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Behavior of Ferroelectric $KNbO_3$ in the Vicinity of the Cubic-Tetragonal Transition

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The results of measurements on single crystals of $KNbO_3$ are reported. From the dielectric constant and spontaneous polarization measurements the coefficients of the first three terms of the free energy expressed as a power series in the polarization can be found. The detailed behavior of single domain crystals in the cubic and tetragonal phases is compared with Devonshire's phenomenological treatment. Agreement with predicted dielectric constant and spontaneous polarization is reasonable. The constants of $KNbO_3$ are compared with those reported for $BaTiO_3$. It is found that in all cases corresponding constants are of the same order of magnitude.

I. INTRODUCTION

THE perovskite ferroelectrics are attractive as testing media for theories because of their relatively simple and symmetrical structure. By now, $BaTiO_3$ has been examined quite intensively in terms of a phenomenological theory proposed by Devonshire[1] and supplemented by Slater.[2] Merz[3] has shown that just above the Curie point the single crystals of $BaTiO_3$ follow the behavior predicted by assuming a free-energy function

$$F=A(T-T_0)P^2-BP^4+CP^6+F_0(T), \qquad (1)$$

where P = electric polarization, T = temperature, A, B, C, and T_0 are constants and $F_0(T)$ is the free energy at zero polarization. A, B, and C were assumed to be temperature-independent.

One of the questions in the development of a valid theory is whether a microscopic treatment is possible which will be correct in the paraelectric as well as the ferroelectric phases. In Slater's treatment, ionic polarizability plays a major role. However, Cohen[4] points out that if one accepts the hypothesis that the lattice is polarized by ionic displacements, the internal fields as calculated by Slater are incorrect in the ferroelectric phase since the fields at the displaced positions differ appreciably from those at the undisplaced atomic sites. If, on the other hand, one can find an empirical function $F(P,T)$ which describes the behavior in both the paraelectric and ferroelectric phases and the transition region between them, then the aim of the microscopic theory can be restricted to predicting the constants of (1) in the one phase with the knowledge that the treatment will be valid in the second phase as well.

We have been investigating $KNbO_3$, a ferroelectric qualitatively similar[5] to $BaTiO_3$. We were interested in discovering whether a thermodynamic treatment such as that applied by Devonshire to $BaTiO_3$ would succeed in describing the observed dielectric constant, spontaneous polarization, and latent heat for $KNbO_3$.

II. PREPARATION OF SAMPLES

Matthias and Remeika[6] first reported dielectric data on $KNbO_3$. We have succeeded in growing some apparently single-domain crystals in the form of small plates of the order of 0.05 mm thick and large enough to accommodate electrodes about 0.5 mm in diameter. These were grown from molten mixtures of Nb_2O_5 and K_2CO_3 in the range 0.50–0.67 molar fraction of the latter.[7] By sawing some of the larger crystals into rectangular plates after electroding, we obtained several with completely electroded faces. This is desirable for reducing clamping and edge-effect errors.

The crystals used in the measurements reported here were selected by microscopic examination in transmitted polarized light. Gold was evaporated on to areas with plane parallel faces showing uniform extinction at room temperature over the entire electrode area. The domain structure was not examined in detail optically beyond this, so that definite conclusions as to the room temperature (orthorhombic phase[8]) domain structure of the crystals could not be drawn. From the dielectric and hysteresis behavior, we could infer that the crystals consisted entirely of "c" domains in the tetragonal phase, i.e., had all domains polarized perpendicular to the crystal faces. In the cubic phase, these are single crystals.

III. DIELECTRIC MEASUREMENTS

Most of the dielectric data were taken by using a modified General Radio 1604B Comparison Bridge and a substitution technique. It was necessary to balance correctly the resistive and capacitive components of the impedance. This was most critical at the elevated temperatures where the conductivity of the crystals becomes a serious problem. Measurements were made at various frequencies from 400 cps to 100 kc/sec to insure that representing the crystals by an equivalent circuit of a capacitance shunted by a resistance was valid. The results reported here are from data taken

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[1] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949); **42**, 1065 (1951).
[2] J. C. Slater, Phys. Rev. **78**, 748 (1950).
[3] W. J. Merz, Phys. Rev. **91**, 513 (1953).
[4] M. H. Cohen, Phys. Rev. **84**, 368 (1951) and **84**, 369 (1951).
[5] Shirane, Danner, Pavlovic, and Pepinsky, Phys. Rev. **93**, 672 (1954).
[6] B. T. Matthias and J. D. Remeika, Phys. Rev. **82**, 727 (1951).
[7] A. Reisman and F. Holtzberg, J. Am. Chem. Soc. **77**, 2115 (1955).
[8] E. A. Wood, Acta Cryst. **4**, 353 (1951).

