

ponents deduced from Eqs. (14) and (15) are listed in Table I.

There are other cooperative phenomena which must be re-examined in light of the possible existence of the spin-glass state. In particular we are now considering the competition between ferromagnetic or antiferromagnetic ordering and spin-glass ordering that will occur at some critical value of $[J]_{av}$. We are also considering the possibility of other types of spin-glass ordering that may occur in other types of random systems, e.g., systems with random uniaxial anisotropy.¹⁶

The authors would like to thank Dr. D. Sherrington and Dr. S. Kirkpatrick for the stimulating preprint of Ref. 6. Also we acknowledge helpful discussions with Professor E. Siggia.

*Work supported in part by the National Science Foundation.

†Alfred P. Sloan Research Fellow.

¹V. Canella and J. A. Mydosh, Phys. Rev. B **6**, 4220 (1972).

²J. Mydosh, in *Magnetism and Magnetic Materials—1974*, AIP Conference Proceedings No. 24, edited by C. D. Graham, Jr., J. J. Rhyne, and G. H. Lander (American Institute of Physics, New York, 1975), p.

131.

³S. F. Edwards and P. W. Anderson, J. Phys. F **5**, 965 (1975).

⁴D. Sherrington and B. W. Southern, J. Phys. F **5**, L49 (1975).

⁵K. H. Fischer, Phys. Rev. Lett. **34**, 1438 (1975).

⁶D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. **35**, 1792 (1975).

⁷G. Toulouse, Nuovo Cimento **23B**, 234 (1974).

⁸A. B. Harris, T. C. Lubensky, W. K. Holcomb, and C. Dasgupta, Phys. Rev. Lett. **35**, 327 (1975), and **35**, 1397(E) (1975).

⁹Y. Imry and S. K. Ma, Phys. Rev. Lett. **35**, 1399 (1975).

¹⁰A. B. Harris and S. Kirkpatrick, to be published.

¹¹K. G. Wilson, Phys. Rev. B **4**, 3174 (1971); K. G. Wilson and M. E. Fisher, Phys. Rev. Lett. **28**, 240 (1972).

¹²For a review of RG see A. Aharony, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1975).

¹³T. C. Lubensky, Phys. Rev. B **11**, 3573 (1975); G. Grinstein and A. Luther, Phys. Rev. B (to be published).

¹⁴K. G. Wilson and J. Kogut, Phys. Rep. **12C**, 77 (1974).

¹⁵R. G. Priest and T. C. Lubensky, to be published.

¹⁶R. Harris, M. Plischke, and M. J. Zuckermann, Phys. Rev. Lett. **31**, 160 (1973); A. Aharony, Phys. Rev. B **12**, 1038 (1975).

Temperature Dependence of Electric Field Gradients in Noncubic Metals*

P. Jena

Department of Physics, Northwestern University, Evanston, Illinois 60201

(Received 2 September 1975)

Temperature dependence of the nuclear quadrupole frequency, ν_Q , of noncubic metals has been studied theoretically. It is shown that the electronic contribution to the field gradient is largely responsible for the observed $T^{3/2}$ behavior. The conclusions are general and apply to all noncubic metals.

The study of electric field gradients, eq , in metals is of great importance since it not only provides a detailed knowledge of the electronic wave functions in the occupied Fermi volume, but can also yield valuable information regarding the nuclear quadrupole moment, Q . Experiments using a variety of probes, such as nuclear magnetic resonance, time-differential perturbed angular correlation, and Mössbauer effect, have been performed on both pure noncubic metals and alloys to study the distribution of eq . In several systems the sign of the nuclear quadrupole coupling, $\nu_Q = e^2qQ/h$, has also been determined.

Recently the temperature dependence of ν_Q of several metals, such as Cd,^{1,2} Zn,³ In,⁴ Sb,⁵ and Ga,⁶ has been studied experimentally. An analysis of these results reveals the interesting feature that ν_Q generally decreases⁷ as $T^{3/2}$ for all these metals, namely,

$$\nu_Q \approx \nu_Q^0 (1 - \alpha T^{3/2}), \quad (1)$$

where ν_Q^0 is the value of the nuclear quadrupole frequency at $T = 0^\circ\text{K}$ and α is a constant. Since the electronic structures of all these metals are very different from each other, this "universal" form of the temperature dependence suggests that

a mechanism common to all metals must be responsible for the behavior.

