Harmonic and anharmonic phonons and associated thermal and electrical properties in thermoelectric clathrates

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論　文　内　容　要　旨

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学位論文の 題　　　目	Harmonic and anharmonic phonons and associated thermal and electrical properties in thermoelectric clathrates (熱電材料クラスレートにおける調和フォノンと非調和フォノンおよび関連する電子物性)		

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Abstract of Thesis

Research background and motivations

Thermoelectric energy conversion attracts a surge of interest, as it is considered to be a potential way to produce electric energy from waste heat as future technology. Thermoelectric efficiency is commonly evaluated by the figure of merit $ZT = (S^2\sigma/\kappa)T$, where S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity. Therefore, a perfect thermoelectric material should be a "phonon-glass electron-crystal" (PGEC) material as proposed by Slack *et al.*. Intermetallic type-I clathrates are regarded as such materials and have been widely studied.

Zintl phase type-I clathrates are featured by the cage framework mainly composed of Si, Ge, or Sn and alkali metal or alkaline-earth metal elements accommodated inside as guest atoms. Anharmonicity of phonons arising from the guest vibrations can suppress thermal conductivity, with exerting little influence on electron conductivity, both factors of which enable clathrates a PGEC material. However, researches so far mainly emphasized on the thermoelectric properties of a limited number of clathrates, and there are only few studies concerning a variety of clathrates to find a general rule of the rattling phonon modes for designing new thermoelectric materials.

The present thesis describes a systematic study on phonons in type-I clathrates. The guest vibration energies, indicated by boson peaks in heat capacity, are shown to be rationalized in terms of a single unified exponential line for a series of clathrates. The unified picture indicates the quasi-harmonic nature of the guest-atom vibrations. Strong anharmonicity in guest-atom vibrations, emerging from quantum tunneling, is also studied by heat capacity measurements. In addition, we show that high quality single crystals are favored for improving thermoelectric performance in the clathrate system by focusing on Cu, Ag and Au containing clathrates.

Main results and discussion

First, we consider the guest atom vibrations at intermediate temperatures (from 2 K to 70 K), where "boson peaks" can be observed for the low-energy phonon modes. We show that the excitation energies of all boson peaks can surprisingly be unified as one single exponential line using a new space parameter (R_{free}) associated with the freedom of motion of guest atoms. By combining experiment data, first principle calculations and a theoretical model based on van der Waals interactions, we point out that the guest-framework interactions are basically van der Waals type interactions, and Coulombic ionic and/or covalent interactions are not significantly important on the energy scale of the boson peaks. We also point out the importance of symmetry-broken for having off-centered guest vibrations. The study on boson peaks in type-I clathrates is helpful for understanding the origin of boson peaks in glass system and contributes to thermoelectric materials design from the viewpoint of rattling phonons.

Then, we consider the guest atom vibrations at extremely low temperatures (below 1K), where tunneling states can be observed for off-centered guest atoms as indicated by a temperature linear as well as time dependent heat capacity. We successfully separate the total linear-T dependent heat capacity contributed from tunneling states and conduction electrons, respectively. Based on the parameters, associated with tunneling states, we show that the phonon anharmonicity, generated by tunneling states, is quite useful for improving thermoelectric performance. We also show that although large free space is important for having off-centered guest atoms, the arrangement of the atoms/vacancies on the framework cages should also be equally considered.

In addition to the guest atom phonon modes, we also studied the electrical and thermal properties of the rattling-system by focusing on the noble metal (mainly Cu, Ag and Au) containing clathrates grown by Sn-flux. By comparing with previously reported data, we show that high mobility and large effective mass are favored for achieving high thermoelectric performance in clathrate-system, and high quality single crystals are very important. At the end of this dissertation, we mention an interesting but non-thermoelectricity related issue: the anomaly of diamagnetic susceptibility in type-I clathrates. Although the extra diamagnetism was once ascribed to the conceptual ring current (RC), it is shown to be less important in the clathrate-system. Possible suggestions, including the imbalance between the Langevin diamagnetism of valence electrons and the Van Vleck paramagnetism, are proposed.

Conclusion

We made a systematic study on guest-atom vibrations by focusing on their harmonic and anharmonic behaviors in type-I clathrates. We discussed the boson peaks appearing at around 15 K as well as the tunneling states below 1K in heat capacity measurements. Our systematic study on the phonons in clathrates provided a quantitative guideline for thermoelectric materials design from the viewpoint of the "PGEC" concept. We also showed the importance of single crystals for enhancing ZT values in clathrates.

論文審査の結果の要旨

非晶質ガラスなどで観測される非調和フォノンが内部空間を有する一連の単結晶物質においても観測される事が判明し、非調和フォノンと物性の関連に関し多くの研究が進められている。本研究では、内部空間を有するクラスレート物質で発現する非調和フォノンに関して、広いエネルギー領域での比熱測定、電子状態測定および第 1 原理計算など利用して物性との観点から議論するとともに、これらの物質で観測される非調和フォノンの発現機構に関して基礎的な理解を進めたものである。

本論文では、非調和フォノンと物性との関連を詳細に研究するため、多くの種類の良質な単結晶クラスレート物質をフラックス法により合成し、比熱、電気伝導度、熱伝導度、熱電変換係数ゼーベックなどの物性測定を行った。比熱データの解析において、10-30K(1-3meV)、および、1K(0.1meV)以下を中心に物性との関連性を議論した。その結果、10-30K で発現する非調和フォノンは、クラスレート物質全般で普遍的に観測される非調和フォノンであり、一つの指数関数で説明できる事を示した。この理由に関して、モースポテンシャルの観点から、ファンデアワールスを基本とする内部空間に作られる弱い束縛ポテンシャルが擬非調和ポテンシャルを形成する事で統一的に説明できる事を示した。また、イオン分極などの効果は、結晶の対称性を反映して重要なエネルギー項とはならない事を第一原理計算の観点から示した。一方、1K 以下で発現するフォノンの非調和性は、クラスレート物質の幾何対称性の低下と関係する多値ポテンシャルを有する非調和ポテンシャルと関係するフォノンの非調和性であり、トンネリングなどの無秩序ガラス状態に関するアンダーソン模型と関係した温度の線形比熱と関係した量子トンネリング現象や電気ダイポールの乱れとして理解できる事を示した。最後に、これらの非調和フォノンの基礎解釈を本物質系の非調和フォノンが関係する熱電変換物性との観点から、議論を行った。

本論文は、一連のクラスレート物質で観測される二つのエネルギー領域の非調和フォノンに関して統一的な基礎理解を与えるとともに、物質の構造とフォノンの非調和性および電子状態を熱電変換物性の観点から詳細に議論した研究である。この成果は、提出者が高度の学識と自立して研究する能力を有することを示している。よって、鄔 家臻（WU, Jiazhen）氏提出の博士論文は、博士（理学）の学位論文として合格と認める。