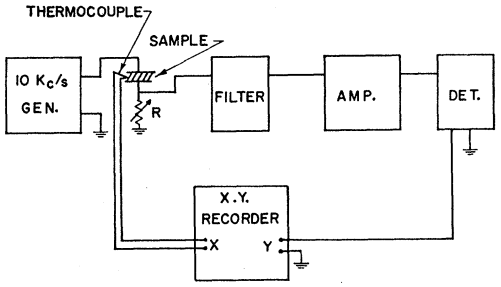

FIG. 1. Block diagram capacitance *vs* temperature recorder.

at 10 kc/sec with measuring field very small compared with the coercive field.

We also ran some dielectric constant *vs* temperature curves using an XY recorder. In this case the sample was set up as half of a voltage divider circuit so that the recorder plotted the reciprocal of the impedance of the sample (a deflection proportional to the capacity) on one axis and the temperature on the other. As long as the loss tangent is less than 0.2 the error is less than $\sim 2\%$. The crystals were checked at several points to insure that this condition (loss tangent <0.2) was satisfied over the temperature region plotted.

The constants A and T_0 are found from the relation of Eq. (14) of the appendix by plotting the reciprocal of the dielectric constant *vs* temperature in the paraelectric phase. Data contributing to the values of A and T_0 given below were taken on nine crystals of thickness ranging from 0.005 cm to 0.014 cm, with round evaporated gold electrodes from 0.05 cm to 0.10 cm in diameter. In addition, three crystals of thickness $\sim$0.006 cm, completely evaporated and then sliced to rectangular plates 0.05×0.07 cm, were measured. Data were taken over the range 410°C to 500°C, about six points being taken for each crystal. The temperature of the furnace in which the measurements were made was regulated to 0.1°C with a Brown chopper amplifier by holding the emf of a thermocouple in the hot space equal to a fixed reference emf.

The results are shown in Table I. The values of A and T_0 are derived for each crystal by least squares matching of straight lines to the plot of $1/K$ *vs* T. Earlier data in the paraelectric temperature region on many other crystals showed the Curie-Weiss Law [Eq. (14)] to be followed quite closely.[9] The result reported for A (2.34×10^{-5} °C^{-1}) was arrived at without end-effect corrections. Crystals 1 to 9 were only partially electroded and hence end effect corrections[10] are required. The second column of Table I shows corrected values. For completely electroded crystals (10 to 12), end effect corrections are negligible because of the high dielectric constant of the material. In calculating other constants, the value 2.60×10^{-5} °C^{-1} will be used for A.

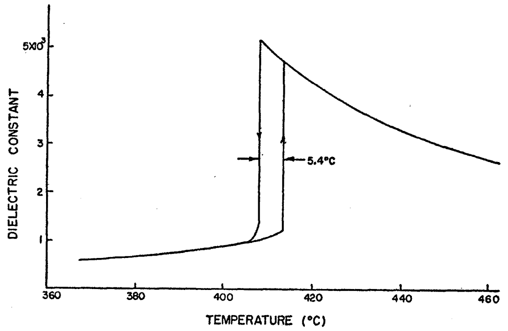

FIG. 2. Dielectric constant *vs* T in vicinity of cubic to tetragonal transition. Measuring field is 10 v/cm at 10 kc/sec.

