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PHYSICAL REVIEW B

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## Off-Center $\text{Cu}^+$ Ions in Potassium Halides Studied with Ionic Thermocurrents\*

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From previous optical and theoretical work it had been concluded that substitutional  $\text{Cu}^+$  ions may occupy off-center positions in certain alkali halides. The method of ionic thermocurrents (ITC) was applied to verify directly the electric dipole properties of  $\text{Cu}^+$  ions in three potassium halides, and to study the temperature dependence of their relaxation behavior. ITC bands were observed for  $\text{Cu}^+$  in KCl, KBr, and KI, with maxima at 62, 70, and 83 °K, respectively. From the integrated ITC currents of crystals with calibrated  $\text{Cu}^+$  concentrations, the electric dipole moment was determined, yielding values of 1.5, 1.9, and 2.6  $e\text{Å}$  for  $\text{Cu}^+$  in KCl, KBr, and KI, respectively. The shape of the ITC bands was found in quantitative agreement with the calculated behavior for dipole reorientation by classical rate theory with a single relaxation time. The activation energy for reorientation of the  $\text{Cu}^+$  dipole was found to be 177, 196, and 232 meV for KCl, KBr, and KI, respectively. Using additional material on  $\text{Cu}^+$  and  $\text{Ag}^+$  ions, some systematic trends in the appearance of the off-center effect, and in the static and dynamic off-center dipole properties of heavy-metal ions, are demonstrated and discussed.

### I. INTRODUCTION

Substitutional  $\text{Cu}^+$  and  $\text{Ag}^+$  ions in alkali halides have attracted considerable experimental and theoretical interest in recent years because they are supposed to occupy (in certain host materials) off-center positions.<sup>1</sup> First indications for this behavior were derived from systematic studies of the uv absorption of  $\text{Cu}^+$  and  $\text{Ag}^+$  centers.<sup>2,3</sup> For  $\text{Cu}^+$  in KCl, KBr, and KI<sup>2,3</sup> and for  $\text{Ag}^+$  in RbCl and RbBr,<sup>4</sup> it was found that the oscillator strength of the parity-forbidden electronic  $d \rightarrow s$  transitions at low temperatures was abnormally large. This was qualitatively interpreted to be caused by mixing of electronic states due to a static odd-parity distortion of the center, produced by an off-center position of the metal ion. After several studies of the  $\text{Ag}^+$  system with partly controversial results, the exact nature of the  $\text{Ag}^+$  off-center effect in RbCl and RbBr and its peculiar relaxation behavior was clarified and comprehensively treated recently.<sup>5</sup>

Among the possible  $\text{Cu}^+$  off-center systems, only KCl: $\text{Cu}^+$  is reasonably well understood. Calculations by Wilson *et al.*<sup>6</sup> with a polarizable point-ion

model yielded an off-center displacement of 1.36 Å in a (111) direction. Measurements of the electric field modulation of the  $\text{Cu}^+$  uv absorption by Sittig<sup>7,8</sup> showed the characteristics of paraelectric alignment of  $\langle 111 \rangle$ -oriented  $\text{Cu}^+$  dipoles at higher temperatures. This effect, however, was found to "freeze-in" at about 65 °K, yielding an Arrhenius-type expression for the dipole relaxation time with an activation energy of 0.155 eV. This is in agreement with the negative result of electrocaloric measurements of KCl: $\text{Cu}^+$  at 4 °K.<sup>9,10</sup> For the KBr: $\text{Cu}^+$  systems, no experimental or theoretical evidence exists (besides the above-mentioned absorption-strength argument) for an off-center effect and paraelectric alignment behavior of the  $\text{Cu}^+$  ion.

A highly sensitive and simple technique to study the field alignment behavior of electric dipole defects is the method of ionic thermocurrents (ITC).<sup>11</sup> In this method the dipole system is polarized in a strong dc electric field in a temperature range in which dipole reorientation is readily possible, and then cooled (under field) to a temperature of frozen-in dipole reorientation. In a subsequent heating process (without applied field), the thermally acti-

