

cent experiments in this laboratory⁷ on the gas-temperature dependence of the angle-averaged sticking coefficient s for H_2 on W(110) and on the isotope effect for s between H_2 and D_2 . A calculation using the square-well potential and quantized motion of the surface atoms gives the correct form for $s(\varphi)$ but predicts that the angle-averaged sticking coefficient s increases with increasing gas temperature, which is at variance with our recent experiments.

These results demonstrate a significant dependence of the sticking coefficient on the angle of incidence. This can have an important bearing on the interpretation of molecular-beam-surface experiments and on catalysis in situations where fluxes may not be isotropic. The results also indicate that our present knowledge of the interaction potential and the energy transfer process in

gas-surface collisions is inadequate and that momentum transfer from the gas to the surface probably cannot account for all the features of condensation rates.

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Superionic Conductors: Theory of the Phase Transition to the Cation Disordered State

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We suggest that it is the interaction of interstitial cation defects with the strain field they induce which is primarily responsible for the phase transition to the cation disordered state of the superionic conductor. This idea is developed in terms of a simple model that yields an analytic solution for the phase transition and relates the necessary strength of the interaction to anomalously large free volumes of cation interstitial formation.

The so-called "superionic conductors," typified by the cation disordered phases of the silver halide-chalcogenides and their various derivatives (e.g., AgI , Ag_2S , Ag_3SI , $RbAg_4I_5$), exhibit remarkable physical properties.¹ Structurally, they may be characterized as consisting of a relatively rigid crystalline framework composed of the nonconducting ionic species, with the conducting cations, usually Ag^+ or Cu^+ , distributed in a statistically disordered fashion among the available sites offered by the crystalline nonconducting framework. There are usually several, and sometimes many, possible sites per conducting cation. As was first recognized by Strock² in 1934, the exceptionally high ionic conductivity¹ and liquidlike levels of cation diffusivity¹ of these solids result from an almost moltenlike state of the disordered cation species. Interestingly, the physical picture of these disordered cations as having "arrived" from some sort of melting tran-

sition is emphasized by the fact that the disordered cation state typically arises as a result of a first-order structural phase transition from a lower-temperature crystalline phase in which the cations are crystallographically ordered. At the transition to the ordered phase the ionic conductivity drops discontinuously by several orders of magnitude to the relatively low levels of ionic conductivity characteristic of typical ionic solids.¹ The accompanying heat of transition is comparable to that of a normal melting transition.³

An as yet unresolved problem in the study of this interesting class of solids is an elucidation of the physics behind the unique phase transition to the superionic conductor phase. It is the purpose of this Letter to present a theoretical model of such a phase transition.

In the low-temperature phase ($T < T_c$) one can imagine that a small fraction of the ordered conducting cation species becomes thermally pro-

moted to certain interstitial sites. Such (Frenkel) defects are believed to be responsible for the low levels of ionic conductivity observed below T_c .⁴ In general, the creation of interstitial defects will lead to a finite change in the volume of the crystal.⁵ The key feature of the present discussion is to suggest that it is the interaction of the cation interstitials with the strain field associated with this net volume change which is the principle factor responsible for the phase transition.

Let us suppose there are N cations belonging to the conducting cation species, and that at a temperature T below T_c , $n = \rho N$ ($0 \leq \rho \leq 1$) of these cations are distributed over a total of Ng energetically less favorable but equivalent interstitial sites. If we imagine the solid to be in an arbitrary state of hydrostatic strain $u = \Delta V/V$ relative to the equilibrium state of the perfectly ordered solid ($\rho = 0$), we may, for sufficiently small u , expand the free energy F of the strained solid in powers of u . To order u^2 the free energy per cation, measured relative to that of the perfectly ordered and unstrained solid, may be written in the form

$$F(\rho, u) = U(\rho) - TS(\rho) + \alpha(\rho)u + \frac{1}{2}\omega(\rho)u^2, \quad (1)$$

where $U(\rho)$ and $S(\rho)$ denote the internal energy and entropy that result purely from the defect population ρ . In the absence of defects U , S , and α must be zero and $\omega(0)$ will be related to the bulk modulus of the ordered solid. The equilibrium value u_0 of u will be zero. For finite ρ , u_0 will not be zero and is determined by minimiz-

ing (1) with respect to u . This yields $u_0 = -\alpha(\rho)/\omega(\rho)$ with the resulting free energy

$$F(\rho) = U(\rho) - TS(\rho) - \frac{1}{2}\alpha(\rho)^2/\omega(\rho). \quad (2)$$

