State density and heat capacity of Jahn-Teller centers in random fields

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(Submitted 25 June 1983)
Pis'ma Zh. Eksp. Teor. Fiz. **38**, No. 3, 135–137 (10 August 1983)

The state density of tunneling Jahn-Teller centers in multicomponent random fields is derived. The density of single-particle excitations is constant over a broad energy range, so that the heat capacity is a linear function of the temperature.

PACS numbers: 71.70.Ej

1. The low-temperature properties of glassy systems (ordinary glasses, spin and dipole glasses, Jahn-Teller glasses, etc.), in particular, the linear temperature dependence of the heat capacity, have been explained under the assumption that the state density remains constant at low energies. Anderson *et al.* and Phillips[1] have linked these properties with the presence of two-level tunneling centers with random spreads in the energies and tunneling parameters. For disordered non-Ising systems, on the other hand, in which the random fields are multicomponent fields, it has been argued that the state density tends toward zero at low energies.[2]

In this letter we derive the state density for one particular system with a degenerate ground state: a system of Jahn-Teller centers in the random deformation fields of randomly distributed point defects. Systems of this type occur in a wide variety of compounds of transition metals and rare earth metals; the microscopic nature of the structural transitions, including transitions to the glassy phase, is accurately known for these compounds, and the properties of the low-temperature phase can be described on the basis of the exact Hamiltonian of the system, rather than some model. When Jahn-Teller centers interact strongly with lattice vibrations, there are several minima on the adiabatic potential corresponding to local distortions of the ligand neighborhood of the Jahn-Teller ion.[3] When tunneling is taken into account, the vibron ground state of the system is twofold or threefold degenerate, and there is yet another level at a distance Δ from it (Δ is the parameter of the tunneling splitting). Random deformation fields, whose dispersion can be much greater than Δ, lift the degeneracy and stabilize the vibron state in one of the minima on the adiabatic potential. In the space of random two- or three-dimensional deformations, however, there are hypersurfaces which preserve the degeneracy of the energy levels in two wells. If we ignore tunneling, we find that the state density is constant at low energies because of these and similar random-field configurations. At energies below the tunneling parameter the state density of course approaches zero, but over the wide energy range between Δ and the width of the random-field dispersion the state density remains constant.

2. Let us consider twofold- and threefold-degenerate Jahn-Teller centers with an octahedral coordination. In the space of functions corresponding to three tetragonal minima of the adiabatic potential, the Hamiltonian of the interaction with deformations is then[3]

$$H=\frac{\Delta}{3}\begin{pmatrix}1&1&1\\1&1&1\\1&1&1\end{pmatrix}+qV\left[e_{E\theta}\begin{pmatrix}-2&0&0\\0&1&0\\0&0&1\end{pmatrix}+\sqrt{3}e_{E\epsilon}\begin{pmatrix}0&0&0\\0&-1&0\\0&0&1\end{pmatrix}\right], \tag{1}$$

where V is the parameter of the interaction with E_g deformations $e_{E\theta}=e_{zz}-(e_{xx}+e_{yy})/2, e_{E\epsilon}=\sqrt{3}(e_{xx}-e_{yy})/2$, and q is the vibron reduction factor. The eigenvalues E_k (**e**) ($k=1, 2, 3$) of Hamiltonian (1) are

$$\left.\begin{aligned}&E_k(\mathbf{e})=2\left[(qVe)^2+(\Delta/3)^2\right]^{1/2}\cos\frac{\Psi+2\pi(k-1)}{3},\quad \cos\Psi=\frac{(\Delta/3)^3-(qVe)^3\cos 3\phi}{[(\Delta/3)^2+(qVe)^2]^{3/2}},\\&\mathbf{e}\equiv\mathbf{e}(e_{E\theta},\ e_{E\epsilon}),\quad e^2=|\mathbf{e}|^2=e_{E\theta}^2+e_{E\epsilon}^2,\quad \cos\phi=e_{E\theta}/e.\end{aligned}\right\} \tag{2}$$

The state density of the system of Jahn-Teller centers $g(E)$ can easily be related to the distribution function of the two-dimensional deformation fields, $f(\mathbf{e})$

$$g(E) = N \sum_{k \neq 0} \int d\mathbf{e} f(\mathbf{e})\, \delta[E_k(\mathbf{e}) - E_0(\mathbf{e}) - E],$$

$$f(\mathbf{e}) = N^{-1} \overline{\sum_s \delta[e_{E\theta} - e_{E\theta s}]\, \delta[e_{E\epsilon} - e_{E\epsilon s}]}, \tag{3}$$

where the subscript "s" specifies the particular Jahn-Teller center, N is the number of these centers, and $E_0(\mathbf{e})$ is the ground-state energy. At a low concentration (x_i) of point sources of the random field in the crystal, the function $f(\mathbf{e})$ has the approximately Lorentzian form[4] $f(\mathbf{e}) = (2\pi)^{-1}\Gamma_0(e_{E\theta}^2 + e_{E\epsilon}^2 + \Gamma_0^2)^{-3/2}$ with a distribution width $\Gamma_0 \sim x_i$ ($x_i \ll 1$).

