TEMPERATURE VARIATION OF THE GRÜNEISEN CONSTANT IN CRYSTALS

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Summary

Barron's theory predicts an abrupt variation in the Grüneisen constant of any crystal around a temperature of $0 \cdot 2 \, \theta_b$. Such a variation is experimentally observed in copper, aluminium, vanadium, diamond and lithium fluoride. Fluorspar does not exhibit a conclusive evidence of such a variation though it appears quite probable. Iron pyrites does not exhibit any abrupt variation in γ till $0 \cdot 17 \, \theta_b$. The curve of γ vs. T/θ_b becomes flatter and flatter as the temperature is decreased. Zinc blende exhibits the drop at a much higher temperature than that predicted by Barron.

1. Introduction

The Grüneisen constant of a solid, defined as $\gamma = \beta V / \chi C_v$, where $\beta =$ volume expansion coefficient of the solid, $V =$ its molar volume, $\chi =$ compressibility and $C_v =$ the molar specific heat at constant volume of the solid, plays an important role in the theory of thermal expansion. Gruneisen (1926) predicted that this ratio γ should be independent of temperature for a monoatomic crystal. This constant is connected with the volume dependence of the frequency of vibration in the solid in the following way: $\gamma = \dfrac{-\partial \ln \nu}{\partial \ln V}$. Grüneisen found that the constancy of γ appeared to be a valid approximation in the polyatomic crystals fluorspar and iron pyrites. Strictly speaking at higher temperatures the Grüneisen constant of a solid as defined above should increase gradually with temperature because of a correction factor in the denominator of the expression for β. But at temperatures, small compared to the Debye temperature of the solid, the correction factor is almost unity and γ should come out as independent of temperature.

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This conclusion of Grüneisen is valid for polyatomic crystals only when all the frequencies of the vibration spectrum show the same dependence on volume. Evidence from the temperature variation of the Raman spectrum of solids indicates that the Grüneisen constant is different for different frequencies. Also the individual Grüneisen constant for each frequency appears to exhibit a temperature dependence.

For a polyatomic crystal, Born (1922) has shown that the Grüneisen constant should exhibit a temperature variation. At very high temperatures, where all the frequencies of the vibration spectrum contribute equally to the specific heat, the Grüneisen constant γ should tend to a limit γ_∞. Similarly at very low temperatures, where only the acoustic branches of the vibration spectrum are effective, γ should tend to a low temperature limit γ_0. According to Born, even polyatomic crystals should rigorously obey Grüneisen's rule of proportionality between expansion and specific heat at very low temperatures.

Recent experiments of Bijl and Pullan (1954, 1955) and Rubin, Altman and Johnston (1954) on copper and aluminium down to liquid helium temperature indicate a sudden drop in the Grüneisen constant at about $0 \cdot 3 \; \theta_{\mathrm{D}}$, where θ_{D} is the equivalent Debye temperature to explain the specific heat at high temperatures.

Barron (1955) has attempted to work out a theory of the temperature variation of Grüneisen constant for a ' p ' atomic lattice on the basis of Born's lattice dynamics. His analysis is applicable to all crystal lattices. The important prediction made by Barron is that the Grüneisen constant for any crystal should show an abrupt variation at a temperature around $0 \cdot 2 \; \theta_{\mathrm{D}}^{(\mathrm{S})}$, where $\theta_{\mathrm{D}}^{(\mathrm{S})}$ is the equivalent Debye temperature to explain the entropy of the solid at high temperatures. Since we are only interested in the order of magnitude of the temperature at which the abrupt variation takes place, we can use θ_{D} in place of $\theta_{\mathrm{D}}^{(\mathrm{S})}$ as Bijl and Pullan have done. The nature and magnitude of the variation depends on the specific nature of the forces operative in the crystal lattice. This theory has received some confirmation in the experiments of Bijl and Pullan mentioned above. But these authors have pointed out that the contribution of the conduction electrons to the thermal expansion of a metal can give rise to a Grüneisen constant varying as $1/T^2$. At very low temperatures this disturbance due to conduction electrons cannot be neglected.

