# Correlation effects of quantum rotors in Ge crystals

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**Abstract**

We address the accurate treatment of dipolar interaction effects between oxygen defects in Ge crystals on the low-temperature properties of bulk systems. On the basis of a quantum rotor model, we reveal that the interaction between adjacent oxygen defects generates nontrivial low-lying excitations that result in power-law specific heats below 0.1 K. In addition, a peculiar hump is observed for the dielectric susceptibilities at approximately 1 K. Further, we contend that the predicted power-law specific heats are well described by the two-level tunneling theory, which is based on the random distribution of interacting oxygen defects in Ge samples.

*Key words:* Interstitial oxygen defect, Germanium crystal, Quantum rotor, Two-level systems

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## 1 Introduction

Point defects often contribute to the low-temperature properties of covalent semiconductors because the presence of light impurities results in the appearance of local vibrational and rotational modes at several degrees Kelvin and below. In crystalline Ge, for instance, interstitial oxygen defects establish a puckered Ge-O-Ge segment that yields a rotational degree of freedom around the Ge-Ge axis (1). At sufficiently low temperatures, those interstitial oxygen atoms are quantum-mechanically delocalized in an annulus around the Ge-Ge axis. This character enables us to employ the quantum rotor model to describe the rotation of rigid $Ge_2O$ units (2; 3; 4).

One notable aspect is that the puckered Ge-O-Ge segment carries electric dipole moments due to the difference in electronegativity between Ge and O (5). In the dilute limit, the interaction between the dipole moments is negligible. However, for actual concentrations of oxygen $\rho \sim 10^{17} - 10^{18}$ cm$^{-3}$, the random distribution of oxygen impurities induces the formation of clusters of closely positioned dipole moments with a large coupling energy. If the coupling is so strong that it interferes with the nearly free rotation of individual $Ge_2O$ units, the quantum nature of the $Ge_2O$ units that are involved in the clusters will be completely different from that of the isolated $Ge_2O$ units (6). It is thus expected that ensembles of clustered $Ge_2O$ units play an important role in the low-temperature properties of Ge:O.

The present work is aimed at showing that the dipolar interaction between $Ge_2O$ units markedly affects the low-temperature properties of oxygen-doped germanium. It is established that the strong dipolar interaction between clus-

tered $Ge_2O$ units results in peculiar low-energy states that in turn give rise to a power-law temperature dependence of specific heat $C(T) \propto T^{0.5}$ below 0.1 K under our numerical conditions (7). Further, the dipolar transitions between the low-lying levels of the interacting $Ge_2O$ units engender a non-trivial maximum in the dielectric susceptibility $\chi(T)$ around 1 K. We also present an interpretation for the power-law specific heat, which is based on the picture of local double-well potentials randomly distributed in Ge:O samples (7).

## 2 Quantum rotor model

Figure 1 illustrates the atomic disposition of a puckered Ge-O-Ge segment together with the six Ge atoms next nearest to the interstitial oxygen. At sufficiently low temperatures, the oxygen atom is quantum-mechanically delocalized around the Ge-Ge axis. The delocalized oxygen is subjected to the repulsive force from the six next-nearest neighboring Ge atoms, thus experiencing an azimuthal potential with sixfold rotational symmetry (1). The two Ge atoms neighboring O are loosely bound around an external axis (2); thus, all three atoms (Ge and O) rotate in phase around the external axis. In addition, the difference in electronegativity between Ge and O is responsible for the occurrence of an electric dipole moment in the direction perpendicular to the Ge-Ge axis. The absolute value of the dipole moment $|\boldsymbol{p}|$ is taken to be 1 Debye [1].

The above-mentioned character allows us to map a rotating $Ge_2O$ unit onto

[1] Although the exact value of $|\boldsymbol{p}|$ might be obtained through a quantum-chemical calculation, such a revision does not change the conclusion of this study.

a quantum rotor consisting of the following Hamiltonian:

$$H = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\theta^2} + V_0 \cos(6\theta + \phi). \tag{1}$$

The first term accounts for the quantum rotation of $Ge_2O$ units having the moment of inertia $I$. The quantity $E_K = \hbar^2/(2I)$ determines the energy scale of the quantum rotation. The second term with a constant $\phi$ corresponds to a hindering potential stemming from the six surrounding Ge atoms. In the following, we set $E_K = 2.3$ K and $V_0 = 1.5E_K$, in agreement with the values deduced from spectroscopic measurements (1).