For examining the thermal hysteresis in the vicinity of the transition, and for rapid checking of the behavior of the crystals, a Moseley XY recorder was used to record capacity *vs* T. Figure 1 shows a block diagram of the circuit. R was always much smaller than the impedance of the sample. The linearity and calibration of the system was checked by substituting calibrated condensers for the sample. Figure 2 is a typical result for one of the crystals. In running through several temperature cycles, it was found that the cubic phase reproduced quite well, but that sometimes the tetragonal phase dielectric constant would be higher than shown. It was usually possible to reduce the dielectric constant below the transition to the values shown by the application for several seconds of a dc voltage of about 1000 v/cm. One can infer that the lower value is for a "*c*" plate while the higher values were for a crystal with some "*a*" domains.

TABLE I. Values of A and T_0 for various crystals.

Crystal No.	A uncorrected	A corrected	T_0
1	2.06×10^{-5}	2.37×10^{-5}	364
2	2.29	2.75	360
3	2.49	2.76	368
4	2.34	2.71	366
5	2.12	2.61	366
6	2.34	2.66	352
7	2.26	2.78	355
8	2.49	2.72	366
9	2.11	2.36	368
		2.64 ± 0.11	
10	2.35	2.35	350
11	2.73	2.73	358
12	2.52	2.52	352
		2.53 ± 0.13	360.4 ± 5.9

The thermal hysteresis reproduced rather well for slow heating and cooling rates, falling between 5°C and 6.5°C for all the crystals so tested. Känzig and Maikoff[11] have estimated thermal hysteresis as $\Delta T = L/C$, where L is the latent heat of the transition and C is the heat capacity. This is based on an assumption that a finite-

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[9] S. Triebwasser and J. Halpern, Phys. Rev. **98**, 1562 (1955).
[10] H. Curtis, J. Research Natl. Bur. Standards **22**, 747 (1939).
[11] W. Känzig and N. Maikoff, Helv. Phys. Acta **24**, 343 (1951).

sized region (domain) must undergo the transition all at once so that the process is always locally adiabatic. Hence the heat absorbed or liberated on heating or cooling must come from the domain itself. This appears to be an over-simplification of the origin of the thermal hysteresis, but at least gives order of magnitude agreement in $BaTiO_3$ and also in $KNbO_3$. Our measurements on a ceramic sample of $KNbO_3$ give C as 35 cal/mole °C and $L=134$ cal/mole at the transition, leading by the above formula to a theoretical value for the thermal hysteresis of 3.8°C.

If the point midway between the two discontinuities is chosen as T_c then, for the crystals for which curves such as Fig. 2 were taken, T_c is 418±5°C. The value of (T_c-T_0) was 58±5°C. Part of the observed fluctuation in T_c and T_0 is experimental. Our crystal holder was an aluminum can in which five crystals were suspended by their lead wires, and a sixth lead was provided as a dummy. The temperature recorded was that in the air space. There could, therefore, be small errors in the absolute temperature values due to fixed gradients in the crystal holder, in addition to possible calibration error in the chromel-alumel thermocouples used. Thermal lag was eliminated by varying the crystal holder temperature sufficiently slowly so that the heating and cooling curves reproduced in the paraelectric phase.

Figure 3 shows the same data as in Fig. 2, but with $1/K$ plotted *vs* temperature. The dashed lines represent Eqs. (14) and (15). The agreement in the paraelectric phase is intrinsic except for the linearity of the data, since the constants A, T_c, and T_0 are so chosen. Within the accuracy of both the theory and the experimental method, the agreement in the ferroelectric phase is quite good. In the theory, we have assumed B and C to be temperature-independent. In addition, we have cut off a power series expansion at a term which is not small compared with the others. Also, we cannot be sure that we have a perfect "c" plate. Equation (16) was approximated for most crystals, the experimental ratio ranging from 4 to 5 depending on choice of T_c within the thermal hysteresis region.

IV. SPONTANEOUS POLARIZATION

The spontaneous polarization and coercive fields of several crystals were measured as a function of temperature using the standard Sawyer-Tower circuit.[12] In Fig. 4, the data for one crystal is compared with the spontaneous polarization calculated from Eq. (12). The theoretical values are shown from T_0 (360°C) to T_c (420°C) for this sample. The constant $B/3C$ is determined empirically from the measured polarization at T_0, where it is given by $P_0^2=2B/3C$. At 300°C ($\tau=-1$), the experimental curve is 7% below the theoretical. By 240°C ($\tau=-2$) the two curves would not resemble each other, the theoretical curve climbing rapidly with decreasing temperature. Undoubtedly, the error introduced by the temperature dependence of A, B, and C is no longer small.

