be explained in terms of this model, the experimental data are not sufficient to characterize adequately the fundamental properties of the system. For example, the densities of the two phases as functions of temperature are as yet undetermined, as are the critical temperature and density. One experimental difficulty in observing this phase separation is the fact that at the temperatures and Li densities of interest, the Li ions are present at supersaturated concentrations.[12] Consequently, the Li ions tend to precipitate out of the Si at the surface and at defects in the bulk. However, the precipitation phenomenon takes place much more slowly than does the expected phase separation, so that although the two-phase system described here is only metastable, this fact should not prevent its observation and characterization.

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Theory of the Temperature Dependence of the Electric Field Gradient in Noncubic Metals*

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The temperature dependence of the electric field gradient $eq(T)$ in noncubic metals is calculated within a pseudopotential approach including the influence of lattice vibrations. The resulting $eq(T)$ factorizes into a Debye-Waller factor and a lattice sum over screened ions. The accurately measured $eq(T)/eq(0)$ values for In, Cd, Zn, Sb, and Sn are quantitatively reproduced using known data for the lattice constants and for the mean-square atomic displacements.

Since the pioneering work of Simmons and Slichter[1] on In metal many more experiments have been performed by nuclear quadupole resonance (NQR) and perturbed angular correlation methods to determine accurately the temperature dependence of the electric field gradient (EFG) $eq(T)$ at a nuclear site in noncubic metals. Recently, Heubes *et al.*[2] discovered in a heuristic way that the $eq(T)$ data in all nontransition metals can be well reproduced by a $T^{1.5}$ dependence. Attempts to explain this temperature dependence have been far from successful. Within the traditionally used *Ansatz*[3] $eq = (1-\gamma_\infty)eq_{\text{ion}} + (1-R)eq_{\text{el}}$ one calculates the point-charge interaction of the ion cores eq_{ion} by a Coulomb potential and separately adds the interaction with the conduction electrons, q_{el}, which has been evaluated by complicated band-structure calculations. The temperature dependence of eq_{ion} due to the variation of lattice parameters is much too small (and in most metals even wrong in sign) to explain the observed $eq(T)$ data.

Simmons and Slichter[1] and Quitmann, Nishiyama, and Riegel[4] considered within rough approaches thermal lattice vibrations as a further possible contribution to $eq(T)$, but in Ref. 1 this contribution has been calculated to be negligible, whereas in Ref. 4 the strength parameter of this contribution was treated as a fitting parameter to the experimental $eq(T)$ data in In.

In this paper we present a theory by which the experimentally observed temperature dependence of $eq(T)$, e.g., in Zn, Cd, In, Sn, and Sb, can be explained quantitatively. Unambiguously the temperature dependence of $eq(T)$ arises from the temperature dependence of the lattice constants and to a larger extent from the strongly temperature-dependent mean-square lattice displacements $\langle u^2\rangle$. A treatment of these two effects within a pseudopotential approach yields in very good approximation the universal $T^{1.5}$ dependence of $eq(T)$ found empirically in Ref. 2.

We start from the *Ansatz*

$$eq(t,T)=(1-\gamma_{\rm eff})\int\sum\nolimits_i{}'\delta(\vec{R}-\vec{R}_i(t))F(\vec{R})d^3R,\quad F(\vec{R})=\int\{Ze\delta(\vec{r}-\vec{R})-e\rho_{\rm sc}(\vec{r}-\vec{R})\}r^{-3}2P_2(\cos\theta_r)d^3r, \tag{1}$$

where the sum runs over all vibrating ions, $\vec{R}_i(t)$, except the probe ion fixed at the origin. $F(\vec{R})$ describes the EFG due to a single screened ion at position $\vec{R}$, the charge of which consists of the point charge Ze and the screening electron charge density[5] $e\rho_{\rm sc}$ which adiabatically follows the vibrating ions. The enhancement of the EFG due to the polarization of the screened probe ion is parametrized by the factor $1-\gamma_{\rm eff}$, which is assumed to be temperature independent.

Since the frequency of the lattice vibrations ($\sim 10^{12}$ Hz) is large compared to the quadrupole interaction frequency observed ($\lesssim 10^8$ Hz), we have to take the time average over the ionic vibrations which are regarded approximately as uncorrelated and isotropic.[6] Combining these conditions with Eq. (1), we derive the following result, more simply expressed in k space[6]:

$$eq(T)=(1-\gamma_{\rm eff})\int\{S(\vec{k})-1\}\exp\{-k^2\langle u^2\rangle/3\}F(\vec{k})d^3k, \tag{2}$$

with $F(\vec{k})$ the Fourier transform of $F(\vec{R})$, and $S(\vec{k})$ the structure factor of the nonvibrating lattice. The influence of the lattice vibrations on the EFG at the probe ion is described by the Debye-Waller factor.