In this Letter I present a theoretical calculation of the temperature dependence of ν_Q in metals that successfully explains the experimental observation. Conventionally⁸ one writes the field gradient as a sum of two contributions,

$$eq = eq_{\text{latt}}(1 - \gamma_\infty) + eq_{\text{el}}(1 - R), \quad (2)$$

where eq_{latt} is the field gradient due to the non-cubic arrangement of ions in the lattice and $1 - \gamma_\infty$ is the well-known Sternheimer⁹ antishielding factor. The term eq_{el} is due to the conduction electrons and $1 - R$ is a correction factor due to the interaction of the conduction electrons with the distorted ion cores. This is of the order of unity and is neglected in most theoretical calculations. While computation of the lattice term in Eq. (2) is straightforward,^{10, 11} the evaluation of the electronic part is rather complicated since it requires a knowledge of the conduction-electron wave functions, $\Psi_{\vec{k}}(\vec{r})$, for all occupied electron states:

$$eq_{\text{el}} = e \int d^3r \rho(\vec{r})(3\cos^2\theta - 1)/r^3, \quad (3)$$

where $e\rho(\vec{r})$ is the total conduction-electron charge density at \vec{r} ,

$$\rho(\vec{r}) = 2 \sum_{\vec{k} < \vec{k}_F} |\Psi_{\vec{k}}(\vec{r})|^2. \quad (4)$$

The sum in Eq. (4) is over the occupied states \vec{k} and the factor 2 is due to spin.

The term in Eq. (3) has recently been calculated at $T = 0^\circ\text{K}$ for the hcp metals Be,¹² Mg,¹³ and Cd¹⁴ using a band-structure procedure. The electronic part combined with the lattice contribution yielded theoretical results for eq in very good agreement with experiment. The lattice contribution to eq in Eq. (2) can be calculated^{10, 11} easily as a function of temperature from a knowledge of lattice parameters. To compute the temperature dependence of the electronic part in Eq. (3), we write $\Psi_{\vec{k}}(\vec{r})$ in terms of orthogonalized plane waves,

$$\Psi_{\vec{k}}(\vec{r}) = N_{\vec{k}}(1 - P_{\vec{k}})\Phi_{\vec{k}}(\vec{r}), \quad (5)$$

where $N_{\vec{k}}$ is the normalization constant, $P_{\vec{k}}$ is the core-projection operator, and $\Phi_{\vec{k}}(\vec{r})$ is the pseudo wave function that contains all of the temperature information. We write $\Phi_{\vec{k}}(\vec{r})$ in terms of perturbation theory,

$$\Phi_{\vec{k}}(\vec{r}) = \Phi_{\vec{k}}^{(0)}(\vec{r}) + \Phi_{\vec{k}}^{(1)}(\vec{r}) + \Phi_{\vec{k}}^{(2)}(\vec{r}) + \dots, \quad (6)$$

where the superscripts (0), (1), (2), ..., indicate various orders of perturbation in the pseudopotential,

V . The form of the various terms in Eq. (6) in nondegenerate perturbation theory is standard. For the discussion to follow, it is useful to write

$$\begin{aligned} \Phi_{\vec{k}}^{(0)}(\vec{r}) &\equiv |\vec{k}\rangle = (\Omega_0)^{-1/2} e^{i\vec{k}\cdot\vec{r}}, \\ \Phi_{\vec{k}}^{(1)}(\vec{r}) &= \sum_{\vec{G}} \mathcal{G}' [(\vec{k} + \vec{G}|V|\vec{k}) / (E_{\vec{k}} - E_{\vec{k}+\vec{G}})] |\vec{k} + \vec{G}\rangle, \end{aligned} \quad (7)$$

etc. In the above equation, $E_{\vec{k}}$ is the free-single-particle energy, and \vec{G} is the reciprocal-lattice vector. The total pseudopotential of the lattice, $V(\vec{r})$, can be written as a sum of potentials centered around the ion site with position vector \vec{R}_ν ,

$$V(\vec{r}) = \sum_\nu v(\vec{r} - \vec{R}_\nu). \quad (8)$$

Following Kasowski,¹⁵ we can write the temperature-dependent pseudopotential matrix element in terms of its value at $T = 0^\circ\text{K}$, namely,

$$\langle \vec{k} + \vec{G} | V | \vec{k} \rangle = e^{-W(\vec{G}, T)} \langle \vec{k} + \vec{G} | V_0 | \vec{k} \rangle. \quad (9)$$

