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ac Hall Measurements in Crystals of Strontium Titanate from 190 to 500°K: Dependence of Hall Mobility on Charge-Carrier Density*

D. PARKER
Lamar State College of Technology, Beaumont, Texas

AND

J. YAHIA†
Oklahoma State University, Stillwater, Oklahoma

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Results of ac Hall mobility measurements in crystals of strontium titanate in different stages of reduction are reported for the temperature range 190–500°K. The charge-carrier concentration of one of these crystals was two orders of magnitude less than for crystals measured in any previously reported work. A dependence of the magnitude of the mobility on the density of charge carriers was found, with the mobility *increasing* with an increase in the degree of reduction of the crystals. The temperature variation of the mobility is essentially the same for all the samples, and assumes the form $\mu_0 e^{\Theta/T}$, with μ_0 and Θ constants. A value for Θ about 700°K was calculated from the data, and values for μ_0 were 0.42, 1.0, and 1.42 cm^2 V^{-1} sec^{-1}, with the lowest value corresponding to the sample with least reduction. A polaron mass was calculated using the value of μ_0 for the least-reduced crystal, and was found to be $3.1m_0$, with m_0 the free-electron mass.

INTRODUCTION

THE compound strontium titanate is a clear, glass-like material with high index of refraction[1] and a large dispersion.[1] It is transparent to 5 μ in the infrared. It is cubic[2] at room temperature, but undergoes a transition to tetragonal at about 110°K.[3,4] The crystal is thought to be ferroelectric below 45°K, and there is some basis for this conclusion: At 40°K and below this temperature, Weaver[5] observed hysteresis loops in the material, and Gränicher[6] has shown that strontium-titanate samples can be made to oscillate like a piezoelectric after polarization by a field in excess of 600 V cm^{-1}. There is, however, some question as to whether strontium titanate is ferroelectric, notwithstanding the observations made above: A hysteresis loop is a necessary but not sufficient condition for ferroelectricity, and, indeed, an unexplained observation with respect to the ferroelectricity of strontium titanate is the lack of a discontinuity of the dielectric constant at 45°K.[5] Frederikse *et al.*[7] refer to a theory of Cochran[8] as being relevant in an explanation of ferroelectric effects found in this material. The energy gap in strontium titanate is ~3.2 eV[9]; thus this material is an excellent insulator when pure and stoichiometric. However, upon reduction at high temperatures in either a hydrogen atmosphere or a forepump vacuum, it becomes semiconducting, and optically a broad absorption band appears, increasing towards the infrared.[9] The crystals obtained by reduction can range from a pale blue (light reduction) to a dark blue or opaque (heavy reduction).

Measurements of electrical conductivity, Seebeck coefficient, and dc Hall effect in reduced and doped strontium titanate have been made by Frederikse *et al.*,[7] in the temperature range from 4 to 300°K. The main conclusions of these authors were as follows: (a) The average effective mass deduced from their data is $\sim 10m_0$ in this material (here m_0 is the free-electron mass); (b) phonon-drag contributions to the thermoelectric power appear to be negligible above 50°K. Tufte and Chapman[10] have also measured the dc Hall mobility in strontium-titanate crystals which were reduced or doped with niobium, in the temperature range from 1.6–550°K. In the high-temperature region, these authors analyze their mobility results in terms of a coupling of the electron to the longitudinal optical modes of the crystal, pointing out, however, that there are two limitations in this analysis: (a) The theory is inexact for a strong electron-phonon coupling; (b) the temperatures of the measurements are not much smaller than $\hbar\omega_l/k$, where $\hbar\omega_l$ is the energy of the relevant mode. An important point, in view of our present measurements, is that Tufte and Chapman find that, empirically, in the range 200–550°K, their mobility data can be fitted very well by an expression of the form μ (cm^2 V^{-1} sec^{-1})$=0.83$ ($e^{600/T}-1$) (cf. their Fig. 7).

Very recently, Frederikse and Hosler[11] have reported

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* The experimental work described herein was performed at Texas A. and M. University, College Station, Texas.

† Present address: Department of Physics, Université de Montréal.