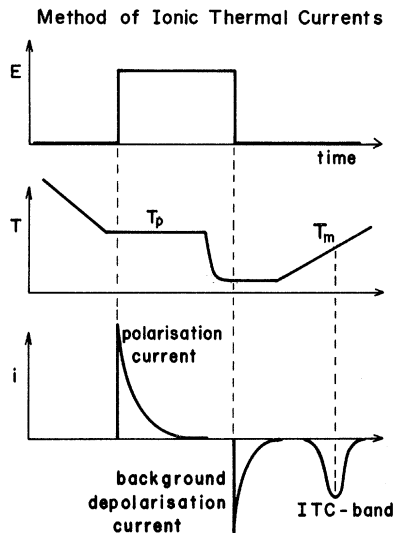


FIG. 1. Schematic representation of the ITC experiment, showing the time variation of the three parameters electric field ( $E$ ), temperature ( $T$ ), and current ( $i$ ).

vated depolarization of the dipole system occurs and is detected by measurement of the depolarization current. This method has been widely and successfully used for the study of the ionic motion of complex defects at high temperatures.<sup>12,13</sup> For molecular and off-center dipole defects which reorient by quantum-mechanical tunneling and therefore are not frozen-in at low temperatures, this method cannot be applied. The off-center heavy-metal ions seem to be exceptions to this, as they display (at least over a certain temperature range) a classical Arrhenius behavior of their relaxation and achieve very long relaxation-time values at low temperatures.<sup>5,7</sup>

In this paper we apply the ITC method for the first time in the low-temperature range to the study of off-center dipole defects. The  $\text{KCl}:\text{Cu}^+$  system (for which the Arrhenius law for dipole relaxation is already established from the electro-optical work<sup>7,8</sup>) will serve as a "test case" for the ITC method. We will then apply this technique to study the electric dipole and relaxation properties of the unknown systems  $\text{KBr}:\text{Cu}^+$  and  $\text{KI}:\text{Cu}^+$ .

## II. EXPERIMENTAL METHOD AND ITC TECHNIQUE

The used crystals were grown from the melt with the  $10^{-4}$ – $10^{-3}$  addition of the appropriate Cu halides. The actual  $\text{Cu}^+$  content in the crystal was determined from the  $\text{Cu}^+$  uv absorption, using the oscillator strength calibration from Ref. 3. An optical He cryostat (Janis) was modified and used for the low-temperature ITC measurements. One of the optical-cryostat windows was replaced by a long brass tube with a Teflon seal at the end,

through which a thin stainless-steel wire extended into the cryostat. Upon insertion of the inner part of the cryostat holding the crystal sample, the end of the stainless-steel wire established contact with the (evaporated) crystal electrode, thus producing the lead for the sensitive current measurement.

The actual experiment followed the usual procedure for ITC measurements,<sup>12</sup> as schematically sketched in Fig. 1. The crystal was cooled to a properly chosen polarization temperature  $T_p$  (between 60 and 80 °K), where a high dc polarization field  $E_p$  (10–40 kV/cm) was applied. After allowing the system to achieve the polarization equilibrium (i. e., allowing the polarization current to decay to zero), the crystal was cooled to liquid-helium (LHe) temperature. At removal of the applied field  $E_p$  at LHe temperature, a strong background depolarization current is observed, which decays in time. After its decay, the temperature is raised with constant rate  $b = dT/dt$ , and the thermally stimulated depolarization current is registered.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows (in an arbitrary normalized scale) the measured ITC currents as a function of the temperature for the three investigated  $\text{Cu}^+$  systems. The observed current for each system consists of a single unsymmetric ITC band, with a maximum at about 62, 70, and 83 °K for  $\text{Cu}^+$  in KCl, KBr, and KI, respectively. For a system of  $N$  identical dipoles with dipole moment  $p$ , which have been polarized in an applied field  $E_p$  at the temperature  $T_p$ , the expected depolarization current  $i(T)$  during a warming process with the rate  $b = dT/dt$  is given by<sup>12,13</sup>

$$i(T) = \frac{Np^2E_p}{3kT_p} \frac{1}{\tau_0} \exp\left(-\frac{\Delta U}{kT} - \int_0^T \frac{1}{b\tau_0} e^{-\Delta U/kT'} dT'\right). \quad (1)$$

This equation should be valid if the dipoles reorient by classical-rate theory with a single relaxation

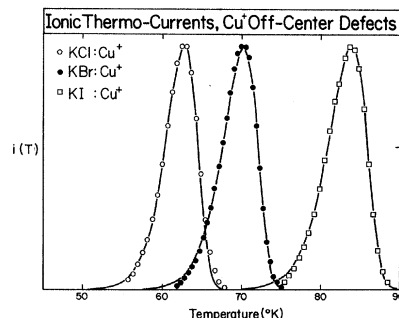


FIG. 2. Measured ionic thermocurrents (in an arbitrary normalized scale) as a function of temperature for the three investigated  $\text{Cu}^+$  systems. The full lines are calculated with Eq. (1) and have been fitted to the measurements by the choice of the parameters  $\Delta U$  and  $\tau_0$ .

