ues appear to be about a factor of 2 higher than those required to account for the estimated decrease in enhancement; but these estimates are rather uncertain because of the many approximations needed to analyze the data.

It should also be pointed out that both the present measurements and mutual-inductance measurements[15] show that the superconducting transition temperature of these lead particles decreases with size. This decrease in T_c appears to be inconsistent with the observation of additional low-frequency modes if the latter tend to lower the McMillan[16] average $\langle \omega^2 \rangle$ and thus increase T_c.

It can be concluded that these observations of the enhancement of the low-temperature specific heat of small lead particles give evidence of the existence of additional low-frequency modes and that the behavior of the specific-heat enhancement at lower temperatures indicates the presence of the size effect.

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Effect of High Pressure on the Quadrupole Interaction in Cd Metal Measured by Perturbed Angular Correlations

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The quadrupole interaction of the 247-keV level of ^{111}Cd in Cd metal under pressures up to 75 kbar has been measured with the aid of time-differential perturbed angular correlations. The quadrupole interaction decreases by about 30% in this pressure range, the variation being nearly linear. We discuss the significance of these data to the understanding of the electric field gradient in Cd metal.

We report here the experimental determination of the pressure dependence of the quadrupole interaction (QI) in Cd metal using the method of time-differential perturbed angular correlations (TDPAC).[1] This measurement is important for several reasons: First, it demonstrates the feasibility of TDPAC to the study of hyperfine interactions in solids under high pressure, which has so far been done only with Mössbauer or NMR/NQR experiments. High-pressure studies could thus be extended to a wider range of materials and problems. Second, the pressure dependence directly brings out the correlation of the QI with the lattice parameters and thus provides valuable insight into the origin of the electric field gradient (EFG) in this metal. Third, the pressure data, in conjunction with the temperature dependence, allow one to isolate the explicit effect of the temperature arising from reasons other than the variation of the lattice parameters with the temperature. This separation is essential before one attempts a theoretical interpretation of the

observed anomalous temperature dependence of the QI in cadmium.[2]

The 247-keV level of [111]Cd was populated by the decay of [111]In (half-life 2.8 days) prepared by irradiating high-purity natural foils of Cd with 26-MeV protons. The targets were used after the irradiation without further treatment. The sources $(1 \times 0.5 \times 0.1$ mm$^3)$ were sandwiched between two foils of pure aluminum, which were used as a pressure transmitting medium. This source assembly was positioned inside a boron-epoxy ring which was then placed between the flat faces of two Bridgman anvils. The pressure calibration was based on the high-pressure phase transitions of Bi at 24.4(10), 27.8(10), and 74(2) kbar.[3] The pressure was monitored by measuring the resistivity of a Bi strip mounted along with the source in the high-pressure cell. The TDPAC experiments were carried out by observing the 173–247-keV cascade γ rays in coincidence at 180°. Details of the experimental setup will be described elsewhere.

Figure 1 shows typical time spectra which display the modulations in the coincidence counting rate due to the precession of the quadrupole mo-
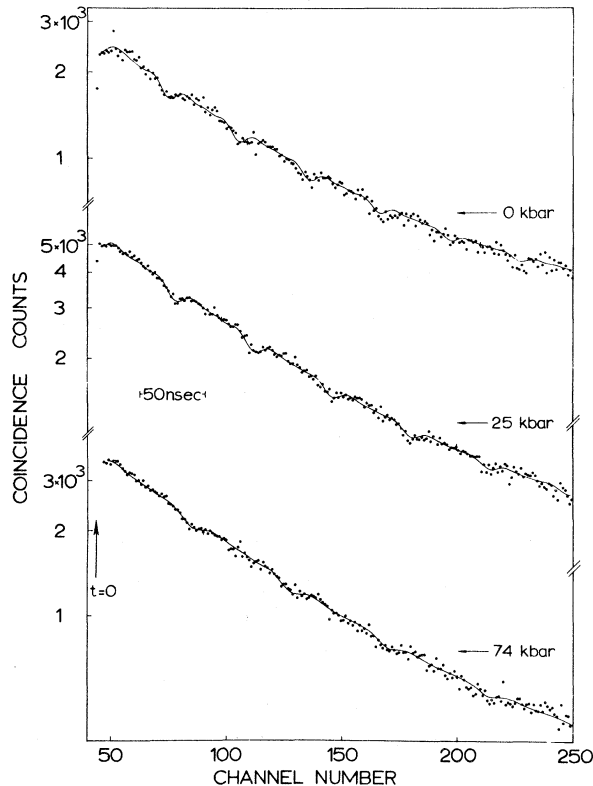
TABLE I. Quadrupole interaction frequencies of [111]Cd in Cd metal at different pressures, at 298°K.

