

X-ray measurements of thermal vacancies in hcp ^4He

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Changes in the x-ray lattice parameter have been used to measure directly the thermal generation of vacant substitutional atomic sites in hcp ^4He crystals held at constant macroscopic volume, for samples with molar volumes in the range 20.2 to 20.9 cm³. A progressive decrease of the apparent formation energy, from 12.6 to 8.6 K, with increase of molar volume, is seen. This variation is consistent with variations observed in the NMR diffusion activation energy for small concentrations of ^3He in ^4He . The magnitudes are also similar, with some exceptions, which suggests that, unlike hcp ^3He , the vacancy in low-density hcp ^4He moves by tunneling. By various means, values for the monovacancy free volume are deduced. Comparisons with other studies of defects in hcp ^4He , such as ion transport, recovery of ultrasonic attenuation, and calorimetry, are less direct and less unambiguous.

I. INTRODUCTION

Remarkable characteristics have been pointed out for the atomic vacancy in solid ^4He (Refs. 1 and 2). These include the possibility of tunneling from site to site at rates which correspond to significant nonlocalization. Indeed, the ground state of this solid helium is speculated to be qualitatively different from usual crystals, in which atoms are each associated with given atomic sites. Experimental investigation of these possibilities in ^4He has mostly been carried out indirectly, however. Examples include measurements of pressure, compressibility, thermal expansion, and heat capacity (which include all excitations but may not clearly discriminate among them if they occur in overlapping temperature ranges), studies of shear strength, ultrasonic response, and thermal conductivity (which are influenced by structure-sensitive factors which may be difficult to control), and measurements of ion mobility and NMR diffusivity (which depend upon the introduction of foreign probes, the ions or ^3He atoms, respectively, which may disturb the intrinsic vacancy structure and properties).

We report here some direct measurements of thermal vacancy content of hcp ^4He crystals over a range of molar volumes, carried out by x-ray diffraction. Free energies of vacancy formation are deduced. They are compared with activation energies from indirect methods. In addition, comparisons with measurements of other kinds yield other properties of the vacancies such as their free volume of formation. The results confirm the idea that the vacancies are indeed unusual in hcp ^4He .

The usual thermodynamic relations hold for the thermal vacancy formation parameters³

$$f = e - Ts, \quad (1)$$

$$s = -(\delta f / \delta T)_V, \quad (2)$$

$$p = -(\delta f / \delta V)_T. \quad (3)$$

Here, f is the Helmholtz partial-molar free energy of formation of a monovacancy in a solid held at constant macroscopic volume, and s is the nonconfigurational entropy of formation of a monovacancy. The pressure of formation at constant volume, p , is related to the more familiar free volume of formation at constant pressure, v , by the relation

$$p = v / \chi v_a, \quad (4)$$

where χ is the isothermal compressibility and v_a the atomic volume.

Thermal vacancy contributions to other properties of a solid are calculated analogously.³ For a monovacancy concentration n/N , useful results are

$$\chi - \chi^0 = \frac{nv}{Nv_a} \left[-\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T + \frac{v}{kT} \right], \quad (5)$$

$$\alpha - \alpha^0 = \frac{nv}{Nv_a} \left[\frac{h}{kT^2} + \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \right], \quad (6)$$

$$C_V - C_V^0 \cong n \left[\left(\frac{\partial e}{\partial T} \right)_V + \frac{e^2}{kT^2} \right]. \quad (7)$$

Here, α is the coefficient of volume thermal expansion, C_V is the isochoric heat capacity, v_a is the atomic volume, h is the enthalpy of formation at constant pressure, and e is the energy of formation. The superscript zeros denote hypothetical solid properties in the absence of thermal vacancies.

II. EXPERIMENTAL METHOD

A. Principles

Solid helium is very compressible. It can be held at essentially constant macroscopic volume, V , in a cell thin enough so that quantitative x-ray diffraction study of the sample crystal can be carried out. Samples can be crys-

tallized from the liquid, oriented, their subgrain structure characterized, and their lattice parameter changes measured with changes in cell temperature.³⁻⁸ The key principle is that the net additional concentration of substitutional atomic sites, c , is given by

$$c = \Delta V/V - \Delta V_x/V_x, \quad (8)$$

where V_x is the unit-cell molar volume determined by x-ray diffraction and Δ denotes changes in the measured volumes with respect to a reference state. With macroscopic constraint, $\Delta V/V$ becomes zero in Eq. (8) and only an x-ray measurement is required.