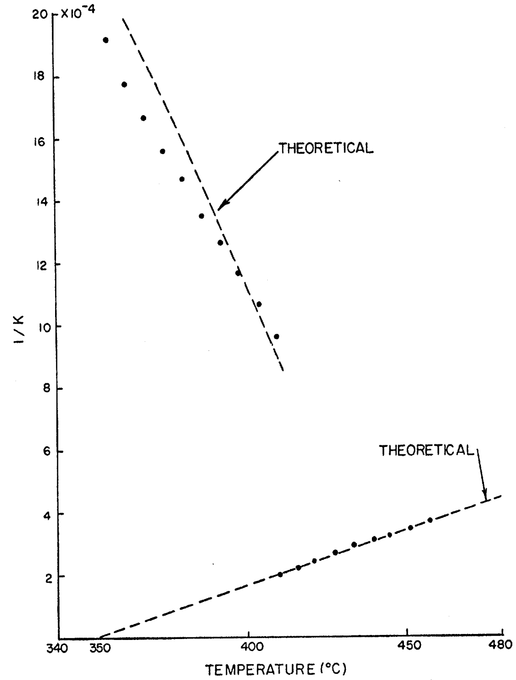

FIG. 3. Reciprocal dielectric constant *vs* T, experimental and theoretical from data of Fig. 2.

The data plotted were taken at 500 cps. Figure 5 shows typical hysteresis loops at 500 cps and 5000 cps at the temperatures indicated.

We reported a spontaneous polarization at the transition of 26 microcoulombs/cm².[9] The uncertainty is about 10% as judged by the scatter of values from crystal to crystal. From Eq. (18), the latent heat of the transition should be 100 cal/mole. Our measured value was given as 135 cal/mole,[9] while Shirane *et al.*[5] report 190 cal/mole.

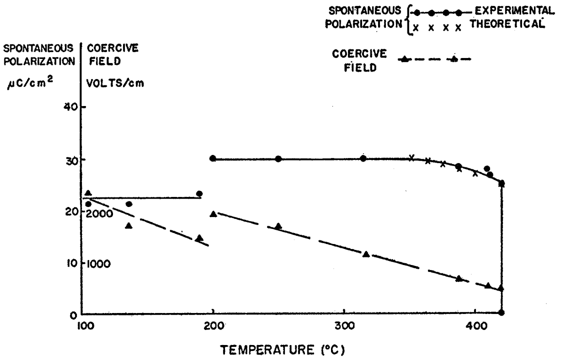

FIG. 4. Spontaneous polarization and coercive field for $KNbO_3$ single crystal at 500 cps.

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[12] C. B. Sawyer and C. H. Tower, Phys. Rev. **35**, 269 (1930).

TABLE II. Comparison of constants for $BaTiO_3$ and $KNbO_3$.

Quantity	BaT_iO_3	Source	$KNbO_3$	Source
A	3.7×10^{-5} °C^{-1}	a	2.60×10^{-5} °C^{-1}	b
P_c	18 μcoul/cm^2	a	26 μcoul/cm^2	b, c
$T_cAP_c^2$	39 cal/mole	$T_c=393$°K	100 cal/mole	b
L	47 cal/mole	d	135 cal/mole 195 cal/mole	c e
B	2.5×10^{-13} cgs	f	5.0×10^{-13} cgs	Eqs. (9) and (10)
C	3.8×10^{-23} cgs	a	4.1×10^{-23} cgs	
$A(T_c-T_0)$	4.1×10^{-4}	$T_c-T_0=11$°C	1.51×10^{-3}	$T_c-T_0=58$°C
$B^2/4C$	4.1×10^{-4}			
P_c^2	2.92×10^9 esu^2/cm^4		6.1×10^9 esu^2/cm^4	
$B/2C$	3.3×10^9 esu^2/cm^4			
$A(T_c-T_0)P_c^2$	1.2×10^6 erg/cm^3		9.2×10^6 erg/cm^3	
$-BP_c^4$	-2.1×10^6 erg/cm^3		-18.6×10^6 erg/cm^3	
CP_c^6	0.94×10^6 erg/cm^3		9.3×10^6 erg/cm^3	

[a] See reference 3.
[b] This paper.
[c] See reference 9.
[d] J. Volger, Phillips Research Repts. **7**, 21 (1952).
[e] See reference 5.
[f] See reference 13.