Pressure (kbar)	ω (10^6 rad/sec)	$\nu = e^2qQ/h$ (MHz)
10^{-3}	117.8(8)	125.0(9)
24.4(10)	105.0(15)	111.4(16)
50(5)	94.7(15)	100.5(16)
74(2)	83.7(15)	88.8(16)

ment of the 247-keV level in the EFG of Cd metal. The solid lines through the points are least-squares fits by the usual TDPAC function[1] appropriate for a randomly oriented, axially symmetric QI for a nuclear level of spin $I = \frac{5}{2}$. The fits yield the basic modulation frequency $\omega = 3e^2qQ/2I(2I-1)\hbar$, where q is the EFG and Q the quadrupole moment of the level. Table I lists the values of ω at different pressures. The ratio q/q_0 of the EFG, obtained from the ω values, is plotted as a function of the pressure P in the curve A of Fig. 2 (q_0 at 298°K and $P = 1$ bar). The average pressure change in the QI is

$$(\partial \ln q/\partial P)_T = -4.30(30) \times 10^{-3}/\text{kbar}. \qquad (1)$$

The EFG in a metallic crystal has two major contributions: $q = q_{el} + q_{ion}$, where q_{el} comes from the conduction electrons, and q_{ion} is produced by the ionic cores of the lattice. While no theoreti-
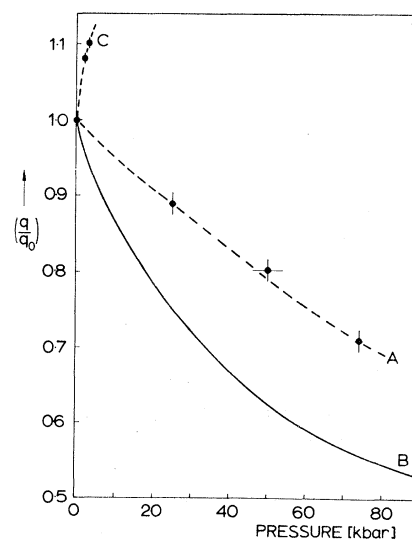

FIG. 1. TDPAC spectra of the QI of the 247-keV level of [111]Cd in Cd metal at different pressures.

FIG. 2. Pressure dependence of the EFG in Cd metal relative to room temperature and pressure. Curve A, experimental data; B, theory of Das and Pomerantz for the ionic part q_{ion} of the EFG; C, experimental temperature dependence relative to room temperature, plotted at equivalent pressures.

cal estimate exists for q_{el}, Das and Pomerantz[4] have calculated q_{ion} and have shown this to depend on the ratio c/a. This prediction is compared with our results in Fig. 2 where curve B represents the theoretical dependence of $q_{ion}/(q_{ion})_0$ on P. The recent data of Perez-Albuerne et al.[5] for c and a at different pressures have been used to obtain this curve. The clear discrepancy between theory and experiment (curve A), is not surprising since the observed EFG q contains a substantial contribution from q_{el}. We note that the ratio of the slopes of these two curves varies with the pressure. This indicates that q_{el} itself has a pressure dependence reflecting the changes in the electronic band structure produced by the compression.

It is interesting to contrast the pressure and

temperature dependences[2] of the QI in Cd. The two points in curve C of Fig. 2 represent the QI at 77 and 4.2°K relative to that at 298°K. They have been located at equivalent pressures at which Cd has the same ratio c/a as at these temperatures. It is clear that a reduction of the ratio c/a achieved by compression decreases the QI, while an equivalent reduction of c/a induced by cooling *increases* it. In order to understand this anomalous temperature behavior, one should separate out from the observed variation, the effects of thermal expansion so that one is left with only the explicit effect of the temperature on the QI. The pressure data are useful for this. Accordingly, we write the observed temperature and pressure dependences in terms of the variations of c and a:

$$\left(\frac{\partial \ln q}{\partial P}\right)_T = \left(\frac{\partial \ln q}{\partial \ln a}\right)_{cT}\left(\frac{\partial \ln a}{\partial P}\right)_T + \left(\frac{\partial \ln q}{\partial \ln c}\right)_{aT}\left(\frac{\partial \ln c}{\partial P}\right)_T, \tag{2}$$

$$\left(\frac{\partial \ln q}{\partial T}\right)_P = \left(\frac{\partial \ln q}{\partial \ln a}\right)_{cT}\left(\frac{\partial \ln a}{\partial T}\right)_P + \left(\frac{\partial \ln q}{\partial \ln a}\right)_{aT}\left(\frac{\partial \ln c}{\partial T}\right)_P + \left(\frac{\partial \ln q}{\partial T}\right)_{ac}. \tag{3}$$