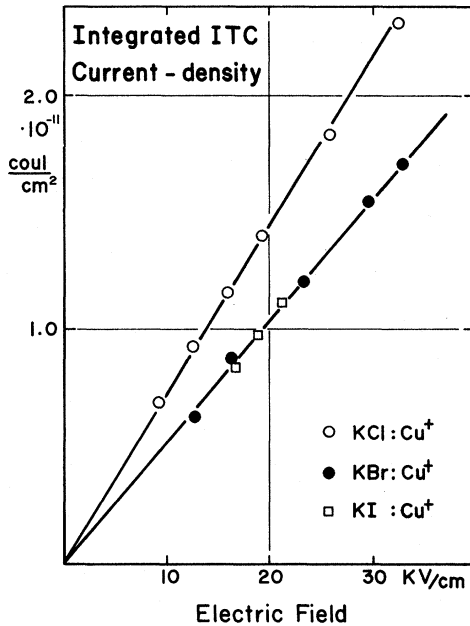


FIG. 3. Measured integrated ionic thermocurrent as a function of the polarization field  $E_P$ .

time  $\tau$  given by

$$\tau = \tau_0 e^{\Delta U / kT}. \quad (2)$$

Equation (1) is valid only for the range  $pE_P < kT_P$ , where the electric polarization of the system is a linear function of the polarization field  $E_P$ . This linear relation was tested experimentally in Fig. 3, in which the measured integrated ITC current is plotted as a function of the polarization field  $E_P$ . For all three  $\text{Cu}^+$  systems, a linear relation is observed. The integrated current density, according to Eq. (1), should be equal to the total dipole polarization achieved by the polarization field  $E_P$  at the temperature  $T_P$ :

$$\frac{1}{F} \int_0^\infty i dt = \frac{Np^2 E_P}{3kT_P}. \quad (3)$$

Thus from the slopes of the measurements in Fig. 3 (with optically calibrated number  $N$  of dipoles), the dipole moment  $p$  can be determined.

For the determination of the activation energy  $\Delta U$  and attempt frequency  $1/\tau_0$  of the relaxation process [Eq. (2)], it is most convenient to use the following relation, derived from Eq. (1):

$$\ln \tau(T) = \frac{\Delta U}{kT} + \ln \tau_0 = \ln \left( \frac{1}{i(T)} \int_T^\infty i(T') dT' \right). \quad (4)$$

By plotting the experimental quantity on the right-hand side (obtained from graphic integration of the ITC curve in Fig. 2) against the inverse temperature, a straight-line dependence should occur. Figure 4 shows a plot of the measured ITC cur-

rents in this form for the three  $\text{Cu}^+$  systems. In all three cases a straight-line dependence is, in fact, obtained, the slopes and intercepts of which yield  $\Delta U$  and  $\ln \tau_0$ , respectively.

With the parameters  $p$ ,  $\Delta U$ , and  $\tau_0$  obtained in this way, the temperature dependence of the ITC current  $i(T)$  can be calculated with Eq. (1) and can be inserted (full lines) into the  $i(T)$  measurements in Fig. 2. For all three  $\text{Cu}^+$  systems, an excellent fit to the measured ITC bands is obtained. The temperature  $T_m$  of maximum ITC current is given by

$$kT_m^{1/2} = [b\Delta u\tau(T_m)]^{1/2}. \quad (5)$$

From a total of 15 measurements for the three  $\text{Cu}^+$  systems, the mean values of the parameters  $T_m$ ,  $p$ ,  $\Delta U$ , and  $\tau_0$  were determined and listed in Table I.