The principle, Eq. (8), depends upon a number of assumptions or demonstrations. The principal ones are (a) that the dilatational field of the force tensor describing the vacancies, in a real crystal, makes equal contributions to the macroscopic and Bragg x-ray dilatations of the crystal lattice, and (b) that the defect population is sufficiently dense and homogeneous to make surface elastic irregularities relatively unimportant. Many treatments of this, both theoretical and experimental, are in the literature.⁹ These many aspects do not explicitly include the case in which the point defects are microscopically considered to be nonlocalized, except in a static sense. However, in the present paper we assume models which, in regions far from the defect core, treat the point defect as an elastic singularity in a continuum and assign tensor components to this singularity. These can include this possibility, even when the nonlocalization, in the sense of Andreev,² is not static. For very rapidly jumping or for tunneling defects the study of x-ray and neutron-scattering effects, in relation to other properties, is just beginning.¹⁰

For present purposes in applying Eq. (8) to hcp ^4He , one also needs to mention a possible concern about crystalline anisotropy. The atomic structure factor of He is unfavorable for measuring x-ray Bragg scattering over a wide angular range, so that with the usual sample one has only a single reflection with which to work, not the more desirable situation of independent a - and c -axis parameters to define the unit cell volume. It has been shown in the metals Cd (Ref. 11) and Zn (Ref. 12), for example, that at constant pressure the a - and c -axis thermal expansions are unequal, and that moreover, apparently due to an orientation dependence of dislocation climb processes during thermal vacancy generation and annihilation, one needs both a - and c -axis lattice parameter changes to obtain suitable thermal vacancy results. However, those metals, unlike hcp ^4He , do not have c/a parameter ratios corresponding to ideal close packing. On the other hand, all available evidence shows that hcp ^4He is close packed. The evidence includes x-ray, elastic, and optical properties including birefringence.¹³ We have checked the c/a ratio on an hcp ^4He crystal with a molar volume of 19.2 cm³, by measuring the lattice spacing of several different reflections. The results agreed with the ideal value 1.633. Finally, evidence about anisotropy of dislocation climb processes in hcp ^4He which might cloud the straightforward interpretation of measurements of the present type has not been found;¹⁴ we proceed in its absence.

B. Practice

Our samples were prepared at essentially constant pressure on the liquid-solid interface by directional solidification in a Lucite [polymethyl methacrylate (PMMA)] cell, 1.6-mm i.d., 3.8-mm o.d., and 14-mm length, in a dilution refrigerator cryostat.¹⁵ In our apparatus, constant-pressure growth produces crystal specimens of better quality for x-ray diffraction study.¹⁶ For our purpose of subsequent measurements at essentially constant volume over the temperature range up to 2 K, Lucite (a) exhibits negligible thermal expansion,¹⁷ and (b) for our cell configuration shows an estimated maximum volume change of only 100 ppm from thermoelastic pressure in the confined helium.

The question arises as to whether the x rays themselves may induce lattice parameter changes through the production of point defects in (insulating) solid helium specimens by photoelectric and Compton processes. Studies of argon at 10 K by Balzer and Giersberg¹⁸ have indeed produced such lattice parameter changes, which they attributed to the formation of vacancy-interstitial ($V-I$) pairs. We note that for our present conditions of macroscopic volume constraint, the formation of $V-I$ pairs would not change the number of substitutional atomic sites, and hence would not change the x-ray lattice parameter, unless a subsequent defect migration and annealing process permitted either the vacancies or the interstitials to disappear preferentially, that is unless the $V-I$ balance would be unbalanced.

A reasonable bound on the possible lattice parameter change in helium can be estimated, using the results of Balzer and Giersberg on argon and a comparison of known properties of the two substances. We assume that (a) the number of displaced atoms is proportional to the energy transferred to photon and Compton electrons, (b) the number of displaced atoms is inversely proportional to the energy required to displace an atom, and (c) the displacement energy is proportional to the vacancy formation energy. Then the ratio of concentration of interstitials created in helium to that in argon is

$$\frac{c_i^{\text{He}}}{c_i^{\text{Ar}}} = \frac{e^{\text{Ar}} \int n(E) [\sigma_p^{\text{He}}(E) E_p^{\text{He}}(E) + \sigma_{C,\text{eff}}^{\text{He}}(E) E_C^{\text{He}}(E)] dE}{e^{\text{He}} \int n(E) [\sigma_p^{\text{Ar}}(E) E_p^{\text{Ar}}(E) + \sigma_{C,\text{eff}}^{\text{Ar}}(E) E_C^{\text{Ar}}(E)] dE} \quad (9)$$