We specify $F(\vec{R})$ by use of the simple pseudopotential $V(R)$ derived from a Coulomb potential $V^{\rm C}(R)$ screened by a free-electron gas[7]:

$$V(R)=\frac{1}{2\pi^2}\int_0^\infty\frac{V^{\rm C}(k)}{\epsilon(k)}\,\frac{\sin(kR)}{kR}k^2dk \tag{3}$$

with $V^{\rm C}(k)$ the Fourier transform of $V^{\rm C}(R)$, and $\epsilon(k)$ the dielectric function,[7] which depends on the Fermi vector $k_{\rm F}$. Common to the use of more sophisticated pseudopotentials (see, e.g., Ref. 5), an essential feature of the radial part of $F(\vec{R})$, $V_2(R)$ [second derivative of Eq. (3)], is the occurrence of long-range oscillations. This oscillating behavior of $V_2(R)$ (period $\pi/k_{\rm F}\sim 2$ Å) leads to the large effect of $\langle u^2\rangle(T)$ on $eq(T)$. The conditions are schematically illustrated in Fig. 1. Typically the nearest-neighbor distances in metals are about 3 Å, whereas the vibration amplitudes are typically about 0.3 Å at the melting point. With increasing temperature and thus increasing $\langle u^2\rangle(T)$ the averaged $V_2(R)$ becomes smaller, as reflected by the Debye-Waller factor in Eqs. (2) or (4). For comparison, $V_2^{\rm C}(R)$ derived by an unscreened Coulomb potential is shown in Fig. 1. A calculation yields no change of $V_2^{\rm C}(R)$ by varying $\langle u^2\rangle$, in contradiction to the assumption made in Ref. 4. Evaluating Eq. (2) by use of the simple pseudopotential Eq. (3) leads to the result[6]

$$eq(T)=(1-\gamma_{\rm eff})eq_{\rm ion}{}^{\rm sc}(T)\exp\{-\tfrac{4}{3}k_{\rm F}{}^2\langle u^2\rangle(T)\}. \tag{4}$$

The lattice sum $q_{\rm ion}{}^{\rm sc}=e^{-1}\sum_i{}'F(\vec{R}_i)=\sum_i{}'V_2(R_i)\times 2P_2(\cos\theta_i)$ over the screened ions, which we calculated over 10^5 ions around the probe ion, depends only on the temperature-dependent lattice constants and on $k_{\rm F}$, which is slightly temperature dependent because of volume expansion. We now are in the favorable position of being able to calculate the ratio $q(T)/q(0)$ without any free parameters. The results are compared with experimental data for In, Zn, Cd, Sb, and Sn in Figs. 2 and 3. All data are plotted against a $T^{1.5}$ scale. Temperature-dependent lattice constants and $k_{\rm F}$ values for these metals are taken from the literature. Concerning the temperature dependence of $\langle u^2\rangle(T)$ we found the remarkable feature that all

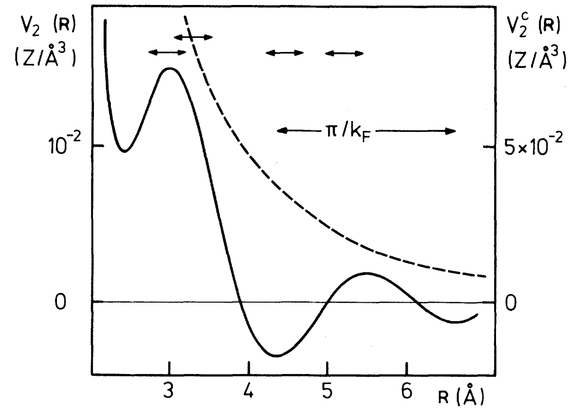

FIG. 1. Influence of the ionic vibrations on the radial part of the EFG in Cd metal. The dashed curve describes the EFG derived from a Coulomb potential (right-hand scale). The arrows indicate the vibration amplitudes of the first- to fourth-neighboring ions at the melting point.

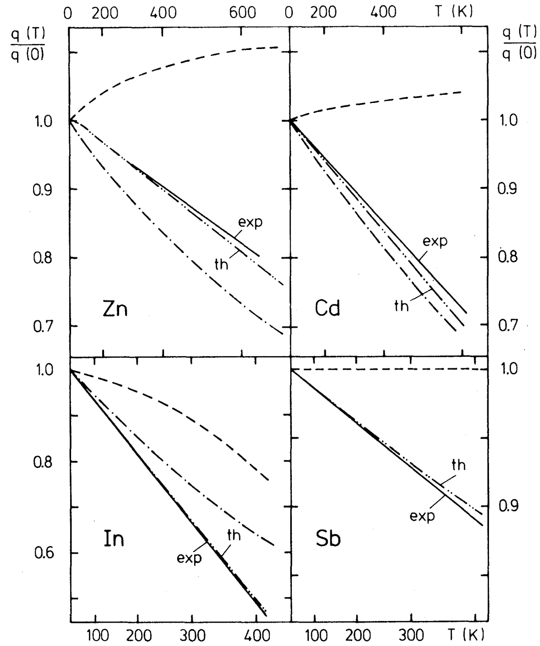

FIG. 2. Comparison of the temperature dependence of the EFG measured for Zn, Cd, In, and Sb with theoretical results (th) [Eq. (4)]. Solid line (exp), experimental $eq(T)/eq(0)$ data (see Ref. 2 and references therein); dashed line, $q_{\text{ion}}^{\text{sc}}$; dot-dashed line, Debye-Waller factor. All curves are separately normalized to unity at 0°K.