Since $\omega(\rho) > 0$ for stability, we see that the effect of the strain field is always to lower the free energy of the disordered solid.

We now investigate the temperature dependence of $\rho(T)$ on the basis of a model defined by the following simplifications:

(a) We set $\epsilon(\rho) = \epsilon_0\rho$, $\alpha(\rho) = \gamma\rho$, and $\omega(\rho) = \omega_0$, where ϵ_0 , γ , and ω_0 are constants. We interpret ϵ_0 as the energy required to promote a cation to an interstitial site, γ as specifying the strength of the interaction between an interstitial cation and the strain field, and ω_0 as a constant related to a mean bulk modulus B according to $\omega_0 = B/n_0$, where n_0 denotes the number of cations per unit volume.

(b) We assume that the dominant contribution to $S(\rho)$ arises from the configurational disorder introduced by ρ . We calculate this on the assumption that the solid is divisible into N identical unit cells each with g equivalent interstitial sites and one ideal site, the cation occupancy of each cell being restricted to one cation at all times. We choose this particular model because the form of resulting entropy, $k_B \ln[g^n N! / (N-n)! n!]$, leads to a simple analytic solution for the phase transition. The more obvious model of simply distributing ρN cations over any of a total of gN interstitial sites will lead to qualitatively similar results, but only on the basis of less transparent numerical computation.

Consequently, the free energy (2) is

$$F(\rho, T) = \rho(\epsilon_0 - \frac{1}{2}\lambda\rho) - k_B T \{ \rho \ln g - \rho \ln \rho - (1-\rho) \ln(1-\rho) \}, \quad (3)$$

where $\lambda = \gamma^2/\omega_0$. Minimization of (3) with respect to ρ yields the following equation for the equilibrium value of ρ :

$$\epsilon_0 - \lambda\rho = k_B T \ln[g(1-\rho)/\rho]. \quad (4)$$

We note that, provided $\epsilon_0 > \lambda/2$, the stability of an ordered cation arrangement at $T=0$ will be ensured. The free energy (3) is of precisely the same form as that studied by Strässler and Kittel⁶ (SK) in a paper dealing with the order of phase transitions in the molecular-field approximation, and we may immediately apply their results to the present problem. Utilizing the property that (3) may be written as the sum of two terms, one symmetric in the operation $\rho \rightarrow (1-\rho)$ and one lin-

ear in ρ , SK show that, provided

$$\lambda/\epsilon_0 > 2/[1 + \frac{1}{2} \ln(g)], \quad (5)$$

a first-order phase transition with respect to ρ will occur at the temperature

$$k_B T_c = (\epsilon_0 - \lambda/2)/\ln g. \quad (6)$$

The two values of ρ at T_c are symmetric about $\rho = \frac{1}{2}$, and if we write $\rho_1 = \frac{1}{2}(1-\Delta)$ and $\rho_2 = \frac{1}{2}(1+\Delta)$, Δ is given by the solution of

$$\frac{2}{\Delta} \ln \left(\frac{1+\Delta}{1-\Delta} \right) = \beta_c \lambda \quad (\beta_c^{-1} = k_B T_c). \quad (7)$$

If, for example, we assume $g=8$, the temperature dependences of ρ calculated from (4) and (7)