If $\Delta = 0$, as in the case of an orbital triplet[3] interacting with E vibrations, for example, the state density is

$$g(E) = 3\pi^{-1} N\Gamma (E^2 + \Gamma^2)^{-1} [1 + E(4E^2 + \Gamma^2)^{-1/2}], \Gamma = 2\sqrt{3}\,|V|\,\Gamma_0. \tag{4}$$

The state density $g(E)$ thus remains nonzero at $E = 0$ and depends slightly on the energy at $E < \Gamma$. At values $E > \Gamma$ the state density falls off with increasing E in proportion to Γ/E^2, reflecting the behavior of the wings of the function $f(\mathbf{e})$ of the Lorentzian type.

We now consider the case $\Delta \neq 0$, assuming $\Gamma > \Delta$. At energies $E \ll \Delta$ the state density is determined by the centers at which the deformations are small ($e \sim E/|V| \ll \Gamma_0$), and $g(E) = 3NE\Gamma^{-2}$ tends toward zero in the limit $E \to 0$. An analogous result is found for $g(E)$ in the case of weak vibron coupling with $E < \Gamma$.

The state density then increases significantly as $E \to 2\Delta/3$, with $g(E) = 8 \times 3^{-5/2} NE\Delta^3 |E^2 - 4\Delta^2/g|^{-3/2}\Gamma^{-2}$, reaching at $E = 2\Delta/3$ the maximum of the energy dependence, $g(E = 2\Delta/3) = 3^{7/4}[\Gamma(1/4)]^{-2}\pi^{1/2}N(\Gamma\Delta)^{-1/2}$, with a characteristic width $\gamma \sim \Delta^2/\Gamma$. At energies $E > 2\Delta/3$, $g(E)$ exhibits a square-root decay, $g(E) = 3\pi^{-1}NE(E^2 - 4\Delta^2/9)^{-1/2}\Gamma^{-1}$, and a weak energy dependence at $\Delta < E < \Gamma$. Only centers with a static Jahn-Teller effect, with $|V|e \sim \Gamma \gg \Delta$, contribute to the state density in the important energy interval $2\Delta/3 < E < \Gamma$.

In the approximation of a two level system, which is valid for $g(E)$ over the entire energy range $E < \Gamma$, the low-temperature heat capacity of a system of Jahn-Teller centers in random fields is

$$C = \frac{1}{4} \int_0^\infty dE\, g(E) \left(\frac{E}{T}\right)^2 \mathrm{ch}^{-2} \frac{E}{2T}. \tag{5}$$

The heat capacity at $2\Delta/3 \lesssim T < \Gamma$ is a linear function of the temperature: $C = 3\pi^{-1}\zeta(2)NT\Gamma^{-1}$. At temperatures $T < 2\Delta/3$ the heat capacity is $C = 13.5\zeta(3)N(T/\Gamma)^2$: quadratic in T and inversely proportional to the square of the random-field dispersion.

3. We have found that the state density remains constant over a broad range of low energies, and the heat capacity is a linear function of the temperature, for orbitally degenerate centers interacting strongly with deformations. It would be interesting to see a test of this conclusion in crystals with randomly distributed Jahn-Teller centers. The predicted effect can occur both in dilute Jahn-Teller systems, where low-temperature long-range correlations of the glass type have been observed,[5] and in concentrated systems, where the strong random fields suppress the cooperative structural transition (see Ref. 6, for example).

Our results may explain the properties of certain types of glasses containing Jahn-Teller ions in a nearly symmetric ligand neighborhood. (The characteristic parameter of the interaction with deformations is $V \sim 1$ eV, while the tunneling parameter is $\Delta \sim 10^{-1}$–$1\ \mathrm{cm}^{-1}$, and the linear T dependence of the heat capacity continues down to extremely low temperatures.)

In glasses with tunneling centers of other types, e.g., centers having ruptured electron bonds, the energy levels may also be degenerate or nearly so for certain directions of the random field.

[1]P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 71 (1972); W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

[2]A. A. Abrikosov, Usp. Fiz. Nauk **97**, 403 (1969) [Sov. Phys. Usp. **12**, 168 (1969)].

[3]F. S. Ham, in: Electron Paramagnetic Resonance (S. Geschwind ed.), Plenum Press, New York. 1970.

[4]M. A. Ivanov and A. Ya. Fishman, Fiz. Tverd. Tela (Leningrad) **25**, 946 (1983) [Sov. Phys. Solid State **25**, 546 (1983)].

[5]M. V. Eremin, T. A. Ivanova, Yu. V. Yablokov, and R. M. Gumerov, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 226 (1983) [JETP Lett. **37**, 268 (1983)].

[6]G. A. Gehring, S. J. Swithenby, and M. R. Wells, Solid State Commun. **18**, 31 (1976).

Translated by Dave Parsons
Edited by S. J. Amoretty