V. DISCUSSION

From Eqs. (9) and (10) and the measured values of A, (T_c-T_0), and P_c, we can calculate the constants B and C for $KNbO_3$:

$$B=5.0\times10^{-13}\ (\mathrm{erg/cm^3})^{-1},$$

$$C=4.1\times10^{-23}\ (\mathrm{erg/cm^3})^{-2}.$$

Table II is a summary of the various constants of $BaTiO_3$ and $KNbO_3$ tabulated for comparison. A few remarks are in order on some of the values given.

First, we notice that in no instance do the constants for the two materials differ by as much as an order of magnitude. This is expected from the general qualitative similarity of behavior of the two crystals. In the case of $BaTiO_3$, Eq. (9) is well satisfied, as is Eq. (10). We have no check of these relations for $KNbO_3$ since no independent measurements of B and C are available. It is also apparent that the value of B measured directly by Drougard, Landauer, and Young[13] gives far better agreement with the theory than that reported by Merz ($B=1.7\times10^{-13}$ cgs-esu), demonstrating further the validity of the former's discussion of clamping effects in the partially electroded samples.

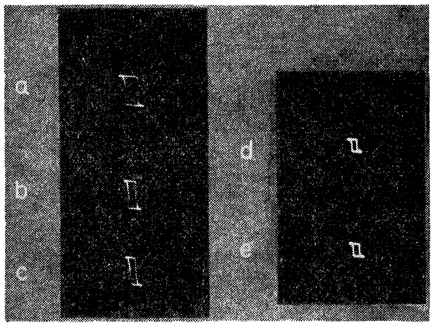

FIG. 5. Hysteresis loops in $KNbO_3$ single crystals: *a*, 315°C; *b*, 387°C; *c*, 409°C; *d*, 300°C; *e*, 340°C. *a*, *b*, and *c* are from the data of Fig. 4, *d* and *e* for a different crystal at 5 kc/sec.

Of greater significance is the temperature dependence of B found by these authors (Drougard *et al.*). They found that B could be written approximately[14]:

$$B(T)=B(T_c)[1-\tfrac{1}{6}(\tau-1)]. \tag{2}$$

This affects Eqs. (15) and (18) appreciably. For example at $\tau=0$, $4\pi/K=(32/3)(B^2/2C)$ and $B(T_0)=B(T_c)[1+\frac{1}{6}]$. This leads to a correction of about 36% in the calculated value of $1/K$ at T_0. If $KNbO_3$ had such a temperature dependence of B, the agreement between the theoretical and experimental curves in Fig. 3 would be poorer. In the case of Eq. (18), there would be an added term:

$$S(P_c,T_c)=-\left(\frac{\partial F}{\partial T}\right)_P=S(0,T_c)-AP_c^2+\frac{\partial B}{\partial T}P_c^4$$

$$=S(0,T_c)-AP_c^2-[\tfrac{1}{6}]\frac{B(T_c)}{(T_c-T_0)}P_c^4 \tag{3}$$

or

$$S(P_c,T_c)-S(0,T_c)=-\frac{1}{(T_c-T_0)}$$

$$\times[(T_c-T_0)AP_c^2+\tfrac{1}{6}B(T_c)P_c^4]. \tag{4}$$

From Table II or the theory, it can be seen that the added term leads to an increase of about $\frac{1}{3}$ in the calculated latent heat. There is at present no information on the temperature dependence of C.

From the present state of knowledge we conclude that there exist for these two systems (and probably for others) expansions of the free energy in even powers of the polarization which describe with reasonable accuracy the phenomena discussed here. Furthermore,

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[13] Drougard, Landauer, and Young, Phys. Rev. **98**, 1010 (1955).