V_0 is the pseudopotential of the lattice at $T = 0^\circ\text{K}$ and $\langle \vec{k} + \vec{G} | V_0 | \vec{k} \rangle$ contains the structure factor at 0°K . The function $W(\vec{G}, T)$ is the usual Debye-Waller factor and is given by

$$W(\vec{G}, T) = \frac{1}{2} \sum_{q,s} \frac{\hbar}{2MN\omega_{qs}} (2\bar{n}_{qs} + 1) |\vec{G} \cdot \vec{\epsilon}_{qs}|^2, \quad (10)$$

where \bar{n}_{qs} is the average occupation number of phonons in the mode qs and the other symbols have their usual meaning. For a system with one atom per unit cell, Eq. (10) can be evaluated in the Debye model¹⁶ and we have

$$W(\vec{G}, T) = (3\hbar^2/2Mk_B\Theta_D) G^2 \varphi(T/\Theta_D), \quad (11)$$

where the Debye integral $\varphi(T/\Theta_D)$ is given by

$$\varphi\left(\frac{T}{\Theta_D}\right) = \left(\frac{T}{\Theta_D}\right)^2 \int_0^{\Theta_D/T} \left(\frac{1}{e^z - 1} + \frac{1}{2}\right) z dz. \quad (12)$$

In Eq. (11), k_B and Θ_D are, respectively, the Boltzmann constant and Debye temperature. For G 's restricted to the first few Brillouin zones and temperatures in the range of experimental interest, it can be seen that $W(G, T)$ is much less than 1 and one can approximate

$$e^{-W(G, T)} \simeq 1 - (3\hbar^2 G^2 / 2Mk_B\Theta_D) \varphi(T/\Theta_D). \quad (13)$$

Substituting this result into Eqs. (9) and (7) and summing up to all orders of perturbation in Eq. (6), one can write the temperature-dependent charge density of Eq. (4) as

$$\rho(\vec{r}) = \rho_0(\vec{r}) - \tilde{\rho}_0(\vec{r}) \varphi(T/\Theta_D), \quad (14)$$

where $\rho_0(\vec{r})$ is the electron charge density at T

$= 0^\circ\text{K}$. $\tilde{\rho}_0(\vec{r})$ is a function of \vec{r} , also at $T = 0^\circ\text{K}$, and its form can be seen easily from Eqs. (4), (6), and (9). The temperature dependence is all included in φ . Substituting Eq. (14) in Eq. (3) we obtain the electronic contribution to the field gradient at temperature T :

$$eq_{el} = eq_{el}^0 [1 - \beta\varphi(T/\Theta_D)], \quad (15)$$

where eq_{el}^0 is the value of electric field gradient at 0°K , and β is a temperature-independent constant that depends upon the details of the pseudopotential, lattice structure, and Debye-Waller factor of the solid.

Since the lattice contribution to the field gradient, eq_{latt} , is weakly dependent upon temperature,¹ one would like to analyze $\varphi(T/\Theta_D)$ to see if it has the same temperature variation as the experimental eq . From Eq. (12), it can be seen easily that as $T \rightarrow 0$, $\varphi(T/\Theta_D) \rightarrow \frac{1}{4}$ (a result of zero-point oscillations) and for $T \rightarrow \infty$, $\varphi(T/\Theta_D)$ increases linearly with T . For intermediate temperatures, this has to be evaluated numerically.