The data derived from the ITC measurement for  $\text{KCl}:\text{Cu}^+$  can be compared to the values obtained from electro-optical and elasto-optical measurements for this system, which have also been included in Table I. Sittig<sup>7,8</sup> derived  $\Delta U$ ,  $\tau_0$ , and  $p$  values from the temperature and frequency dependence of the electric field modulated absorption, while Dultz<sup>14</sup> obtained  $\Delta U$  and  $\tau_0$  values from the temperature dependence of the elasto-optical effect. In the electro-optical experiment the temperature of maximum field modulation shifts with the modulation frequency. Extrapolation of the field-modulation data<sup>7,8</sup> to a modulation frequency of  $10^{-1}$  Hz (which would correspond roughly to the conditions of our ITC warming rate) would yield an electro-optical  $T_m$  value of 68 °K. The elasto-

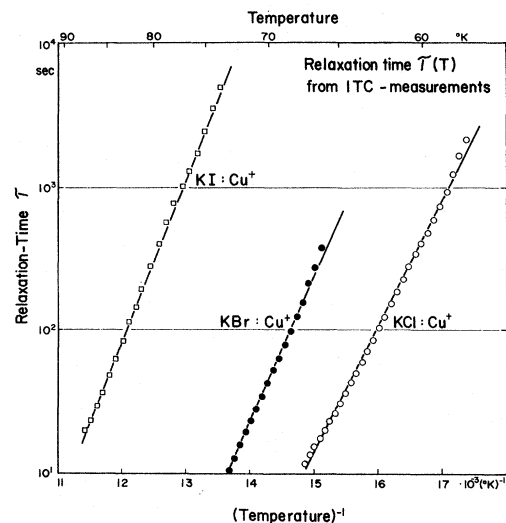


FIG. 4. Logarithmic plot of the relaxation time  $\tau$  [obtained from the ITC measurements according to Eq. (4)] against the inverse temperature for the three  $\text{Cu}^+$  systems.

TABLE I. Mean values of the parameters  $T_m$ ,  $\Delta U$ ,  $p$ , and  $\tau_0$  as determined from 15 ITC measurements for Cu<sup>+</sup> in KCl, KBr, and KI. [For KCl:Cu<sup>+</sup>, the previous results from electro-optical (Refs. 7 and 8), elasto-optical (Ref. 14), and theoretical (Ref. 6) work are listed too.]

Quantity	Method	KCl:Cu <sup>+</sup>	KBr:Cu <sup>+</sup>	KI:Cu <sup>+</sup>
$T_m$ (°K)	ITC	62 ± 2	70.2 ± 0.4	82.9 ± 1.7
	Electro-optic	68	...	...
	Elasto-optic	61	...	...
$\Delta U$ (meV)	ITC	177 ± 27	196 ± 22	232 ± 28
	Electro-optic	155	...	...
	Elasto-optic	160	...	...
$p$ (eÅ)	ITC	1.49 ± 0.20	1.92 ± 0.10	2.6 ± 0.13
	Electro-optic	1.73	...	...
	Theory	1.36	...	...
$\tau_0$ (sec)	ITC	~10 <sup>-13</sup>	~10 <sup>-13</sup>	~10 <sup>-14</sup>
	Electro-optic	5 × 10 <sup>-12</sup>	...	...
	Elasto-optic	10 <sup>-11</sup>	...	...

optical effect<sup>14</sup> under a slow continuous warming of the crystal (similar to the one in the ITC experiment) showed a maximum at  $T_m = 61$  °K, in excellent agreement with our ITC value ( $T_m = 62$  °K). The values for the activation energy  $\Delta U$  derived from the optical work are systematically somewhat lower than the ITC value, but lie within experimental uncertainty. The values for the attempt frequency (which can be determined only within about one order-of-magnitude uncertainty in all experiments) differ by about two orders of magnitude.

One can check if the measured  $\Delta U$  and  $\tau_0$  values are compatible with a reasonable value for the distance between neighboring potential wells. In the most simple treatment, one can choose two adjoining harmonic potentials (with a curvature determined by the frequency  $1/\tau_0$ ) and ask at what distance  $d$  of their minima they are separated by an energy barrier of the height  $\Delta U$ . Using the  $\Delta U$  and  $\tau_0$  values for the ITC and elasto-optical measurements, one obtains  $d = 0.2$  Å and  $d = 20$  Å, respectively. The large difference directly reflects the large discrepancy and uncertainty in the frequency value  $1/\tau_0$ . With an assumed mean value for  $1/\tau_0$  of about  $10^{12}$  sec<sup>-1</sup>, one obtains just the right order for the distance of the adjoining wells (which would be  $d = 1.7$  Å for an ion displaced by  $1.5$  Å in a  $\langle 111 \rangle$  direction from the center).