In order to solve these equations one has to perform, in addition, a uniaxial stress experiment using a single crystal. In the case of Cd, however, a hydrostatic compression is practically equivalent to a uniaxial stress along the c axis due to the very large anisotropy of the compressibility of Cd at low pressures.[5] This simplifies the problem somewhat. From the data of Ref. 2, we have, at room temperature and pressure, the value

$$(\partial \ln q/\partial T)_P = -4.91(15)\times 10^{-4}/°\text{K}. \tag{4}$$

The linear expansivities[6] and compressibilities[5] at 298°K, together with (1) and (4), enable us to obtain

$$(\partial \ln q/\partial T)_{ac} = -5.9(6)\times 10^{-4}/°\text{K}, \tag{5}$$

$$(\partial \ln q/\partial \ln c)_{aT} = 1.87(30). \tag{6}$$

These values have been obtained by assuming a wide choice of the values of the third unknown variable, i.e., $-3 < (\partial \ln q/\partial \ln a)_{cT} < +3$. The large uncertainty in this value has nevertheless only a small effect on the accuracy of (5). The limits of this range are not likely to be much wider since one expects $(\partial \ln q/\partial \ln a)_{cT}$ to be of the same order as $(\partial \ln q/\partial \ln c)_{aT}$.

The explicit effect of the temperature on the QI given by (5) is independent of q_{ion}. Therefore, it

should be ascribed entirely to the EFG due to the conduction electrons, q_{el}. In attempting to understand this behavior of the conduction electrons, one is reminded of the strong temperature variation of the Knight shift in Cd which has been explained by the redistribution of the relative s and p character of the electronic wave functions by the electron-phonon interaction.[7] While the Knight shift is sensitive to the s character, the QI depends on the p admixture and it is possible that this interaction is responsible for the temperature effects of the QI also. The pressure and temperature data on the QI in Cd should now provide sufficient motivation for a detailed theoretical investigation.

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Rotational Levels of Shallow Acceptor States: The Undulation Spectra of N in GaP

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We report the first direct evidence of rotational levels of vibronic states in solids. These levels are associated with the ground states of shallow acceptors and provide the basis of a detailed understanding of the fine structure or "undulations" in emission spectra derived from bound excitons in GaP. This explanation is contrasted with one proposed recently by Hopfield, Kukimoto, and Dean.

We demonstrate in this Letter that rotational structure[1-3] in the vibronic states of shallow acceptors[4] explains the undulatory spectra[5] associated with the decay of bound excitons in GaP. Such rotational structure in solids has been predicted[1-4] but never identified.

The undulatory spectra shown in Fig. 1 have been obtained in photoluminescence from crystals of GaP which contain N and are codoped with various shallow acceptors: Figure 1(a), for a Zn-doped sample at low temperature, includes an absorption spectrum for comparison; and Fig. 1(b), for a C-doped crystal, shows the effects of a higher temperature. The N exciton in undoped GaP generates two sharp intense lines separated by ~ 0.8 meV.[6] The lower of these lines, N_2, at $E_2 = 2.3163$ eV comes from decay of the $J = 2$ state of the bound exciton and exhibits about 1% of the oscillator strength of the higher-lying line N_1, derived from $J = 1$.[6] [These states are shown on the right-hand side of Fig. 1(c).] At the lowest temperatures of measurement ($\sim 2°K$), the much greater population of the lower state causes N_2 to dominate. In crystals containing increasingly higher concentrations of neutral acceptors, the emission intensity of N_2 is *gradually transferred* into a broad undulatory band N_p which begins near N_2 and extends to lower energy. This is the band shown in Figs. 1(a) and 1(b).

Recently Hopfield, Kukimoto, and Dean, to explain the spectra N_p, suggested that the energy of the initial (exciton) state was significantly lowered by interaction with nearby acceptors and that interference effects accounted for the undula-

tions.[5] Such a model predicts that the absorption spectra will be similarly perturbed. A comparison of the emission and absorption spectra in Fig. 1(a) shows that this prediction is not borne out. The absorption shown in Fig. 1(a) is completely
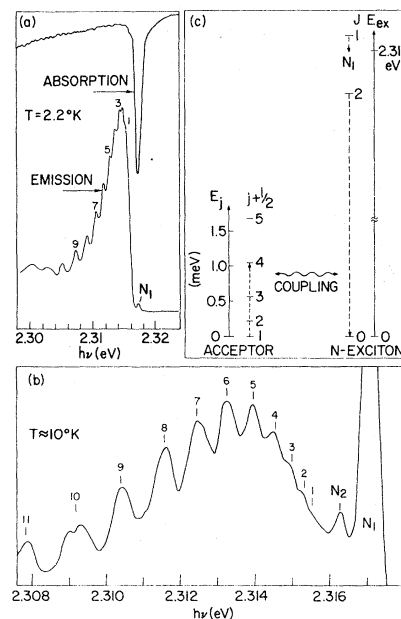

FIG. 1. Undulation spectra and energy levels for C- and Zn-doped GaP containing N. (a) Emission and transmission spectra taken at low temperature from a sample containing $\sim 10^{18}$ cm^{-3} Zn acceptors. The peaks are numbered according to $j + \frac{1}{2}$. (b) Emission at a higher temperature from a C-doped sample. (c) Coupled vibronic acceptor levels (left) and bound-exciton levels (right) which account for the spectra. The spacing of the vibronic levels is appropriate for C acceptors.