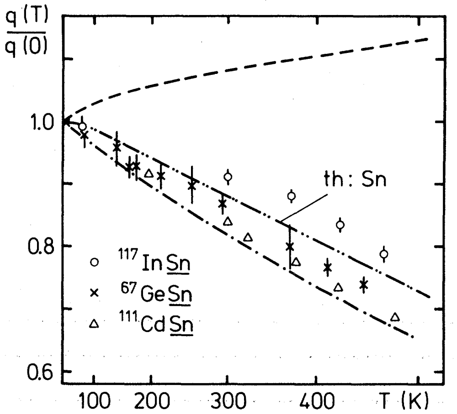

FIG. 3. Temperature dependence of the EFG at the site of various impurities in Sn metal (see Ref. 8) compared with theoretical values for Sn*Sn* [Eq. (4)]. For the identification of the curves see the caption of Fig. 2.

experimental data in cubic metals (e.g., Al, Au, Pb, α-Fe, Ti) can be perfectly reproduced by a $T^{1.5}$ dependence between $T = 0$°K and the melting point.[9] This variation with T holds for the poorer $\langle u^2\rangle(T)$ data in noncubic metals, also; the most accurate data are available for Sn and Zn.[10] We thus extrapolated a $T^{1.5}$ dependence for $\langle u^2\rangle(T)$ in In, Sb, and Cd; absolute values for $\langle u^2\rangle$ were taken from x-ray or neutron scattering and/or from Debye temperatures Θ_D.[11]

We can summarize the following essential features of $eq(T)$ in noncubic metals as inferred from Eq. (4) and Figs. 2 and 3:

(1) As shown in Figs. 2 and 3, the main change of $q(T)$ stems in all cases analyzed from the variation of the Debye-Waller factor, which always decreases with temperature. The variation of the term $q_{\text{ion}}^{\text{sc}}(T)$ ranges from an increase (Zn, Cd, Sn) to a decrease (In) with temperature. For Sb this term is nearly constant; thus the change of the Debye-Waller factor is identical to the theoretical curve (Fig. 2). The product of these two terms yields, in all cases analyzed, a striking $T^{1.5}$ dependence, in quantitative agreement with experiment. This universal behavior of $eq(T)$ over temperature ranges from a few degrees Kelvin to the melting point should bring some new information about the correlation between the temperature dependence of the lattice constants and $\langle u^2\rangle(T)$.

(2) The simple pseudopotential used yields remarkable agreement with experiment. Thus the oscillating slope of the radial part of the EFG [Eq. (3)] seems to be satisfactorily described by such a potential.[12] Additionally this feature supports the analysis of the temperature dependence of the nuclear-quadrupole relaxation rate in liquid metals where the same potential has been utilized to evaluate the averaged EFG.[13]

(3) Equation (4) might be used in future work as a reliable starting point to analyze the many $eq(T)$ data observed by perturbed angular γ-ray distribution methods for (substitutional) impurities in metals (see Fig. 3 for impurities in Sn). Because of the different size mass and charge of the impurity ion compared to the host ion, the impurity may locally influence the lattice parameters, $\langle u^2\rangle$, and k_F; the changes of these quantities are most probably correlated.

(4) Concerning the magnitude of eq we have compared Eq. (4) for $T = 0$°K with experimental data on $|eq|$ for Be, Mg, Zn, Cd, In, and Sn. Taking the factor γ_∞ for the ion cores from the literature we found $|\gamma_{\text{eff}}/\gamma_\infty| \sim 6$ within roughly a factor of 2 for all these metals. Thus the empirical finding recently made by Raghavan, Kaufmann, and Raghavan[14] is reflected in the theory presented here. An open problem for the future is to calculate from first principles the quantity γ_{eff} on which the magnitude of eq sensitively depends.

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Note added.—While this paper was being submitted, Jena[15] published a semiquantitative treatment of $eq(T)$ on which we comment in Ref. 15.

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[12] Starting from Eqs. (3) and (4) we have *quantitatively* analyzed the pressure and concentration dependence of the EFG in In, Cd, and CdMg alloys, respectively. These analyses provide an independent critical test for the model developed here, especially for the free-electron approach, Eq. (3). See K. Nishiyama and D. Riegel, to be published.

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