In the electro-optical experiment, the dipole moment  $p$  can be directly derived from the size of the measured field modulation  $\Delta K/K$  if the optical anisotropy of the used optical absorption is known. In the ITC technique, on the other hand, a calibration of the dipole concentration  $N$  is necessary in order to determine  $p$ . In view of this difference, the agreement between the  $p$  values obtained using the two techniques must be regarded as very good.

In comparing the two techniques, one finds that the ITC method offers the advantage of unsurpassed

experimental simplicity, highest sensitivity even for very small dipole concentrations, and very direct evaluation of  $\Delta U$  and  $\tau_0$ . However, the ITC technique does not allow one to determine the symmetry of the off-center dipoles. In the given temperature range of relaxation,  $pE_p \ll kT_p$  always holds, so that both the achieved dipole polarization ( $Np^2E_p/3kT$ ) and the relaxation time  $\tau$  is independent of the applied field direction. Therefore, neither the size nor the position and shape of the ITC band reveals any anisotropic effect. The inherent anisotropy of the electro-optical and elasto-optical method, on the other hand, gives direct information on the symmetry of the dipoles, even in the high-temperature range. The optical methods revealed  $\langle 111 \rangle$  off-center positions for Cu<sup>+</sup> in KCl<sup>8,14</sup> and  $\langle 110 \rangle$  off-center positions for Ag<sup>+</sup> in RbCl and RbBr.<sup>5</sup> Since the ITC experiments in this work do not answer the question for the symmetry of the Cu<sup>+</sup> off-center dipoles in KBr and KI, electro-optical experiments are planned to achieve this.

The present work—and its planned continuation and extension—is part of a systematic attempt to establish experimental correlations between the off-center effect and the crystal properties over a wide range of host materials. These empirical correlations are important to develop a more general theoretical understanding about the conditions for the appearance of the off-center effect, and the static and dynamic off-center dipole properties in various host materials. While for the Li<sup>+</sup> ion the off-center effect seems to be a singular event (appearing only in KCl),<sup>9</sup> the heavy-metal ions Cu<sup>+</sup> and Ag<sup>+</sup> go off center in various host lattices, displaying definite trends in their static and dynamic behavior. Summing up the results from this ITC work and from previous optical,<sup>2,3</sup> electro-optical,<sup>5,7,8</sup> and theoretical work<sup>6</sup> on Cu<sup>+</sup> and Ag<sup>+</sup> in the chlorides, bromides, and iodides of Na<sup>+</sup>, K<sup>+</sup>, and Rb<sup>+</sup>, the following systematic trends appear (Fig. 5).

For the Cu<sup>+</sup> ion the off-center behavior occurs in the potassium and rubidium halides (with RbI not yet explicitly checked out, but very likely expected). Cu<sup>+</sup> in NaCl is centrosymmetric, while the other Na halides are not yet investigated, but likely to be on-center systems, too. If the expectations for the uninvestigated systems come out in the above way, a very simple trend appears. The small Cu<sup>+</sup> ( $r = 0.96$  Å) ion goes off center in crystals where it replaces a cation of appreciably larger size [K<sup>+</sup> ( $r = 1.33$  Å) and Rb<sup>+</sup> ( $r = 1.48$  Å)], but remains centrosymmetric when replacing the Na<sup>+</sup> ion which is of about equal size ( $r = 0.95$  Å).

Thus a simple size misfit to the replaced cation appears to be the predominant criterion for the appearance of the off-center effect. Second, the size of the off-center displacement is found to increase