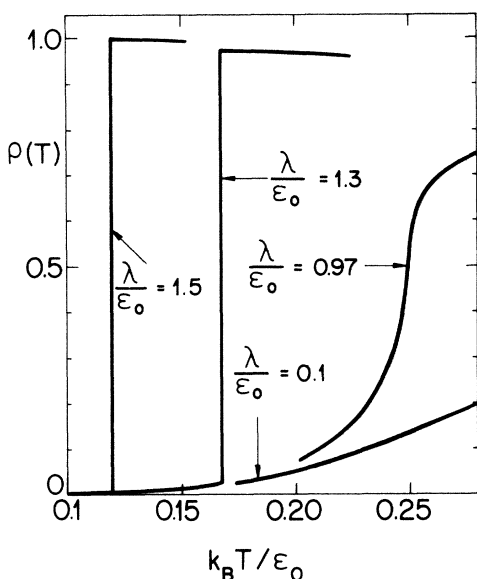


FIG. 1. The interstitial defect population calculated for $g=8$ as a function of temperature for increasing values of the interaction parameter λ . A first-order phase transition is possible for $\lambda/\epsilon_0 > 0.98$.

for various increasing values of λ/ϵ_0 appear as shown in Fig. 1.⁷ We note that for $\lambda\beta_c$ large, $\Delta \sim 1$, so that $\rho_1 \sim 0$ and $\rho_2 \sim 1$. In this limit the precise magnitude of the jump in ρ at T_c is given by $\rho_2/\rho_1 = \exp(\beta_c \lambda/2)$. The heat of transition, Q , is easily calculated to be

$$Q = Nk_B T_c \Delta \ln g. \quad (8)$$

The increase in volume of the solid due to defect formation is $\Delta V(T) = Vu_0(T)$, or, since $u_0 = -(\gamma/\omega_0)\rho$,

$$\Delta V(T) = -(\gamma/\omega_0)V\rho(T) = -(\gamma/B)m(T). \quad (9)$$

This result, which depends only on the assumptions made under (a), tells us that the ratio $-\gamma/B$ is just the conventional "free volume" of defect formation v_0 . Thus γ may be experimentally determined via the relation $\gamma = -v_0 B$.

Bearing in mind the stability condition, $\epsilon_0 > \lambda/2$, the full criterion for the occurrence of the first-order transition from an ordered to a disordered cation arrangement⁸ is $2\epsilon_0/[1 + \frac{1}{2} \ln(g)] < \gamma^2/\omega_0 < 2\epsilon_0$. We note the crucial role of the availability of a relatively large number of interstitial sites per cation in providing a finite width to the energy range defined by the latter criterion. Since $\gamma = -v_0 B$, we may re-express the criterion

on γ as one on v_0 :

$$[2\epsilon_0 n_0 / B(1 + \frac{1}{2} \ln g)]^{1/2} < n_0 |v_0| < (2\epsilon_0 n_0 / B)^{1/2}. \quad (10)$$

If we use as typical values those appropriate for the low-temperature hexagonal β phase of AgI, $\epsilon_0 \approx 0.35$ eV,⁴ $B \approx 2.5 \times 10^{11}$ dyn cm⁻²,⁹ and $n_0 = 1.45 \times 10^{22}$ cm⁻³, and apply (8) to arrive at the estimate¹⁰ $\ln g \approx Q/Nk_B T_c \approx 2$, then (10) becomes $\sim 0.18 < n_0 |v_0| < \sim 0.26$. Since such values of v_0 are unusually large we conclude that the required magnitudes of γ imply *anomalously large free volumes* of cation interstitial formation below T_c . The very high polarizabilities of *both* the conducting and nonconducting ionic species are likely to be an important factor in leading to such magnitudes in the superionic conductor compounds. Unfortunately, relevant data on v_0 appear to exist only for β -AgI. The low-temperature value estimated by Hoshino,¹¹ $n_0 v_0 \leq -0.15$, is indeed anomalously large and confirms the approximate satisfaction of (10).