[1] S. B. Levin, N. J. Field, F. M. Plock, and L. Merker, J. Opt. Soc. Am. **45**, 737 (1955).

[2] R. W. G. Wyckoff, *Crystal Structure* (Interscience Publishers, Inc., New York, 1948), Chap. 7, Table 12.

[3] R. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963); **125**, 1915 (1962).

[4] L. Rimai and G. A. de Mars, Phys. Rev. **127**, 702 (1962).

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[8] W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1960), Vol. IX, p. 387.

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[10] O. N. Tufte and P. W. Chapman, Phys. Rev. **155**, 796 (1967).

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dc Hall mobility measurements on some 30 crystals of reduced and doped strontium titanate in the temperature range 1 to 1000°K. These authors conclude from their data that above room temperature, the interaction of *two* longitudinal optical modes with the electron determines the mobility behavior.

Our work describes detailed measurements on the temperature variation of the *ac Hall mobility* for three crystals of strontium titanate in different stages of reduction, in the temperature range 190–500°K. These measurements corroborate the dc results of the workers mentioned above as to order of magnitude of the electronic mobility in reduced strontium titanate in the temperature range investigated. In addition, two features are presented which were not brought up in the former measurements: (a) Most conspicuous is the fact that the magnitude of the mobility depends on the degree of reduction of the crystal, being smaller for lower degrees of reduction, and (b) the slope of the straight-line $\ln\mu$-versus-T^{-1} plot seems more or less independent of degree of reduction and is about 0.06 eV (here μ is the mobility).

EXPERIMENTAL

The crystals used in these measurements were cut from boules obtained from the National Lead Company.[12] Wafers approximately 1.5 mm thick were cut from the boule, using a diamond wheel, and from these wafers a string saw was used to cut samples in the shape of rectangular parallelepipeds of dimensions $\sim 10\times 3\times 1.5$ mm. The samples were reduced by being placed in an evacuated quartz tube (forepump vacuum $\sim 10^{-3}$ Torr) which was itself in the center of a cylindrical high-temperature oven. It was found that the samples were readily reduced, requiring times of reduction (at equivalent temperatures) considerably less than those given by Frederikse *et al.*[7] for a comparable reduction in resistivity. Generally, an exposure time about $\frac{1}{2}$ h at 850°C was more than enough to bring the value of the resistance of test samples to values of a few ohm.

Six contacts to the crystals were made by first drilling shallow holes (10 mil in diam, approximately 10 mil deep), using an ultrasonic drill,[13] and then filling these holes with indium solder.[14] Platinum wires were then bent until they made good pressure contacts with these indium spots, and a gold paste was applied to the junction. The gold paste lowered the contact resistance in all cases, provided that the paste covered an area of the crystal larger than the indium spots. It was noted that where the indium had been removed, the gold paste by itself did not make so good a contact as the combination described above; also, as is usually the case, the indium contacts deteriorated after a high-temperature run. A sizeable contact resistance was observed, even on the low-resistivity samples. For example, the ratio of the total applied voltage (across the current contacts) to the drop across the longitudinal Ohmic probes was about 1.5 to 2.0 for sample No. 2 and about 3 to 10 for sample No. 1, with the largest ratio corresponding to the lowest temperature. With perfect contacts, geometrical factors would make this ratio about 1.2. In processing our data, we assume that the longitudinal probe voltage divided by the separation of these probes gives a representative electric field in the sample. The current probes were found to be nonlinear, with the worst situation occurring in the high-resistivity samples at low temperatures. Since these measurements were made, Carnes and Goodman have reported[15] the results of a detailed study of metal contacts on strontium titanate which will explain the source of this nonlinearity.