To determine the temperature dependence of $\varphi(T/\Theta_D)$ at an intermediate T , I have plotted in Fig. 1 $\ln[\varphi(T/\Theta_D) - \varphi(0)]$ as a function of $\ln(T/\Theta_D)$. It is seen that $\varphi(T/\Theta_D)$ increases on the average as $(T/\Theta_D)^{3/2}$ for temperature up to Θ_D and does not approach the infinite-temperature limit even for $T/\Theta_D \sim 3$. This observation clearly establishes the average $T^{3/2}$ variation of the electric field gradient at low temperatures. Since the Debye integral in Eq. (12) is independent of the details of the electronic structure, and the

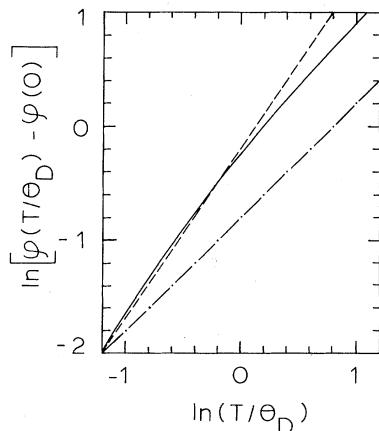


FIG. 1. The solid curve is the plot of $\ln[\varphi(T/\Theta_D) - \varphi(0)]$ versus $\ln(T/\Theta_D)$. The dashed and dot-dashed curves represent the $T^{3/2}$ and T^1 behaviors, respectively. The range of T/Θ_D which is most significant experimentally is $0 < T/\Theta_D \lesssim 2.5$.

nuclear quadrupole moment Q is believed to be temperature independent, the above conclusion applies to all metals and explains the "universal" temperature dependence of ν_Q in terms of the electronic part of the field gradient.

The calculation of the constant β in Eq. (15) is rather difficult because of its complicated dependence on the pseudopotential and band structure of the solid. It is, however, interesting to note that $\beta\varphi(T/\Theta_D)$ in Eq. (15) also provides one with a scheme to study the relative slopes, α , of the electric field gradient in Eq. (1). Neglecting the influence of the band structure in the determination of the relative slope and noting that $\varphi(T/\Theta_D) \sim (T/\Theta_D)^{3/2}$, one can evaluate the relative α 's semiquantitatively. From Eqs. (11)–(13) it is easy to see that this slope α should scale as $1/\Theta_D^{5/2}M$, where M is the mass of the ion. Since this result is obtained by neglecting the effect of pseudopotentials of metals, comparisons of relative slopes should be made with caution. This comparison would perhaps be more meaningful between elements of the same group of the periodic table. Thus the ratio of the slopes α computed for Cd and Zn is 1.8 which is in good agreement with the experimental ratio 1.6. For a numerical comparison of ν_Q/ν_Q^0 with experiment, I have chosen metallic Cd and Zn. The lattice contribution for hcp metals was computed by using the expression¹¹

$$q_{latt} = 2[0.0065 - 4.3584(c/a - 1.633)]a^{-3}, \quad (16)$$

where c and a are lattice parameters. Taking γ_∞ as computed by Das and Pomerantz¹¹ and the lattice parameters¹⁷ at several temperatures, I have computed $eq_{latt}(1 - \gamma_\infty)$ for Cd and Zn. The quantities eq_{el}^0 and β in Eq. (15) were determined empirically by subtracting the lattice contribution from experimental values of eq extrapolated to 0°K and at room temperature. Equation (15) was then used to compute eq_{el} at other temperatures. Table I compares theoretical and experimental ratios of ν_Q/ν_Q^0 at several temperatures. The agreement with experiment is good, particularly for low temperatures.

The deviation of $\varphi(T/\Theta_D)$ from $T^{3/2}$ behavior in Fig. 1 and the remaining discrepancy between experiment and theory in Table I at high temperatures could be due to several reasons: (i) $\varphi(T/\Theta_D)$ in Eq. (12) is evaluated in the harmonic approximation and anharmonic effects are important at higher temperatures; (ii) the temperature dependence of Θ_D and the use of actual phonon frequencies could also influence the result of

TABLE I. Temperature dependence of the normalized nuclear quadrupole frequency, ν_Q/ν_Q^0 , in Cd and Zn.