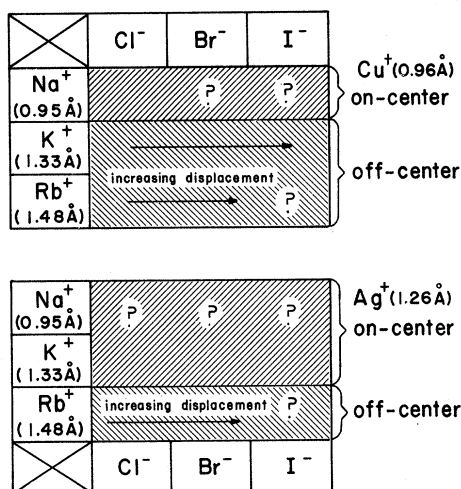


FIG. 5. Summary of the  $\text{Cu}^+$  and  $\text{Ag}^+$  off-center properties in the chlorides, bromides, and iodides of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Rb}^+$  as obtained from ITC, optical, and theoretical work. (The systems marked with a question mark are not yet explicitly checked for off-center behavior.)

among both the potassium and rubidium halides systematically with the anion variation  $\text{Cl}^- \rightarrow \text{Br}^- \rightarrow \text{I}^-$ . This is as expected because an increase in the size of the nearest-neighbor ion increases the polarization interaction and decreases the repulsion interaction with the metal ion, both producing a larger off-center effect.

For the  $\text{Ag}^+$  ion, with a considerably larger ionic radius ( $r = 1.26 \text{ \AA}$ ), the behavior looks similar, but shifted vertically in the crystal tableau in Fig. 5. The  $\text{Ag}^+$  ion is on center when replacing the (equal size)  $\text{K}^+$  ion or the smaller  $\text{Na}^+$  ion (the latter was never checked explicitly, but is unquestionably true). For the rubidium halides, the cation size misfit is large enough to produce an off-center position, again with a displacement increasing with the anion size. Similar to the case of the  $\text{Cu}^+$  ion, a large off-center displacement is expected for the  $\text{Ag}^+$  ion in  $\text{RbI}$ , but has not yet been experimentally verified.

It is in agreement with this general picture that for the  $\text{Tl}^+$  ion [which has a size ( $r = 1.4 \text{ \AA}$ ) com-

parable to the  $\text{Rb}^+$  ion size], no off-center behavior was found so far in any alkali-halide crystal.

The relaxation behavior shows a clear trend of increasing relaxation times with increasing off-center displacement for the  $\text{Ag}^+$  and  $\text{Cu}^+$  systems studied so far.  $\text{Ag}^+$  in  $\text{RbCl}$  ( $b = 0.78 e \text{ \AA}$ ) reorients by rapid tunneling below  $5^\circ \text{K}$  and has not yet been investigated at higher temperatures.  $\text{Ag}^+$  in  $\text{RbBr}$  ( $b = 0.95 e \text{ \AA}$ ) displays considerably slower tunneling reorientation below  $5^\circ \text{K}$  and reorientation by classical-rate theory above that temperature. For these  $\langle 110 \rangle$ -oriented  $\text{Ag}^+$  dipoles, two distinctly different relaxation rates are observed for  $90^\circ$  and  $60^\circ$  reorientation; therefore, two different activation energies  $\Delta U$  are obtained for  $\text{RbBr}:\text{Ag}^+$ . The three off-center  $\text{Cu}^+$  systems studied in this paper continue the trend of increasing activation energy  $\Delta U$  with increasing off-center dipole moment  $p$  (Fig. 5). Different from the  $\text{Ag}^+$  systems, only a single thermally activated relaxation process is observed for the  $\text{Cu}^+$  dipoles. Low-temperature reorientation by tunneling with any appreciable rate can be excluded from our measurement for the  $\text{Cu}^+$  dipoles: From the size of the background current at the low-temperature side of the ITC band (i.e., at  $\sim 50, 60,$  and  $70^\circ \text{K}$  for  $\text{KCl}$ ,  $\text{KBr}$ , and  $\text{KI}$ ), it can be concluded that at these temperatures any present reorientation processes must have rates smaller than  $10^{-4} \text{ sec}^{-1}$ . Taking into account the temperature dependence of the reorientation by tunneling, this yields completely negligible and unmeasurable (upper-limit) tunneling rates at low temperatures.

The dependence of  $\Delta U$  on  $p$ , for the three  $\text{Cu}^+$  systems investigated, follows with good accuracy a  $\Delta U \propto p^{1/2}$  dependence. The question, if such an empirical relation could reflect any physical significance, should be delayed until more off-center systems are investigated. A systematic program, using both ITC and optical techniques, is under way to determine the static and dynamic physical parameters for the  $\text{Ag}^+$  and  $\text{Cu}^+$  off-center systems, which have not yet been investigated.