Here $n(E)$ is the number of incident photons with energy E , σ_p is the atomic photoelectric cross section, $\sigma_{C,\text{eff}}$ is the effective atomic Compton cross section, and E_p and E_C are the respective energies of the photoelectrons and Compton electrons created. This ratio can be evaluated for present conditions, by using cross sections of McMaster *et al.*,¹⁹ the energy spectrum for a Cu x-ray tube operated at 40 kV (Ref. 20), and the various physical properties of the two solids.²¹ The result is that the ratio, Eq. (9), is about 10^{-2} .

Balzer and Giersberg¹⁸ observed lattice parameter changes of 6×10^{-4} after 20 h of irradiation with a Cu tube at 40 kV/20 mA. Our samples had, by the end of their study, including temperature cycling, about 20 h at

40 kV/30 mA. We therefore expect at most 10 ppm total influence of this possible effect on our studies.

The first sample was examined with the x-ray diffractometer drive mechanism of Heald,³ while for the others a later x-ray instrument⁶ was used. Results were obtained for a range of relatively large molar volumes. Many attempts were made to prepare and examine crystals at a smaller molar volume, 18.8 cm³, the one at which thermal vacancies in hcp ³He were measured by Heald and co-workers.^{3,5} Unfortunately, we could not obtain consistent results with temperature variation from any of these samples, which in our apparatus were unstable to rotation, perhaps provoked by minute thermal gradients. Success of single-crystal x-ray techniques, including the present one, depends upon reasonable orientational and positional stability of the crystal in the diffractometer.

III. DATA

Data for lattice parameter changes on sample no. 1 were taken as noted in Sec. II, with a device from which absolute lattice parameter measurements are not available. They are shown in Fig. 1. The measurements do not extend to a low enough temperature to determine accurately the low-temperature reference value of the lattice parameter. Therefore, a single parameter fit is all that is justified to infer a vacancy formation energy.

Sample no. 13 was the subject of extensive studies not only of hcp, reported here, but also of bcc and of the hcp-bcc mixed phase.⁷ It was originally grown at 3.110 MPa with an apparent melting temperature of 1.787 K, but with a bit of liquid trapped in the sample fill line. After subsequent annealing, x rays showed bcc phase from 1.735 down to 1.70 K, then bcc-hcp mixed phase down to about 1.6 K. At lower temperatures the annealed sample gave Laue diagrams showing a single hcp crystal, upon which (10 $\bar{1}$ 0) Bragg reflection measurements were made. Vacancy data, obtained during cooling, are shown in Fig. 2. Because of irregularities including weakening of the hcp reflection as the sample neared

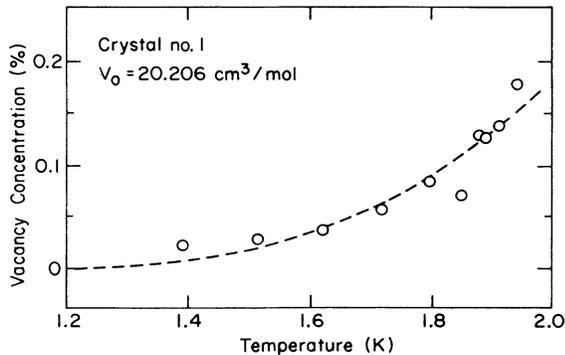


FIG. 1. Thermal-vacancy data on 20.206 cm³/mol hcp ⁴He obtained on cooling. The dashed line is a fit to Eq. (10) with $s=0$, because the data do not extend to a suitable low temperature at which the thermal-vacancy content is negligible.

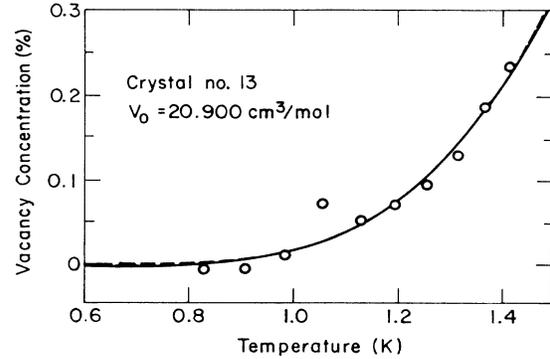


FIG. 2. Thermal-vacancy data on 20.900 cm³/mol hcp ⁴He obtained on cooling after transition of the sample from the mixed bcc-hcp phase. The solid line is a least-squares fit to Eq. (10) in which both e and s are varied. The dashed line is for a fit with $s=0$.

the mixed phase, useful vacancy data stop more than 0.3° below the melting temperature.