The method used to make the Hall measurements on the most heavily reduced sample (where the current probes were linear) is described in detail in an article by Hermann and Ham.[16] In this method of measurement, *the sample is rotated* in a fixed magnetic field at 20 cps. An electric field is applied at $13\frac{1}{3}$ cps, and the Hall signal, preamplified by field-effect transistors mounted on the rotating shaft near the sample, is synchronously detected at $33\frac{1}{3}$ cps. Hall mobilities as small as 0.2 cm^2 V^{-1} sec^{-1} in samples of resistance $\sim 10^9$ Ω can be measured with negligible detector loading. This method therefore appears to be well suited to measurements of Hall mobilities in oxide semiconductors, where low mobilities and high impedances are often encountered, provided that Ohmic contacts can be obtained. When Hall measurements were attempted on the high-resistance samples by this method, the abovementioned current probe nonlinearity (which produced only a slight distortion of the current waveform) was found to mix the current frequency and the rotation frequency ($d\Phi/dt$ voltage), and thus produce a false Hall signal. This signal is exactly linear in the B field, is nonlinear in the rms current, and is at some arbitrary phase relative to the true Hall signal. The problem was avoided by rotating the sample at 4 rpm instead of 1200 rpm (thus reducting the $d\Phi/dt$ voltage by a factor of 300) and reversing the polarity of the output of the synchronous detector every half-revolution. The current frequency was switched to $33\frac{1}{3}$ cps (the frequency of the detection system). The polarity reversal was obtained by means of a cam, microswitch, and reversing relay. The reversing mechanism was carefully symmetrized so that a constant $33\frac{1}{3}$-cps signal into the synchronous detector (giving an average dc level at the synchronous-detector output) would average to zero. Thus an error in setting the bucking signal would only

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[12] National Lead Company, Titanium Division, Research Laboratory, P. O. Box 58, South Amboy, N. J.

[13] Gulton Industries, Inc., 212 Durham Ave., Metuchen, N. J.

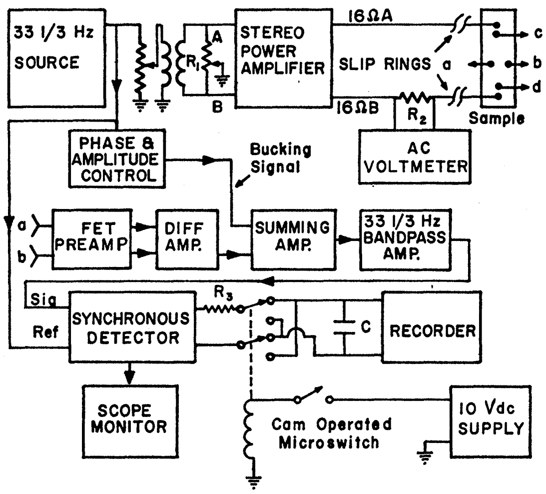
[14] Available from Indium Corporation of America.

[15] J. E. Carnes and A. M. Goodman, J. Appl. Phys. **38**, 3091 (1967).

[16] A. M. Hermann and J. S. Ham, Rev. Sci. Instr. **36**, 1553 (1965).

cause 1/15-cps oscillations of the output about the correct value. In principle, this is still a three-frequency method, although both Hall components ($33\frac{1}{3}\pm 1/15$ cps) as well as the unwanted mismatch are now within the band pass of the detection system.

A block diagram of the modified system is shown in Fig. 1. The Hall data for sample No. 2 were obtained by the usual (1200-rpm) method, and those for Nos. 1 and 3 were obtained by the modified method. The resistivity data for samples Nos. 2 and 3 were taken simultaneously with the Hall data by connecting the longitudinal voltage probes through slip rings to an oscilloscope differential amplifier and then to an ac voltmeter. Because of the rather high resistance of sample No. 1, the resistivity data and Hall data were taken on separate temperature sweeps, so that the FET preamp could be used to monitor the longitudinal probe voltage. Sample temperatures, both above and below room temperature, were obtained by standard methods and monitored using a thermistor mounted in the rotating sample holder.



NOTES:

1. Hall Probes are set near AC ground with R_1
2. $R_2 = 1\Omega$ 1% for samples 2 & 3 and 100Ω 1% for sample 1.
3. R_3C = 75 seconds
4. The microswitch is opened (closed) when the plane of the sample is parallel (antiparallel) to the B field.

FIG. 1. Block diagram of 4-rpm method (see text).