In view of this complication in metals, it appears profitable to turn to dielectric crystals for a verification of Barron's theory. There are some dielectric crystals like diamond, lithium fluoride and iron pyrites which have high Debye temperatures and so experiments up to liquid air or liquid hydrogen temperature are sufficient to cover the temperature range of interest to theory. Fortunately such experiments have been carried out long back so that data are available to make a comparison with theory.

2. RESULTS AND DISCUSSION

In Table I we have collected the Debye temperatures and the Grüneisen constants for various values of T/θ_D for six substances: namely, vanadium, diamond, lithium fluoride, fluorspar, iron pyrites and zinc sulphide. The substances are chosen to cover metallic, covalent and ionic lattices and monoatomic, diatomic and triatomic lattices.

TABLE I

The Grüneisen constants of vanadium, diamond, lithium fluoride, fluorspar, iron pyrites and zinc blende at different temperatures

Vanadium	..	T/θ_D	0·63	0·52	0·43	0·25	0·16	..	..	..	..	..
$\theta_D = 450°$ K.	..	γ	1·30	1·34	1·29	1·25	1·05	..	..	..	..	..
Diamond	..	T/θ_D	0·445	0·301	0·337	0·283	0·230	0·182	0·150	0·125	..	..
$\theta_D = 1860°$ K.	..	γ	1·29	1·32	1·30	1·31	1·27	1·20	1·10	1·03	..	..
Lithium fluoride	..	T/θ_D	0·45	0·38	0·32	0·28	0·15	0·12	..	..	..	..
$\theta_D = 610°$ K.	..	γ	1·62	1·59	1·57	1·56	1·48	1·29	..	..	..	..
Fluorspar	..	T/θ_D	1·04	0·96	0·87	0·79	0·70	0·62	0·44	0·36	0·26	0·20
$\theta_D = 474°$ K.	..	γ	1·91	1·86	1·84	1·82	1·80	1·75	1·71	1·69	1·65	1·60
Iron pyrites	..	T/θ_D	0·97	0·88	0·81	0·73	0·66	0·58	0·50	0·37	0·24	0·17
$\theta_D = 645°$ K.	..	γ	1·81	1·75	1·70	1·64	1·59	1·55	1·50	1·45	1·40	1·37
Zinc blende	..	T/θ_D	1·09	0·77	0·62	0·53	0·44	0·19	..	..	..	..
$\theta_D = 175°$ K.	..	γ	0·70	0·57	0·45	0·32	0·15	-0·36	..	..	..	..

The values of θ_D and γ for vanadium have been taken from Erfling (1942). The values of γ for diamond are derived from Krishnan (1946). For lithium fluoride, Blackman (1935) gives θ_D as $610°$ K. at high temperatures. The γ values are taken from the experiments of Adenstadt (1936) which covered a range of T/θ_D values from $0·45$ to $0·12$. The values of γ for fluorspar have been calculated from the measurement of Valentiner and Wallott (1915) and Press (1949). For iron pyrites the expansion data of Valentiner and Wallott (1915) and Sharma (1951) have been used. The expansion at low temperatures for this substance was checked by Srinivasan (1955) and found to be in good agreement with Valentiner and Wallott's values. The θ_D values for these two crystals have been taken from Grüneisen (1926). The γ values for zinc blende have been taken from Adenstadt (1936) and the θ_D value from Gunther (1916).