Data on sample no. 14, also at a relatively large molar volume, also showed some irregularities at the highest temperature. We believe this was related to mixed phase problems. In Fig. 3 are shown (10 $\bar{1}$ 1) lattice parameter changes measured upon first cooling, which is often the most favorable case; data above 1.65 K are excluded. For both samples nos. 13 and 14 the molar volumes were determined directly by x-ray diffraction.

IV. DISCUSSION

The data were fitted by a relation of the form

$$c(T) = \exp(-f/kT), \quad (10)$$

with the e and s assumed to be temperature-independent quantities. The results are shown in Table I, which also summarizes other properties of the samples.

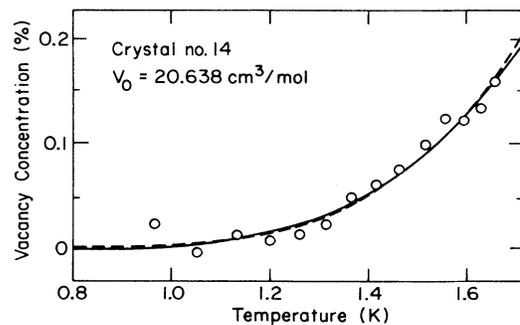


FIG. 3. Thermal-vacancy data on 20.638 cm³/mol hcp ⁴He obtained on warming. The solid line is a least-squares fit to Eq. (10) in which both e and s are varied. The dashed line is for a fit with $s=0$.

TABLE I. Measured characteristics of hcp ${}^4\text{He}$ samples. V_0 is the low-temperature x-ray molar volume and T_m and P_m are the melting temperature and pressure, respectively (see text). e is the apparent formation energy, obtained either under the assumption that the formation entropy s is zero or is left as a fitting parameter.

Sample no.	$V_0(\text{cm}^3/\text{mol})$	$T_m(\text{K})$	$P_m(\text{MPa})$	$e(s=0)(\text{K})$	$e(\text{K})$	s/k
1	20.206 ^a	1.979	3.710	12.6±0.1	a	a
13	20.900 ^b	c	c	8.6±0.1	8.2±0.1	-0.2±0.1
14	20.638 ^d	1.798	3.137	10.62±0.05	9.59±0.05	-0.61±0.03

^aFrom observed T_m . See the text, Sec. III.

^bFrom (10 $\bar{1}$ 0) lattice parameter measured at 0.822 and 0.921 K, and assumption that $c/a = 1.633$.

^cSee the text, Sec. III.

^dFrom (10 $\bar{1}$ 1) lattice parameter measured at 0.947 K, and assumption that $c/a = 1.633$.

A. Vacancy formation volume

Table II shows vacancy free volumes estimated by several methods. Compressibility and thermal expansion measurements,²² when combined with the present vacancy data, can be used in Eqs. (5) and (6), respectively, to obtain v/v_a . For this purpose we ignore the smaller derivative terms in the equations and, since $T \ll \Theta_D$, the Debye temperature, we attribute all of the observed temperature dependence of each property to the vacancies. Results of applying the elastic theory of Holder and Granato,²³ with published elastic constant data,²⁴ are also shown.

Some trend is shown in Table II for v/v_a to decrease as the molar volume increases, although the agreement between the different methods at a given molar volume is only fair. Heald and co-workers³ found the same trend with volume for vacancies in bcc ${}^3\text{He}$, and in addition, better agreement between the results from different which is unavailable in pure ${}^4\text{He}$. Here, it is difficult to attribute the disagreement to any specific cause or assumption. We are not aware of any microscopic calculation of the vacancy free volume in hcp ${}^4\text{He}$ with which the present experimental estimates can be compared. (Goldburg and Guyer²⁵ have made estimates of tunneling rates in hcp ${}^4\text{He}$, which depend upon local lattice distortions.)