RESULTS AND DISCUSSION

The results of our measurements are shown in Figs. 2–4. In Fig. 2, ln$R$ is plotted as a function of T^{-1} for the three samples. It will be seen from this figure that for the most highly reduced sample (No. 2), the Hall coefficient is almost independent of temperature, implying a complete ionization of the (shallow) donor centers over the temperature range measured, and also suggesting that these centers, because of their high density, are more effective in controlling the conductivity behavior than any compensating centers existing in the crystal. For samples Nos. 1 and 3, the Hall coefficient is fairly independent of temperature at the lower temperatures, but, as the temperature increases above 250°K, the coefficient drops slowly in value. This behavior is similar to that noted by Frederikse *et al.*[7] for some of their samples, and is explained by them as being due to an acceptor-donor compensa-

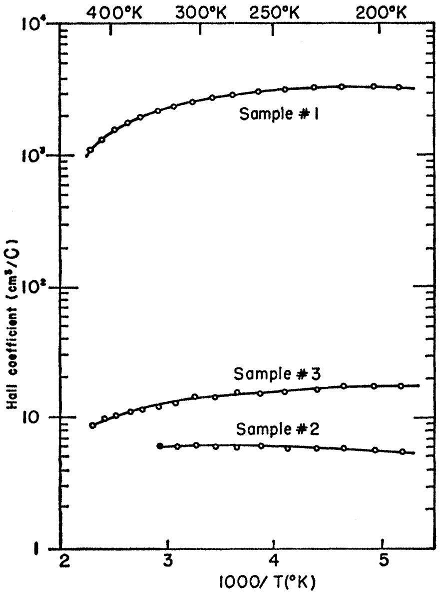


FIG. 2. Hall coefficient as a function of temperature for crystals of strontium titanate.

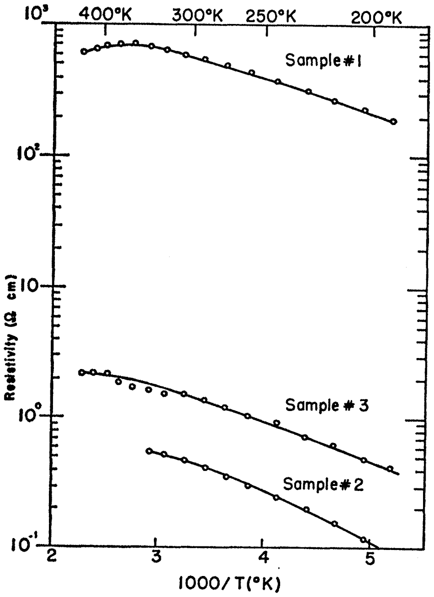


FIG. 3. Resistivity as a function of temperature for crystals of strontium titanate.

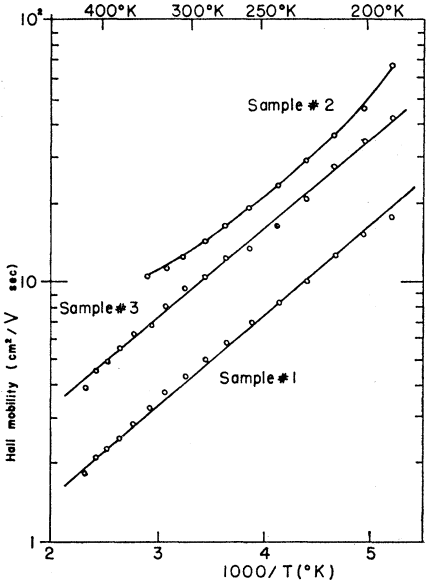


FIG. 4. Log mobility versus inverse temperature for crystals of strontium titanate.

tion mechanism. Their conclusion is that the charge carriers originating from the shallow-donor centers introduced by the reduction do not dominate the picture when their density is below a certain value, about $1\text{–}3\times10^{18}$ cm^{-3}. Thus for "smaller" reductions one can expect the compensating centers to have an influence on the temperature dependence of the Hall coefficient and resistivity. These centers might be foreign ions, vacancies, interstitials, etc.