## 3 Paired and clustered rotors

When quantum rotors become sufficiently close to each other, the interaction between them should be taken into account. Let us consider two rotors with dipolar moments $\boldsymbol{p}_i$ and $\boldsymbol{p}_j$ separated by a distance vector $\boldsymbol{R}$. The dipolar interaction energy is

$$W_{ij} = \frac{1}{4\pi\varepsilon}\left\{\frac{\boldsymbol{p}_i \cdot \boldsymbol{p}_j}{R^3} - 3\frac{(\boldsymbol{p}_i \cdot \boldsymbol{R})(\boldsymbol{p}_j \cdot \boldsymbol{R})}{R^5}\right\}, \tag{2}$$

where $\varepsilon$ is the dielectric constant of Ge crystals. Discarding a numerical factor, the energy scale of the dipolar interaction potential (2) is characterized by the quantity $J = p^2/(4\pi\varepsilon R^3)$. For the case $E_K \gg J$, the rotors are nearly isolated so that the interaction potential (2) can be treated as a perturbation. When $E_K \leq J$, on the other hand, the quantum nature of coupled rotors is completely different from that of the isolated ones because of thier strong dipolar interaction.

Note that the thermal fluctuation suppresses the dipolar interaction between the rotors. We thus introduce the upper cut-off length $R_c$, which is defined by $J(R_c) \sim k_{\mathrm{B}}T$; within this cut-off length, the dipolar interaction energy is so large that the two rotors correlate via dipolar interaction. We also should note that the inhomogeneous distribution of rotors in a Ge:O sample leads to the formation of clusters consisting of two or more rotors. Figure 2 shows the number of n-sized clusters for a random distribution in a cubic system. Two different values are assumed for the upper cut-off length $R_c$; these cut-off lengths correspond to the thermal energy $k_{\mathrm{B}}T$ of the order of milli-Kelvin. In both cases, most rotors do not form clusters, and remain isolated ($n = 1$). This suggests, *at first glance*, that the presence of a small number of clustered rotors is considered to be negligible when considering the properties of Ge:O within milli-Kelvin range. However, we will see that ensembles of clustered rotors $n \geq 2$ markedly contribute to the low-temperature properties of Ge:O in spite of their being a minority. This is because clustered rotors yield peculiar low-energy excitations originating from the dipolar interaction between rotors that manifest themselves at 1 K and below (7).

## 4 Low-temperature specific heat

In order to evaluate the low-temperature specific heat of Ge:O, we consider the density of state $P(\varepsilon)$ regarding the lowest energy excitation $\varepsilon$ for strongly paired rotors. It has been shown that low-lying states of interacting quantum rotors are well described by the two-level tunneling theory (8; 9); this scenario is based on the fact that the dipolar interaction term $W_{ij}(\theta_i, \theta_j)$ given in Eq. (2) forms a double-well potential in the $\theta_i$-$\theta_j$ plane when the separation $R$

is sufficiently small. For such strongly paired rotors, the height of the tunneling barrier $U$ between two potential minima scales as $U \sim J \propto R^{-3}$. This leads the tunneling amplitude $\Delta_p$ that expresses the coupling between two localized wavefunctions to yield

$$\Delta_p = \gamma \exp\left(-aR^{-3/2}\right). \tag{3}$$

Let us consider the density of states $P(\varepsilon)$ of the lowest energy excitation $\varepsilon$. Assuming that the spatial distribution of rotors is random with no correlation, the density of states $P(\varepsilon)$ is

$$P(\varepsilon) = \int d\boldsymbol{R}\, \delta\left\{\varepsilon - \Delta_p(R)\right\} \propto \frac{1}{\varepsilon\left\{\log(\gamma/\varepsilon)\right\}^3}. \tag{4}$$

When the rotors are strongly coupled, the energy splitting $\varepsilon$ is much smaller than the parameter $\gamma$. Then, the function $P(\varepsilon)$ given in Eq. (4) obeys asymptotically the power law of $P(\varepsilon) \propto \varepsilon^{-\alpha}$, where the exponent $\alpha$ is of order unity or less. Consequently, the ensemble of the two-level tunneling systems contributes to the specific heat $C(T)$ of the bulk system as (8; 9)

$$C(T) \propto \int \frac{P(\varepsilon)}{k_B T^2} \mathrm{sech}^2\left(\frac{\varepsilon}{2k_B T}\right) d\varepsilon \propto T^{1-\alpha}. \tag{5}$$

This suggests that the specific heats for Ge:O should exhibit power-law behavior at sufficiently low temperatures, whereas the quantitative determination of $\alpha$ requires numerical simulations.