B. Comparison to vacancies in bcc ${}^4\text{He}$ and hcp and bcc ${}^3\text{He}$

Direct measurements of vacancy free energy in bcc ${}^4\text{He}$, which exist only in a narrow range of temperature and pressure, for molar volumes of about 21.10–20.84 cm^3 , give $f = 9 \pm 1$ K (Ref. 7). Within the estimated experimental uncertainties this agrees with the present vacancy free energy for hcp ${}^4\text{He}$ at the same molar volume. For ${}^3\text{He}$, it is interesting to note that a reasonable extrapolation, to smaller molar volumes, of the x-ray vacancy formation free energies of Heald and co-workers³ for the bcc phase falls through their measured value for the hcp phase in that solid. See Fig. 4. So, the constant-molar-volume vacancy formation energy appears rather similar in the respective helium solids at large molar volume, whether the structure is bcc or hcp. We remark, incidentally, that deep inelastic neutron-scattering measurements of momentum density show that for ${}^4\text{He}$ there is a closely similar kinetic energy per atom in hcp, bcc, and even liquid, in specimens held at the same molar volume (but of course different values of pressure and temperature).²⁶

The present measurements in ${}^4\text{He}$ do not cover a large enough range of molar volumes to establish a precise volume dependence for the vacancy formation energy, for example, to compare that dependence to the variation with volume of other crystal energies. But one can speculate a little, if one ventures to pursue the analogy with

TABLE II. Estimated vacancy free volumes of formation, v , in hcp ${}^4\text{He}$. v_a is the atomic volume; HG, elastic theory, Ref. 23; α , coefficient of thermal expansion; χ , isothermal compressibility; $\Delta f/\Delta V$, volume dependence of x-ray vacancy free energy f . See the text, Sec. IV A.

Sample no.	$V_0(\text{cm}^3/\text{mol})$	HG	α	v/v_a χ	$\Delta f/\Delta V$
1	20.206	1.28	0.70	0.61	1.4
13	20.638	1.31	0.51	0.52	1.25
14	20.900	1.18	0.29	0.30	

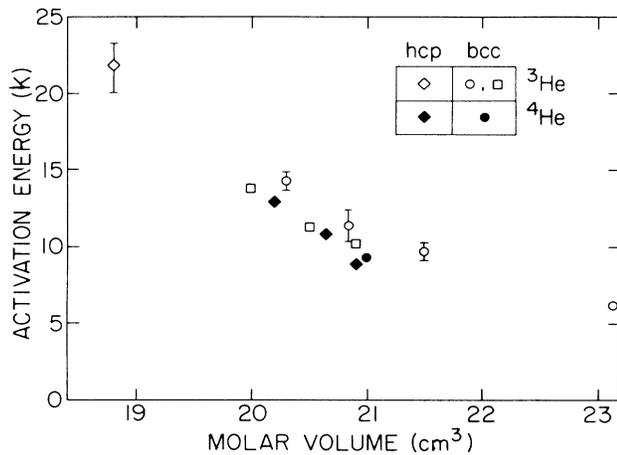


FIG. 4. Thermal-vacancy free energies deduced from x-ray measurements. There is apparently a common dependence of the free energy for thermal-vacancy formation, within the respective experimental uncertainties, for both isotopes of helium and both the bcc and hcp crystal structures, at least in the intermediate range of molar volumes shown. (◆) present work, hcp ^4He ; (●) Ref. 7, bcc ^4He ; (◇) Ref. 3, hcp ^3He ; (○) Ref. 3, bcc ^3He ; (□) Ref. 4, bcc ^3He , data reanalyzed with the assumption $s=0$, which was used in Ref. 3.

^3He , for which data over a wider range of molar volumes is available. Suppose vacancy formation energy values for hcp ^4He lie parallel to the ^3He values in Fig. 4, extending to smaller molar volumes. Then, for example, at 18 cm^3 the vacancy energy f might be about 25 K. At this molar volume the melting temperature T_m is 2.8 K (Ref. 27). The estimated ratio (f/T_m) might then be about nine, to be compared to ratios in the range six to five from samples at the three present molar volumes in the range $20.2\text{--}20.9\text{ cm}^3$. This ratio would not appear to be either the same as, or as constant as, the ratio 10.8 ± 1 deduced by Muzusaki and co-workers for ^3He impurity NMR diffusion in hcp ^4He samples.²⁸

One might be tempted to extend this speculation further, to properties of thermal vacancies in fcc ^4He , in order to estimate vacancy energies in the fcc phase. However, the similarities noted in the first paragraph of this section and Fig. 4 probably arise from the dominance of (zero point) kinetic energy effects in the crystals at the large molar volumes. It is known that as helium is compressed to smaller molar volumes, the lattice dynamical properties, for example, as summarized in the temperature dependence of the calorimetric Debye characteristic temperature,²⁹ or in the phonon spectrum,³⁰ approach those of the other noble-gas solids in a classical regime. So rough estimates for fcc could with better likelihood be made through comparisons with neon and argon.