Figure 3 shows the $\ln\rho$-versus-T^{-1} plots for samples 1, 2, and 3. These data are in agreement with our Hall data, in that the samples show a correlation between degree of reduction, or density of charge carriers, and electrical resistivity, the most highly resistive samples being the least reduced. Note that the $\ln\rho$-versus-T^{-1} plot is more or less linear at low temperatures and *increases* with increase in temperature, similar to results obtained by Tufte and Chapman.[10] This implies that the temperature variation of mobility in this range is more important than the variation with temperature of the density of charge carriers. At high temperatures the resistivity appears to go through a broad maximum, decreasing at still higher temperatures. This is probably due to the competition between density and mobility terms in the expression for the resistivity, with the density term dominating at high temperatures.

Figure 4 shows a plot of $\ln\mu$ versus T^{-1}, and it may be seen that this plot is quite linear for samples Nos. 1 and 3, but that sample No. 2 shows some nonlinearity at low temperatures. Starting from the linear connection between $\ln\mu$ and T^{-1} and from the fact that strontium titanate is believed to be quite ionic,[17] it seems plausible to suppose that the dominant interaction describing the behavior of the mobility for all three crystals is one invoking an interaction of the Fröhlich type.[18] Moreover, we find from our data that the slope of the $\ln\mu$-versus-T^{-1} line corresponds to an energy 0.06 eV, or $\hbar\omega_l=0.06$ eV in terms of the theory referred to above, where ω_l is the frequency of the interacting mode. It seems probable, therefore, that the interaction is with the second highest longitudinal optical mode in strontium titanate, since Eagles[19] has calculated that for this mode, $\hbar\omega_l=0.058$ eV. (The calculation of Eagles is based on room-temperature infrared-reflection data in this material by Spitzer *et al.*[20]) For this mode, Eagles has calculated a value for the coupling constant $\alpha=0.50\times(m_{\text{eff}}/m_0)^{1/2}$. If one takes for the rigid-lattice mass m_{eff} the value $2m_0$, as seems indicated from the work of Barker[21] and Frederikse and Hosler,[11] one obtains $\alpha=0.7$. (Note that m_0 is the free-electron mass.) For this value of α (less than unity), one can probably use the perturbation-theoretic treatment[18] of mobility of a slow electron in a polar lattice to estimate, from fundamental theory, effective masses for the charge carriers in terms of the experimental results. One may also start from a different point, using the approach of Low and Pines, which is especially appropriate for the intermediate coupling range, $1<\alpha<6$, and which reduces to the perturbation-theory result for α small enough. We shall now use this latter formalism to derive values for coupling constants and polaron masses for our crystals.

According to these authors, the mobility μ is given by[22]

$$\mu=\frac{1}{2\alpha\omega_l}\frac{e}{m_p}\left(\frac{m_{\text{eff}}}{m_p}\right)^2 e^{\hbar\omega_l/kT}, \quad \hbar\omega_l\gg kT.$$

Here ω_l is the circular frequency of the interacting mode, m_{eff} is the rigid-lattice mass, m_p is the polaron mass, and α is the coupling constant.

Rather than use the value of α from the work of Eagles quoted above, we solve for values of α and m_p, using the equation for the mobility, the Low and Pines relation between m_p and m_{eff} for α small, $m_p=m_{\text{eff}}\times(1+\frac{1}{6}\alpha)$, and our experimental results for the pre-exponential factor μ_0 (0.4, 1.0, and 1.46 cm^2 V^{-1} sec^{-1}) and for the term ω_l ($28\pi\times10^{12}$ sec^{-1}). The results of this calculation are shown in Table I. In the last

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[17] A. H. Kahn, H. P. R. Frederikse, and J. H. Becker, in *Transition Metal Compounds*, edited by E. R. Schatz (Gordon and Breach Science Publishers, Inc., New York, 1964).

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[19] D. M. Eagles, J. Phys. Chem. Solids **26**, 672 (1965).

[20] W. G. Spitzer *et al.*, Phys. Rev. **126**, 1710 (1962).

[21] A. S. Barker, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1965).