Figure 3 shows the numerical results of specific heat $C\,(T)$ for various concentrations of rotors $\rho$. The Debye specific heat $C\,(T) = aT^3$ with $a = 5.83 \times 10^{-2} \mu\mathrm{J\ g^{-1}K^{-4}}$ is also plotted. The value of $a$ is evaluated based on the experimental data obtained at the temperature range of 2.8 to 100 K. As ex-

pected, we find a power-law temperature dependence of the form $C(T) \propto T^{0.5}$ below the Schottky peak. The exponent 0.5 seems to be independent of the impurity concentration $\rho$, whereas the magnitude of $C(T)$ shifts downward with decreasing $\rho$. Furthermore, the magnitudes of $C(T)$ for temperatures $T < 0.1$ K are proportional to $\rho^2$, while those for $T > 0.1$ K (around the Schottky peak) show a trivial linear dependence on $\rho$. All these peculiarities in $C(T)$ are attributed quantitatively to the $\varepsilon$ dependence of the distribution function $P(\varepsilon)$, as demonstrated in detail in Ref. (7).

## 5 Dielectric susceptibility

We now focus on the dc dielectric susceptibility $\chi(T)$ for Ge:O samples. The contribution from an individual cluster is given by

$$\chi^{\mathrm{cls}}(T) = -\frac{2}{3\varepsilon Z} \sum_{\mu} \sum_{j,l \neq j} f_{jl} e^{-\frac{E_j}{k_{\mathrm{B}} T}}, \tag{6}$$

$$f_{jl} = \frac{|\langle E_j | P_\mu | E_l \rangle|^2}{E_j - E_l}, \tag{7}$$

where $Z$ is a partition function and the operator $P_\mu$ represents the $\mu$-component of the total dipole moment for the cluster. The dielectric susceptibility $\chi(T)$ for a whole Ge:O sample is obtained by summing up $\chi^{\mathrm{cls}}(T)$ of all clusters involved in the system.

For later use, we examine the difference in dielectric properties between an isolated rotor and paired rotors. Figure 4 displays the low-lying energy levels of (a) an isolated rotor and (b) single paired rotors (7). Vertical lines indicate the allowed dipolar transitions; dashed lines refer to the allowed transitions involving the ground state, and solid lines, to the remainder. For an isolated

rotor, only two dipolar transitions contribute to the dielectric susceptibility $\chi(T)$ below a few Kelvin. On the other hand, for single paired rotors, many eigenlevels lower than $4E_K$ contribute to the dielectric susceptibility, as shown in Fig. 4(b). Particularly important is the occurrence of the allowed transitions at around $E \sim E_K$ connecting nearly degenerate eigenlevels. The small energy differences $|E_j - E_l|$ of two nearly degenerate eigenstates $|E_j\rangle$ and $|E_l\rangle$ magnify the absolute value of the factor $f_{jl}$ appearing in Eq. (7), leading to an anomalous maximum in $\chi(T)$ at the temperature $T \sim E_K/k_B$.

Figure 5(a) shows the calculated results of the dielectric susceptibility for Ge:O at various oxygen concentrations. The solid lines show the total susceptibility $\chi(T)$, while the dashed ones show the contribution of the ensemble of isolated rotors. It should be noted that an increase in $\rho$ gradually enhances the maximum of $\chi(T)$ at approximately 1 K, which comes from an increase in the number of paired and clustered rotors in the Ge:O sample. To aid in illustration, Fig. 5(b) exhibits the differences $\Delta\chi(T)$ between the solid lines and the dashed lines displayed in Fig. 5(a). The magnitude of $\Delta\chi(T)$ depends almost squarely on the oxygen concentration $\rho$. This $\rho^2$ dependence of $\Delta\chi(T)$ can be explained by using the same scenario as that for the power-law specific heat, which indicates that the presence of paired and clustered rotors affects the dielectric properties of Ge:O at low temperatures.

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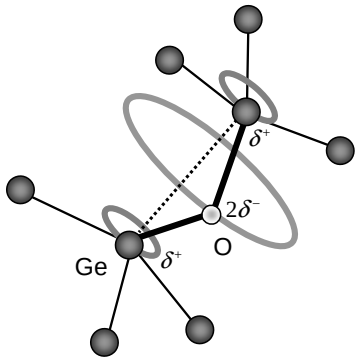


Fig. 1. Microscopic details of a rotating $Ge_2O$ unit. The whole $Ge_2O$ unit rotates in phase around an external axis. The difference in electronegativity between Ge ($\delta^+$) and O ($2\delta^-$) is responsible for the occurrence of an electric dipole moment.