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## Sublimation and Vapor Pressure of Ar<sup>36</sup>†

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The sublimation and vapor pressure of Ar<sup>36</sup> were measured in the temperature range 23.752–87.375 K. Pressures below 1 Torr were measured with a McLeod gauge and corrected for effects of thermal transpiration and mercury streaming. The estimated accuracy of these pressure measurements ranges from 1% near 1 Torr to 10% near 10<sup>-5</sup> Torr. Above 1 Torr a calibrated Bourdon gauge was used to give pressures to ±0.03 Torr. Temperatures were measured to ±3 mK with a Pt resistance thermometer. Equivalent sublimation-pressure data on normal Ar are compared with our Ar<sup>36</sup> data in the temperature range 62.315–84.503 K. This comparison yields vapor-pressure ratios which are in reasonable agreement with theory and other experiments.

### INTRODUCTION

Properties of rare-gas solids are interesting because the interatomic forces are weak, short ranged, and relatively well understood. In particular, sublimation pressure is calculable from lattice-dynamical theories and consequently can be used as a test of such theories. The purpose of this paper is to present an accurate table of sublimation-pressure data for Ar<sup>36</sup> which extend over several orders of magnitude. Since the sublimation pressure of normal argon (Ar<sup>N</sup>) has been measured previously with the same apparatus,<sup>1</sup> we then compare the sublimation pressure of Ar<sup>N</sup> with that of Ar<sup>36</sup> and discuss the observed difference.

Vapor and sublimation pressures of Ar<sup>N</sup> have recently been measured in the range 75–85.2 K by Chen, Aziz, and Lim.<sup>2</sup> Lee, Fuks, and Bigeleisen<sup>3</sup> have, also recently, made differential measurements comparing the vapor and sublimation pressures of Ar<sup>N</sup> and Ar<sup>36</sup>. Their data, in the form of  $P(\text{Ar}^N)$  and  $P(\text{Ar}^{36}) - P(\text{Ar}^N)$ , extend from 62–102 K. Earlier measurements on the argon isotopes have been made by Clusius and co-workers<sup>4</sup> in the range 84–88 K, and by Boato and co-workers<sup>5–7</sup> in the ranges 84–119 and 72–83.7 K.

The vapor-pressure ratios for isotopes of solid Ne and Ar have been calculated by Klein, Blizard, and Goldman<sup>8</sup> using the improved self-consistent phonon scheme of Goldman, Horton, and Klein.<sup>9</sup>

### THEORY

Applying classical thermodynamics to a solid-vapor system (or liquid-vapor system) in equilibrium

yields the Clusius–Clapeyron equation which may be written<sup>10</sup>

$$\frac{d(\ln P)}{d(1/T)} = \frac{-L}{R[1 - P(v_c - \mathcal{B})/RT]} \quad (1)$$

In Eq. (1)  $P$  is the pressure,  $T$  is the temperature,  $L$  is the heat of sublimation,  $R$  is the gas constant, and  $v_c$  is the molar volume of the solid (or liquid). The second virial coefficient  $\mathcal{B}$  is defined by the gaseous equation of state  $Pv_g = RT(1 + \mathcal{B}/v_g)$ , in which  $v_g$  is the molar volume of the gas. Over a sufficiently narrow temperature interval Eq. (1) can be integrated to give the classical vapor-pressure equation:

$$\ln P = A/T + B, \quad (2)$$

where

$$A = -L/R[1 - P(v_c - \mathcal{B})/RT].$$

Using statistical mechanics to calculate the Gibbs free energy of the gaseous phase, a somewhat different vapor-pressure equation is obtained:

$$\begin{aligned} \ln P - P(v_c - \mathcal{B})/RT \\ = F/RT + \frac{5}{2} \ln kT + \frac{3}{2} \ln(m/2\pi\hbar^2). \end{aligned} \quad (3)$$

In Eq. (3),  $F$  is the Helmholtz free energy of the solid,  $k$  is Boltzmann's constant,  $\hbar$  is Planck's constant divided by  $2\pi$ , and  $m$  is the mass of a single atom. The remaining symbols are the same as those defined in Eq. (1).

The improved self-consistent theory of Goldman, Horton, and Klein<sup>9</sup> for the Helmholtz free energy of the anharmonic crystal has been used to calculate