C. Relation to NMR measurements of ^3He impurity diffusion

For certain regimes of ^3He impurity concentration and of temperature, activated behavior of NMR relaxations is observed.^{28,31-35} The deduced activation energies are summarized in Fig. 5. The ^3He impurity NMR relaxa-

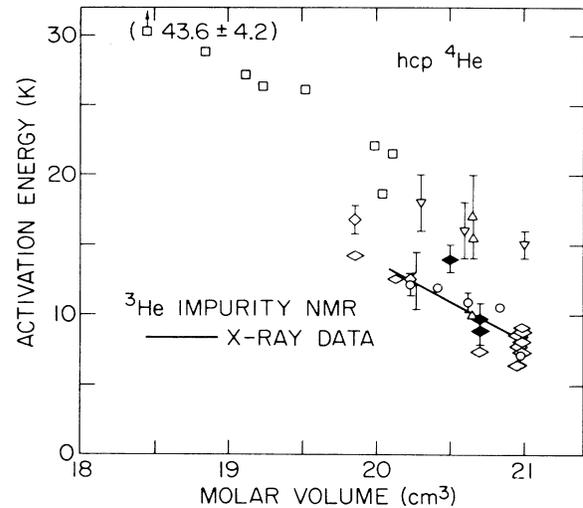


FIG. 5. Activation energies deduced from ^3He impurity NMR diffusion in hcp ^4He . Solid line represents present hcp ^4He x-ray data from Fig. 4. (□) Ref. 28, 4.8% ^3He ; (▽) Ref. 31, 1.94% ^3He ; (◆) Ref. 32, 2.17% and 0.75% ^3He ; (○) Ref. 33, 5×10^{-4} ^3He ; (◇) Ref. 34 T_1 , $5\text{--}8 \times 10^{-4}$ ^3He ; (◇) Ref. 34 T_2 ; (△) Ref. 35, 4%, 2.17%, 0.12% ^3He .

tion data extend over the molar volume range $17.3\text{--}20.9\text{ cm}^3\text{ mol}$, and a trend of decreasing activation energy is apparent, from over 40 K down to below 10 K, respectively. There is, however, a considerable range of values, inferred from the various measurements, at any given molar volume, especially for volumes larger than 19.5 cm^3 . For not very large ^3He concentrations, there does not seem to be any simple dependence of the activation energy upon concentration, although to probe intrinsic vacancy properties one prefers the smallest possible concentration.

In pure hcp ^3He , NMR activation energies are volume dependent and appear significantly larger than x-ray and ultrasonic values,³ suggesting that thermally activated motion is involved in hcp phase. Here for hcp ^4He , given the data for molar volumes less than 19.8 cm^3 alone, one might expect the same (see Fig. 5). However, in the range $19.8\text{--}21\text{ cm}^3$, NMR measurements of ^3He impurity diffusion in hcp ^4He by different investigators cover quite a range, the bottom of which is around 7 K near $21\text{ cm}^3\text{ mol}$. It is not clear whether there is a qualitative change in NMR behavior around $19.8\text{ cm}^3\text{ mol}$.

We conclude that NMR measurements have been most successful in elucidating ^3He -concentration-dependent phenomena in the temperature-independent exchange plateau. On the other hand, from Fig. 5 we conclude that interpretation of temperature-dependent NMR data in terms of thermal vacancy properties is ambiguous. Some of the ^3He NMR phenomena are no doubt influenced by thermal vacancies, but without independent measurements of vacancy content in a similar impure specimen, the interpretation is not straightforward. Perhaps NMR work in oriented single-crystal specimens of this hcp phase would also help.

D. Relation to ion mobility measurements

Essentially the same value of activation energy as in the present x-ray work is observed in careful measurements at this molar volume in hcp ^4He , of activation energy for positive ion motion.^{36,37} There are complications upon a brief simple interpretation, however. Such positive ion motion has a variety of possible mechanisms.^{38,39}