We stress that in the particular model studied here, the nonconducting framework of the superionic compound is considered structurally rigid and consequently the model disregards the experimental fact that the nonconducting framework generally undergoes a change in lattice structure at T_c . The explicit model results and criteria that we have found above are therefore likely to have only a qualitative significance. A model which incorporates the effect of a change in structure of the nonconducting framework and which also allows for a vibrational contribution¹² to the entropy of disorder is currently under study.

Measurements of v_0 below T_c would be particularly relevant to the ideas expressed in this Letter.

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⁷It follows from Eq. (7) that if $\epsilon_0/\lambda > g/(1+g)$ the value of $\rho(T_c)$ will exceed the infinite-temperature value of ρ , $\rho_\infty = g/(1+g)$, so that $d\rho/dT$ will be < 0 above T_c . Below T_c , $d\rho/dT$ will always be > 0 . For such a “supertransition” (Ref. 6), it follows from Eq. (9) that the volume-expansion coefficient $\alpha_p(T)$ will undergo a sign change at T_c . Note that the transitions shown in Fig. 1 are “supertransitions.”

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¹²Note that if the vibrational contribution to $S(\rho)$ is of the form $S(\rho)_{\text{vib}} = k_B \rho \ln g_{\text{vib}}$, where g_{vib} denotes a characteristic constant, it follows from Eq. (3) that the effective degeneracy factor appearing in our model will be just $g_{\text{eff}} = g_{\text{vib}} g$.

Particle Release from Niobium Irradiated with 14-MeV Neutrons*

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The particle release from cold-rolled niobium surfaces under 14-MeV-neutron impact to a total dose of 4.6×10^{15} neutrons/cm² was investigated under ultrahigh-vacuum conditions and at ambient temperature. The type and amount of material released and deposited on a substrate surface was determined independently by four analytical techniques. Surprisingly, there were two types of deposits—one in the form of large chunks, the other a more even layer covering the surface. The chunk emission cannot be explained by existing neutron-sputtering theories.

It has been suggested¹⁻³ that the bombardment of the first wall of fusion reactors by MeV neutrons may lead to both serious wall erosion and plasma contamination. Unfortunately, the experimental information available on particle release by MeV-neutron impact on solids is very scarce and contradictory (for reviews, see Refs. 1–3). For example, for monocrystalline gold irradiated with 14-MeV neutrons, the particle release yield $S = 3 \times 10^{-3}$ atom/neutron was reported.⁴ However, for iron irradiated with neutrons of a softer energy spectrum (from a fission reactor), $S = (5.7 \pm 0.8) \times 10^{-3}$ atom/neutron was reported.⁵ A theoretical estimate of S for niobium irradiated with 14-MeV neutrons by one of us (M.K.) yielded $S \approx 6 \times 10^{-5}$ atom/neutron—a value which was approximately 2 orders of magnitude smaller than the above-mentioned experimental value for gold. More recently Behrisch⁶ and Behrisch and Vernickel⁷ estimated a yield value for 14-MeV-neutron-bombarded niobium that was only about a quarter of that of Kaminsky. On the basis of such an estimated value, these authors con-

cluded that neutron sputtering would have a negligible effect on wall erosion and plasma contamination during the operation of a fusion reactor. In view of the great discrepancy between the theoretical estimates and the available experimental results, it seemed imperative to conduct new experiments under controlled conditions.

The present experiments were undertaken to provide information on the erosion of surfaces of cold-rolled polycrystalline niobium under 14-MeV-neutron impact in an ultrahigh-vacuum environment. The Lawrence Livermore Laboratory's rotating-target neutron source⁸⁻¹⁰ was used in conjunction with an insulated-core-transformer accelerator. The total neutron emission rate over the entire 4π solid angle of a fresh neutron-source target was about 3×10^{12} neutrons/sec. The irradiation run was monitored with two proton-recoil detectors.^{9,10} The drift in counting efficiency of each recoil detector is thought to be less than 5%.¹¹ The total dose was calibrated independently by activation analyses,¹⁰ for example, by use of the reaction $^{93}\text{Nb}(n, 2n)^{92}\text{Nb}$. The