[22] F. E. Low and D. Pines, Phys. Rev. **98**, 414 (1955).

column of this table, the ratio m_p/m_0 is computed on the basis that $m_{\mathrm{eff}}=2m_0$.[11,21]

At this point, the question regarding which preexponential factor is appropriate to a calculation of a "true" α and m_p occurs: Should the μ_0 corresponding to the most reduced crystal or the least reduced crystal be used? Qualitatively, one would expect that the latter should be used. The reason for this is that in the pure and stoichiometric crystal, one would expect to measure the "true" electron-phonon interaction, uncomplicated by the presence of a free-electron system which has the effect of shielding this interaction. This point has been raised earlier by von Hippel *et al.*[23] Using this picture, it is clear why the crystals with greater degree of reduction have the larger mobilities: The electron-phonon interaction being shielded, m_p decreases, and, as we have seen, $\mu_0 \sim m_p^{-3}$. Also, it is entirely consistent with our picture that the temperature variation of the mobility should *not* depend strongly on degree of reduction of the crystal. The temperature variation is governed by terms representing absorption and emission of phonons of the form $1/(e^{\hbar\omega_l/kT}-1)$ (absorption) and $e^{\hbar\omega_l/kT}/(e^{\hbar\omega_l/kT}-1)$ (emission). It is true that $\omega_l=(\epsilon/n^2)^{1/2}\omega_t$, where ω_l is the frequency of the longitudinal optical mode, ω_t is the residual ray frequency, ϵ is the static dielectric constant, and n^2 is the high-frequency dielectric constant. This term will depend somewhat on the variation of ϵ and n^2 with degree of reduction.

Another, far more precise formulation of the shielding problem is to be found in the work of Ehrenreich.[24] This author has given a complete discussion of the effect of screening by conduction electrons of the electron-phonon interaction of the Fröhlich type. He derives the Hamiltonian directly, using Poisson's equation for the potential of the electron Φ, including polarization charge density *and* screening charge density in the source term. He finds that $4\pi Q=-a^2\Phi$, where Q is the screening charge density arising from the presence of the excess electrons, and a is a complicated expression which reduces to the reciprocal of the Debye screening length for the limiting case of parabolic bands and Boltzmann statistics. The reduced expression is $a^2=4\pi ne^2/\epsilon_s kT$, where n is the density of charge carriers, e^2 the electronic charge, and ϵ_s the static dielectric constant. (It probably reduces to the Fermi-Thomas expression for high densities and low masses and temperatures, although this is not immediately seen from the general expression for a.) The matrix element for scattering is recalculated, using the solution to the Poisson equation, and it is found that this element is modified, in that the factor $1/q$ appearing in it is replaced by $q/(q^2+a^2)$ (q is the phonon wave number). This screening reduces the effectiveness of the interaction and leads to a decreased transition probability for scattering or to an increased absolute value of mobility. The temperature dependence of the mobility is not affected by the presence of this screening.[25] We see, then, that this calculation predicts a dependence of mobility on charge-carrier density such as the one which we have observed.

TABLE I. Coupling constants and polaron masses for crystals of strontium titanate from experimental data and Low-Pines theory (see text).

Sample number	Room-temperature resistivity (Ω cm)	Room-temperature Hall constant (cm^3 C^{-1})	μ_0 (cm^2 V^{-1} sec^{-1})	α	m_p/m_0
1	650	2300	0.4	3.3	3.1
3	1.8	12.5	1.0	2.1	2.7
2	0.54	5.8	1.46	1.7	2.6

Finally, if one takes the position that μ_0 for the most lightly reduced crystal (0.4 cm^2 V^{-1} sec^{-1}) is the proper preexponential factor to compare with theory, one obtains a value of $m_p=3.1m_0$. We believe that the actual polaron mass will be somewhat larger than this value and will be determined only by measurements on stoichiometric and extremely pure strontium titanate.

ACKNOWLEDGMENTS

We are indebted to G. Baum for preparing the crystals used in these measurements, and to Professor M. Cohen for referring us to the calculations of Ehrenreich on screening. One of the authors (D.P.) would like to thank Professor J. S. Ham for helping him with this work.

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[23] A. von Hippel *et al.*, J. Phys. Chem. Solids **23**, 779 (1962).

[24] H. Ehrenreich, J. Phys. Chem. Solids **2**, 131 (1957).

[25] Reference 25, Eq. (52).