Measurements of ion mobilities in hcp ^4He have been made by several groups of investigators.^{36,37,40-46} An early general finding was that a given molar volume, positive ion mobility and ^3He impurity diffusion have about the same thermal-activation energies in a range below the melting temperature. Ifft and co-workers⁴⁰ found that the activation energy for positive ion mobility in hcp ^4He was equal to a single value they obtained for the positive ion mobility in bcc ^3He at the same molar volume (but the ion current was five times as large in the ^3He). Sai-Halasz and Dahm⁴¹ measured activation energies for positive ion mobilities in hcp ^4He which were similar to those of Ifft but noted that they were equal to or somewhat greater than those from NMR work on ^3He -doped samples; their activation energies for negative ion mobility were in a range 25–50% greater. This was carried further by Lau and co-workers,⁴² who reported a range of activation energies at the same molar volume, for different specimens. They supposed that the different specimens had different crystal orientations, and fitted the mobilities to an orientation-dependent function. In their apparatus they could not independently check their specimens for single crystallinity nor orientation. They could not verify that their observed upper and lower limits of mobility at a given molar volume corresponded to the c - and a -axis limits (or vice versa), but they do remark that trial of an assumed 1° wider range of activation energies did not fit their data well.

It is supposed³⁹ that the structure of the positive ion in solid helium has as its center He_2^+ (or possibly a linear He_3^+), and that owing to the field gradient of the ion there is an enhanced density near the core arising from electrostriction. If the crystal is treated as an elastic continuum, the enhancement of density near the core is considerable, but no microscopic model calculations of the atomic arrangements surrounding the positive ion have been published. Nor have quantitative pictures of how vacancies provide mobility of the ion been constructed. Qualitatively it seems plausible that something like a bulk vacancy hopping or tunneling mechanism could operate both in the case of the positive ion and the case of the ^3He impurity, and both such nonintrinsic probes likely produce local compression of the crystal lattice.

The situation is different for negative ions, which are thought to consist of bubbles with an enclosed electron, bubbles whose motion may either move through internal surface adatom diffusion or alternatively, through bulk vacancy flow.³⁹ In this case one does not necessarily expect any correlation between bulk vacancy formation energy and the motion of a negative ion. For many years vacancies have been freely and somewhat loosely invoked as contributors to ion and impurity mobilities in the solid heliums, so the present direct x-ray results can be used to

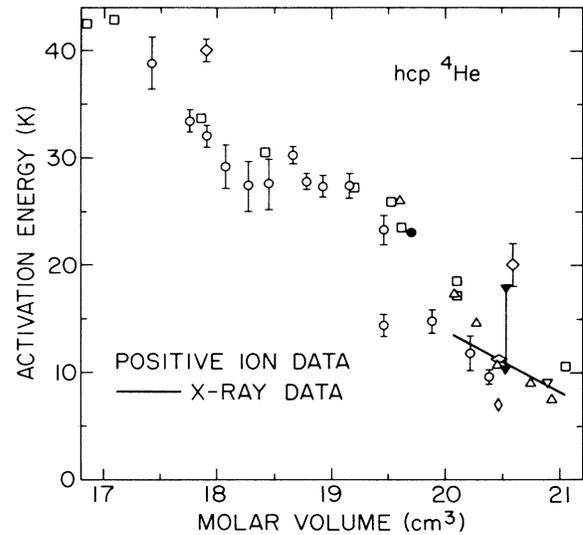


FIG. 6. Activation energies deduced from positive ion mobility in hcp ^4He . Crystalline anisotropy of this mobility may account for some of the range of values at a given molar volume (Ref. 41). Solid line represents the present hcp ^4He x-ray data from Fig. 4. (Δ) Ref. 35; (∇) Ref. 36; (\square) Ref. 40; (\diamond) Ref. 41; (\blacktriangledown) Ref. 42; (\circ) Ref. 43; (\diamond) Ref. 44; (\bullet) Ref. 45; (\diamond) Ref. 46.

point out some cautions. For example, we note that in bcc ^4He it is the *negative* ion activation energies which correspond to the x-ray value,⁷ not the positive ion value as in the presently considered hcp phase near 21 cm^3 .

Figure 6 shows these reported activation energies for mobility of positive ions and also has a line representing vacancy formation energies from the present x-ray work. It seems that, aside from apparent experimental scatter in early work,⁴³ all published measurements of positive-ion mobilities, except perhaps those of Efimov and Mezhov-Deglin,⁴⁶ have activation energies equal to or greater than these values derived from x-ray vacancy formation studies.

Suppose the ion-diffusion activation energies e_D have the form

$$e_D(V) = e_f(V) + e_m(V, \phi), \quad (11)$$

where the motion energy e_m has some orientation (ϕ) dependence in the hcp lattice, corresponding to the observed range of activation energies. Then at least at the larger molar volumes shown in Fig. 6, the smallest values of e_D for ions, and the ^3He impurity motion energies, are equal to the x-ray formation energies within experimental uncertainties. This would be consistent with operation of a tunneling mechanism, at least for some direction (basal plane?), in both cases.