[14] Equation (2) is an empirical relation based on the data of Fig. 3 of reference 13.

three terms in this expansion do fairly well for the detailed description in the vicinity of the cubic-to-tetragonal transition. One can hope, then to be able to treat microscopically the problem of the cubic perovskite and use the A, B, C, and T_0 as measured to find additional details in the interaction as discussed by Slater. Kittel[15] has shown how this treatment can be extended to predict the existence of antiferroelectricity.

ACKNOWLEDGMENTS

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APPENDIX: THERMODYNAMICS OF THE DEVONSHIRE THEORY

We represent the free energy, F, as a function of the polarization by the polynomial

$$F(P,T)-F(0,T)=A(T-T_0)P^2-BP^4+CP^6. \qquad (5)$$

In a fixed external field, E, the equilibrium value of the polarization will be that for which the thermodynamic potential

$$G=F-EP \qquad (6)$$

is a minimum. Hence the equilibrium value of P must satisfy

$$E=(\partial F/\partial P)=2A(T-T_0)P-4BP^3+6CP^5. \qquad (7)$$

For $E=0$, minima of G are given by

$$P=0, \quad P=\pm P_0, \qquad (8)$$

where

$$P_0^2=(B/3C)\{1+[1-(3C/B^2)A(T-T_0)]^{\frac{1}{2}}\}. \qquad (8')$$

[The other two roots of the quintic (7) for $E=0$ give maxima of G.] If the minimum at $P=0$ is the lower of the two, $F(0)<F(P_0)$, then the crystal will be unpolarized in zero field: that is it will be in the cubic (paraelectric) phase. If $F(P_0)<F(0)$, there will be a spontaneous polarization of magnitude P_0: the crystal will be in the tetragonal (ferroelectric) phase. The transition occurs at the temperature for which $F(0)=F(P_0)$. Then, from (5) and (8′), we find for the transition temperature, T_c,

$$A(T_c-T_0)=B^2/4C, \qquad (9)$$

and for the polarization at this temperature,

$$P_c^2=B/2C, \quad \text{where} \quad P_c=P_0(T_c). \qquad (10)$$

If A, B, and C are independent of the temperature, (8′) can be expanded in terms of

$$\tau=(T-T_0)/(T_c-T_0), \qquad (11)$$

as

$$P_0^2=(B/3C)[1+(1-\tfrac{3}{4}\tau)^{\frac{1}{2}}]. \qquad (12)$$

Dielectric Constant

Since the dielectric constant, K, is large, it may with sufficient accuracy be set equal to $4\pi(\partial P/\partial E)_T$. Then, by differentiating (7) with respect to P, we obtain

$$4\pi/K=2A(T-T_0)-12BP^2+30CP^4. \qquad (13)$$

Hence, for the paraelectric state in zero field,

$$4\pi/K=2A(T-T_0)=(B^2/2C)\tau. \qquad (14)$$

For the ferroelectric state in zero field, we find, from (9), (11), (12), and (13),

$$4\pi/K=(B^2/2C)(16/3)[(1-\tfrac{3}{4}\tau)+(1-\tfrac{3}{4}\tau)^{\frac{1}{2}}]. \qquad (15)$$

It follows from (14) and (15) that at the transition

$$K_{\text{paraelectric}}=4K_{\text{ferroelectric}}, \qquad (16)$$

as has been pointed out by Kittel (reference 15).

Latent Heat

If we assume A, B, and C are independent of temperature, then the entropy is

$$S(P,T)=-(\partial F/\partial T)_P=S(0,T)-AP^2. \qquad (17)$$

Hence, the latent heat of the transition in zero field is

$$L=T_c\Delta S=T_cAP_c^2. \qquad (18)$$

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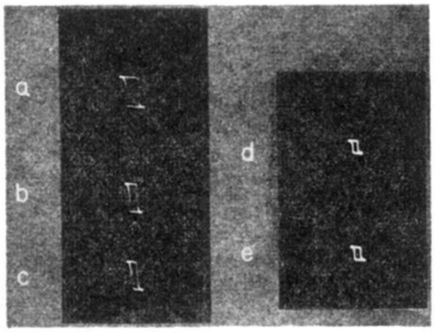
[15] C. Kittel, Phys. Rev. 82, 729 (1951).



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