = (\frac{1}{2}s + \Delta s_\pm)/k$ and $W_\pm = \frac{1}{2}h + \Delta h_\pm$.
A test of the Teltow formulation is to see if
a sum of two exponentials will describe the
intrinsic conductivity and gives results consis-
tent with analyses of conductivity over a wid-
er temperature range which includes the ex-
trinsic region.

The electrical conductivity of "pure" Harshaw
KCl crystals has been measured from 480 to
750°C using standard ac bridge techniques at
1 kHz and a furnace design which permits the
taking of measurements every 3° or so. A high-
er density of data points than reported for oth-
er experiments of this type has thus been ob-
tained. In Fig. 1 the data from our measure-
ments of the conductivity of Harshaw KCl are
shown by open circles and the data from the
measurements of the conductivity of zone-re-
fined KCl (data of Ref. 2, run No. 9) are shown
by solid squares. The precision of our mea-
surements is estimated to be ±1% for the con-
ductivity and ±0.5°C for the temperature. The
least-squares computer fit of Eq. (1) with the
59 experimental data points for $T > 560$°C is
shown by the solid line in Fig. 1.

Two difficulties are encountered in the use
of Eq. (1) to analyze conductivity data. One
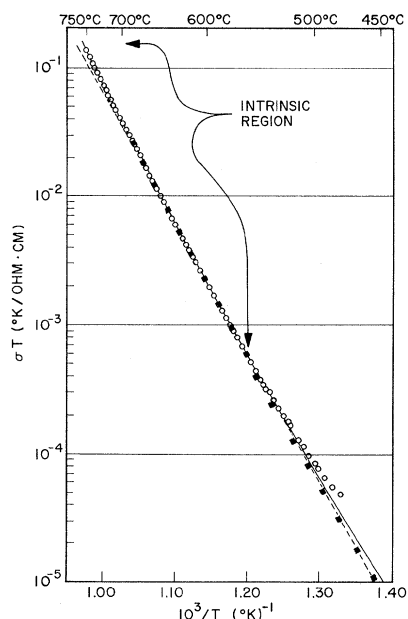is the determination of the temperature at which

FIG. 1. The electrical conductivity of KCl as a function of temperature. Open circles, experimental data for Harshaw KCl; solid squares, experimental data for zone-refined KCl (Ref. 2, run No. 9); solid line, least-squares fit of Eq. (1) with the intrinsic region ($T > 560°C$); dashed line, results from Beaumont and Jacobs' (Ref. 2) analysis of intrinsic and extrinsic conductivity of KCl.

the intrinsic region begins and the other is the verification of the uniqueness of the parameters obtained by the computer fit.

Two KCl crystals containing small but different amounts of aliovalent cation impurities have equal values of electrical conductivity only in the intrinsic region. The data for the Harshaw KCl and the zone-refined KCl are equal with a mean deviation of 1.2% for $T > 560°C$. Therefore, the temperature range above 560°C can safely be designated as the intrinsic region (Fig. 1).

The reliability of our computer program was

determined by manufacturing data for a sum of exponentials with known parameter values and affixing computer-generated random errors, so that the least-squares fit to Eq. (1) with the test data and with the experimental data gave equal rms deviations. The analysis of ten sets of 59 test data points permitted us to verify the uniqueness of our results and to estimate the precisions of $S_\pm$ and $W_\pm$. The corrected values and related uncertainties of these four parameters are given in row 1, Table I, along with the rms fractional deviation between Eq. (1) and the experimental data for $T > 560°C$.

Beaumont and Jacobs[2] have measured the electrical conductivity of several undoped KCl single crystals (of which the squares of Fig. 1 are one sample) for $690 > T > 370°C$. For their analysis they used the Teltow equations, which required a seven-parameter least-squares computer fit. Their values for the parameters of Eq. (1) are shown in row 2, Table I. Despite the conclusion from the Teltow model that the conductivity should reduce to a four-parameter description, Eq. (1), in the intrinsic region, the following facts may be observed:

(1) The analysis of the intrinsic and extrinsic regions together for undoped KCl gives entropy and enthalpy values significantly different from those obtained in the analysis of the intrinsic region alone.

(2) The computed values for conductivity resulting from the analysis of the intrinsic and extrinsic regions together are below the experimental data for all temperatures above 665°C and are low by more than 10% above 730°C.