T (°K)	Zn		T (°K)	Cd	
	Expt.	Theor.		Expt.	Theor.
300 ^a	0.92	0.92	219	0.93	0.93
400	0.89	0.89	245	0.92	0.92
490	0.86	0.87	303 ^a	0.90	0.90
560	0.83	0.85	338	0.89	0.89
630	0.79	0.84	415	0.86	0.87
			465	0.81	0.86
			523	0.79	0.85

^aThe constant β in Eq. (15) was obtained by fitting the theoretical result for ν_Q to experiment at 300°K for Zn and 303°K for Cd.

Eqs. (11) and (12); and (iii) the effects of temperature on the Fermi-surface topology could also be important.

In summary, I draw the conclusion that the temperature dependence of ν_Q of a metal is primarily due to the conduction-electron effects and that the effect of the electron-phonon interactions on the crystal potential is responsible for the larger part of the temperature dependence. A more detailed calculation of the eq_{el} term using a band-structure procedure and experimental phonon frequency would be useful in obtaining better agreement with experiment. Experimental study of the temperature dependence of ν_Q in more metals as well as alloys would be useful to establish further evidence for the $T^{3/2}$ behavior.

The author is grateful to Professor E. F. W. Seymour for suggesting this problem and for many helpful discussions. He is also thankful to Professor K. S. Singwi and Professor D. L. Williams for helpful and stimulating discussions and to J. Rath for a critical reading of the manuscript.

*Work supported by the National Science Foundation through Northwestern University Materials Research Center.

¹R. S. Raghavan and P. Raghavan, Phys. Lett. **36A**, 313 (1971).

²J. Bleck, R. Butt, H. Haas, W. Ribbe, and W. Zeitz, Phys. Rev. Lett. **29**, 1371 (1972).

³H. Bertschat, E. Recknagel, and B. Spellmeyer, Phys. Rev. Lett. **32**, 18 (1974).

⁴R. R. Hewitt and T. T. Taylor, Phys. Rev. **125**, 524 (1962).

⁵R. R. Hewitt and B. F. Williams, Phys. Rev. **129**, 1188 (1963).

⁶S. L. Segel, R. D. Heyding, and E. F. W. Seymour, Phys. Rev. Lett. **28**, 970 (1972).

⁷P. Hubes *et al.*, in *Contributed Papers of the International Conference on Hyperfine Interactions Studied in Nuclear Reactions and Decay, Uppsala, Sweden, 1974*, edited by E. Karlsson and R. Wappling (University of Uppsala, Uppsala, Sweden, 1974), p. 208. It is worth pointing out that a better fit to experimental data of eq in Eq. (1) can be obtained if the exponents for Sb, Cd, and β -Ga were chosen to be 1.47, 1.46, and 1.25, respectively.

⁸R. E. Watson, A. C. Gossard, and Y. Yafet, Phys. Rev. **140**, A375 (1965).

⁹R. M. Sternheimer, Phys. Rev. **95**, 736 (1954).

¹⁰F. deWette, Phys. Rev. **123**, 103 (1961).

¹¹T. P. Das and M. Pomerantz, Phys. Rev. **123**, 2070 (1961).

¹²N. C. Mohapatra, C. M. Singal, T. P. Das, and P. Jena, Phys. Rev. Lett. **29**, 456 (1972).

¹³P. Jena, S. D. Mahanti, and T. P. Das, Phys. Rev. **B 7**, 975 (1973).

¹⁴N. C. Mohapatra, C. M. Singal, and T. P. Das, Phys. Rev. Lett. **31**, 530 (1973).

¹⁵R. V. Kasowski, Phys. Rev. **187**, 891 (1969).

¹⁶J. M. Ziman, *Principles of the Theory of Solids* (Cambridge Univ. Press, Cambridge, England, 1964), p. 60.

¹⁷Lattice parameters were interpolated for Zn from *Gmelins Handbuch der Anorganischen Chemie, Zink, Ergänzungsband* (Verlag Chemie, Weinheim, Germany, 1956), p. 282; and for Cd, *ibid.*, *Cadmium, Ergänzungsband* (Verlag Chemie, Weinheim, Germany, 1959), p. 56.