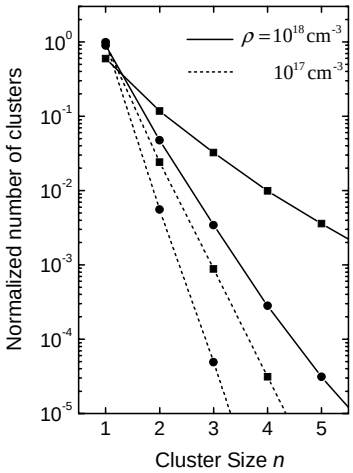


Fig. 2. The number of $n$-sized clusters in a cubic system. The concentrations of rotors are taken to be $\rho = 10^{17}\text{cm}^{-3}$ (dashed lines) and $10^{18}\text{cm}^{-3}$ (solid lines). Solid squares and circles correspond to the definition of the upper cut-off lengths $R_c = 30\text{Å}$ and $R_c = 20\text{Å}$, respectively.

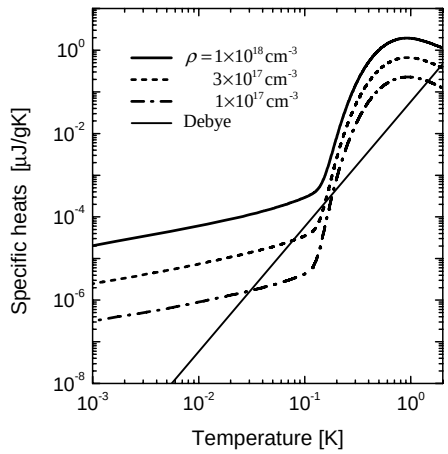


Fig. 3. Calculated results of specific heat $C(T)$ for Ge:O. The concentration of rotors $\rho$ is varied as shown in the figure. The dashed-dotted line follows the Debye specific heat for pure Ge crystals as deduced from Ref. (10).

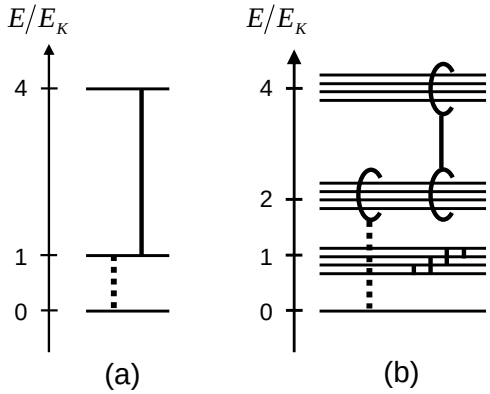


Fig. 4. Schematic illustration of allowed dipolar transitions: (a) an isolated rotor, and (b) single paired rotors. Vertical lines (solid and dashed) indicate the allowed dipolar transitions. In (b), rings bundling four eigenlevels indicate that the corresponding vertical line connects all of the four eigenlevels bundled.

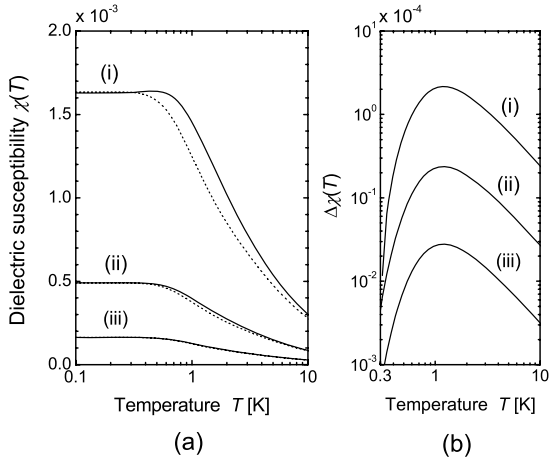


Fig. 5. (a) Semi-logarithmic plot of dc dielectric susceptibility $\chi(T)$ at various oxygen concentrations: (i) $\rho = 10^{18}$ cm$^{-3}$, (ii) $3 \times 10^{17}$ cm$^{-3}$, and (iii) $10^{17}$ cm$^{-3}$. Solid lines show the total susceptibility $\chi(T)$, and dashed lines show the contribution of the ensemble of isolated rotors. (b) Double-logarithmic plot of differences $\Delta\chi(T)$ between the solid lines and the dashed lines in (a).