

A Self-Consistent Statistical Description of Thermodynamic Properties of Solids: Premelting Effects

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We propose a new self-consistent statistical method for calculating the Gibbs-Bogolubov functional (GBF) for the free energy of anharmonic crystals with various potentials of interatomic interactions [1]. In the framework of the present method, the GBF of a crystal is a function of temperature and pressure, and depends on variational parameters which determine the thermal lattice expansion and the quasi-elastic bonds of atoms. The variational procedure of the determination of the equilibrium value of the GBF, allows one to calculate thermodynamic properties and equations of state of crystals at an arbitrary temperature and pressure [1, 2]. The computed thermodynamic properties of the heavy rare gas crystals [1–3] and some metals [4] agree well with the experimental data over a wide range of temperatures and pressures.

It is shown that the anharmonicity of atomic vibrations is responsible for a high-temperature instability of the phonon subsystem of the crystal [1]. This instability is associated with the attraction between phonons, which enhances with temperature. This attraction manifests itself in an anomalous growth in the phonon concentration with increasing temperature as the system approaches a critical temperature, resulting in the accumulation of an excess of the potential energy of the crystal in comparison with a quasi-harmonic solid [5, 6]. A number of thermodynamic properties of the crystal, such as the isobaric specific heat, the thermal expansion, and the Grüneisen parameter, show anomalous behavior in the temperature range where the instability of the phonon subsystem evolves. It is established [5, 6] that the structure defects (vacancies, dislocations, etc.) of the crystal are centers of the relaxation of the excessive potential energy, which favors a reduction of the energy required to create a defect. Such reduction of the defect formation energy is most pronounced in the vicinity of the instability temperature, so that a phase with a large number of structure defects (a liquid) becomes thermodynamically favorable. Thus, we may conclude that the premelting effects in solids are associated with the evolution of the instability of the phonon subsystem, while the melting transitions at rather small external pressures are directly related to the system's proximity to the instability point, i.e. they are attributed to the anharmonicity of the atomic motion.

- [1] A.I. Karasevskii and V.V. Lubashenko, *Phys. Rev. B* **66**, 054302 (2002).
- [2] A.I. Karasevskii and W.B. Holzapfel, *Phys. Rev. B* **67**, 224302 (2003).
- [3] A.I. Karasevskii and W.B. Holzapfel, *Low Temp. Phys.* **29**, 711 (2003).
- [4] A.I. Karasevskii and V.V. Lubashenko, *Phys. Stat. Sol. (b)*, 1274 (2004).
- [5] A.I. Karasevskii and V.V. Lubashenko, *Phys. Rev. B* **71**, 012103 (2005).
- [6] A.I. Karasevskii, W.B. Holzapfel, and V.V. Lubashenko, *J. Low Temp. Phys.* **139**, 609 (2005).