Recent results for the conductivity of nearly pure KBr reported by Dawson and Barr[3] are similar to these results for KCl. Dawson and Barr analyzed their conductivity data over a wide temperature range ($T > 290°C$) and over the intrinsic region ($T > 560°C$) alone. They

Table I. Entropies and enthalpies for electrical conductivity in potassium chloride. The rms deviation was computed using Eq. (1) and the experimental data for $T > 560°C$. The value used for the jump-attempt frequency ν was 4.276×10^{12} sec^{-1}.

	S_-	W_- (eV)	S_+	W_+ (eV)	Rms deviation (%)
Intrinsic conductivity (this work)	11.6 ± 0.3	2.36 ± 0.03	2.1 ± 0.6	1.66 ± 0.04	1.3
Intrinsic and extrinsic conductivity[a]	9.0	2.17	4.5	1.84	6.2

[a]Ref. 2.

reported that, although the analysis for the wide temperature range gives results in agreement with their analysis of diffusion data, the analysis of the intrinsic-extrinsic regions gives entropy and enthalpy values significantly different from those obtained by their analysis of the intrinsic region only. The computed values of conductivity resulting from their intrinsic-extrinsic analysis are below the values computed from the intrinsic analysis for all temperature above 589°C, are more than 10% low for $T > 660$°C, and fall 20% low near 700°C.

In summary, our analysis shows that a reliable least-squares fit of Eq. (1) to the intrinsic conductivity of KCl can be obtained and that the parameters of the fit are uniquely determined within the uncertainties given in row 1, Table I. On the other hand, results of an analysis using the Teltow equations for both the intrinsic and the extrinsic regions of undoped KCl crystals do not agree with the intrinsic data. Furthermore, these analyses give enthalpies that differ by about 10% and entropies that differ by as much as a factor of 2 or more.

Two possibilities for bringing the conductivity theory into agreement with experiment seem to exist. One possibility is the existence of other charge carriers, such as trivacancy complexes, Frenkel defects, or electrons (or holes) thermally liberated from impurity traps. One or more of these carriers, associated with higher activation energies, might appear in the intrinsic region in sufficient concentrations to account for the discrepancy. On the other hand, it seems likely that the Teltow formulation oversimplifies the four-defect model. The addition of long-range Coulomb interactions to the Teltow equations has been made by Lidiard[4] using the Debye-Hückel theory for electrolytic solutions. However, we have found in preliminary calculations that the discrepancy between theory and experiment is only slightly lessened by the use of the Lidiard formulation of conductivity theory. The vacancy concentration in the intrinsic may well be too large for the Debye-Hückel approximations to be valid.[5-7] For example, the ratio of $e^2 K / \epsilon k T$ is assumed to be much less than 1 in the Debye-Hückel treatment, where K and ϵ refer to the Debye-Hückel screening constant and the static dielectric constant, respectively.[5] In fact, the ratio increases with temperature in the intrinsic region of KCl from about 0.3 to 1.0. Defect interactions may therefore be underestimated in the Lidiard formulation. Moreover, a variation with temperature of the free energy of motion may be an important effect which would become apparent in a more careful treatment of the influence of the lattice vibrations. In any event, one is forced to conclude that no consistent set of temperature-independent parameters in the Teltow equations can adequately describe both the intrinsic and extrinsic regions of electrical conductivity of KCl.

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[1]J. Teltow, Ann. Physik 5, 71 (1949).

[2]J. H. Beaumont and P. W. Jacobs, J. Chem. Phys. 45, 1496 (1966).

[3]D. K. Dawson and L. W. Barr, Phys. Rev. Letters 19, 844 (1967).

[4]A. B. Lidiard, Phys. Rev. 94, 29 (1954).

[5]R. H. Fowler and E. A. Guggenheim, Statistical Thermodynamics (Cambridge University Press, Cambridge, England, 1939), Chap. 9.

[6]A. R. Allnatt and M. H. Cohen, J. Chem. Phys. 40, 1871 (1964); E. Koch and C. Wagner, Z. Physik Chem. 38, 295 (1937).

[7]A. R. Allnatt and P. C. Hoines, J. Chem. Phys. 46, 1154 (1967).