There are some residual questions, for example, the possibility of anisotropy of the ^3He impurity diffusion. For pure ^3He , Sullivan, Deville, and Landesman⁴⁷ argue that very little anisotropy of the spin-lattice relaxation time T_1 is expected in the hcp lattice. Also, it is unknown whether the specimens were single crystals in a given NMR or ion mobility experiment. Finally, from

Fig. 6 (as also from Fig. 5) it is not clear whether there is a qualitative change in behavior around a molar volume about 19.5 cm^3 .

E. Relation to calorimetric studies

For hcp ^4He detailed calorimetric data and analyses, including analyses of previous work, have been published by Ahlers,^{29,48} by Edwards and Pandorf,⁴⁹ and by Gardner and co-workers.⁵⁰ Ahlers concluded from consideration of temperature-dependent contributions to the respective equations of state that at low temperatures there were striking similarities in the thermodynamic properties of hcp ^3He and hcp ^4He . But he noted that the reduced Debye characteristic temperature Θ/Θ_0 has two points of inflection for hcp ^4He , which "is not a feature expected for the lattice heat capacity and is most likely caused by an excess heat capacity at large T/Θ_0 attributable to a premelting phenomenon." Figure 8 of Gardner *et al.*⁵⁰ shows for hcp ^4He samples at molar volumes near those of the present measurements the rather small "excess" heat capacities involved. The corresponding temperature intervals lie within 80 mdeg of the transition temperature, and the deviations lie beyond a T^7 term in their fitted heat capacity. Gardner and co-workers noted that their "pretransition anomalies" were correlated with the transition temperature rather than with Θ/Θ_0 or with the type of two-phase mixture formed in their sample cell at the transition.

It is interesting to ask what contribution to the heat capacity would be expected if the thermal vacancies measured in the present work contributed like localized vacancies. Putting the current activation energies in Eq. (7) yields values which are larger than the total measured heat capacity at molar volumes near 21 cm^3 . From Fig. 6 one sees that the same result appears from using most of the positive ion energies, and from Fig. 5 again the same for NMR data except those of Miyoshi and co-workers³¹ and some values of Mikheev and co-workers.³⁵ Actually, even taking a model calculation of vacancy bandwidth into account for the hcp phase, Goldburg and Guyer²⁵ concluded long ago that while Miyoshi's data were consistent with heat capacity work, the lower activation energy values of Grigor'ev and co-workers³² were not (i.e., their calculation yielded a very small bandwidth).

So one is left with a dilemma similar to that for bcc ^3He , which has been indicated by Heald and co-workers³ and others earlier, and for bcc ^4He by Granfors and co-

workers.⁷ The argument of Hetherington,⁵¹ for example, leads to skepticism that the x-ray effects measured by Heald and co-workers indicate thermal vacancy concentrations of such magnitude. On the other hand, there have been qualitative confirmations of the Heald activation energies in quite independent work on pure bcc ^3He , for example ultrasonic attenuation measurements by Beamish and Franck⁵² at intermediate molar volumes, ^3He NMR measurements by Chapellier *et al.*⁵³ and pressure measurements by Iwasa⁵⁴ also at large molar volumes. Unfortunately, there has been no x-ray work (that is, no direct measurements of thermal vacancy concentrations themselves) published from outside our laboratory. We do note that the bcc ^4He x-ray work of Granfors and co-workers⁷ obtained a consistent activation energy and vacancy content near melting for that substance from two quite different methods.

So, for some reason, possibly concerned with a limited density of states near the bottom of a relatively wide vacancy band, fairly large thermal vacancy concentrations in low-density hcp ^4He do not seem to make very large contributions to the heat capacity. The "pretransition anomalies" seen in heat capacity work in very narrow temperature intervals seem unlikely to be connected with thermal vacancies but rather to possible extrinsic factors such as small pressure gradients in the samples.

V. CONCLUSION

The present direct measurements of vacancy content of hcp ^4He have provided for the first time a firm basis for a variety of comparisons between measurements of activated phenomena in this solid. Extension of direct x-ray measurements to molar volumes below 20 cm^3 would make possible further comparisons, and may clarify whether there are, in some regimes, differences in the vacancy properties of hcp ^3He and hcp ^4He and whether there is a qualitative change in vacancy properties of hcp ^4He around a molar volume of 19.5 cm^3 .

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