The variation of γ as a function of T/θ_D is plotted for all these substances in Fig. 1. In the inset the curves of Bijl and Pullan (1955) for copper and aluminium are reproduced.
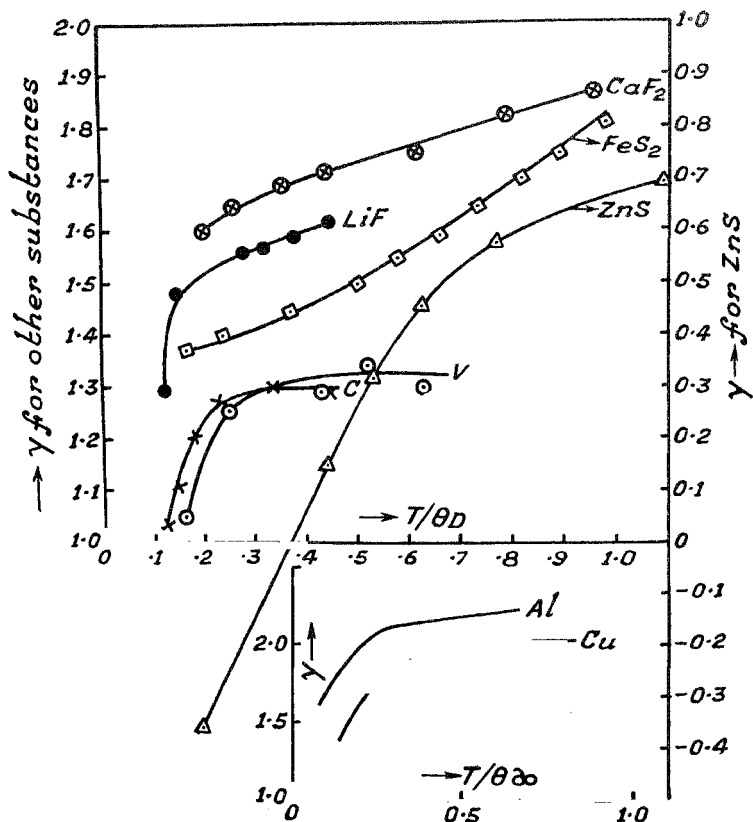
FIG. 1. Temperature Variation of the Grüneisen Constant in Crystals.

In vanadium the curve of γ vs. T/θ_D exhibits a sudden drop around $0.3\theta_D$. The behaviour of vanadium is exactly similar to that of copper and aluminium observed by Bijl and Pullan. While the change in the Grüneisen constant observed by Bijl and Pullan on copper and aluminium is large (around 0.5), in vanadium it is only about 0.25.

A study of the curve for diamond also indicates an unmistakable and sharp drop in γ around $0\cdot 28\ \theta_D$. The Grüneisen constant remains almost independent of temperature from $0\cdot 28\ \theta_D$ to $0\cdot 45\ \theta_D$. The change in the Grüneisen constant is of the same order as in vanadium.

Lithium fluoride is a diatomic crystal having the face centred cubic structure of rocksalt. Above $0\cdot 3\ \theta_D$ the Grüneisen constant increases with temperature unlike the case of diamond where it is a constant. The sharp drop in γ around $0\cdot 2\ \theta_D$ is very pronounced. The fall in γ is of the same order of magnitude as in the two preceding crystals. Fluorspar has three atoms per unit cell. Unfortunately for this substance the experiments have not been carried down to temperatures much below $0\cdot 2\ \theta_D$. The Grüneisen constant for this substance increases almost linearly with temperature beyond $0\cdot 35\ \theta_D$. An examination of the curve reveals a tendency for γ to drop off below $0\cdot 35\ \theta_D$. Yet experiments are needed up to liquid hydrogen temperatures to establish this drop.

When we come to iron pyrites we notice that the shape of γ *vs.* T/θ_D curve is entirely different from that for other substances. No abrupt variation in γ is observed around $0\cdot 2\ \theta_D$. On the contrary the curve becomes flatter and flatter as the temperature approaches $0\cdot 2\ \theta_D$. Barron's theory does not seem to hold for this crystal.

In zinc blende γ does show a sharp drop. But this drop occurs at $1\ \theta_D$ which is a temperature far removed from that predicted by Barron's theory. But it should be mentioned that this crystal exhibits a negative expansion coefficient below $-195°$ C. In fact it is not known why substances like zinc sulphide and α-silver iodide should exhibit a negative expansion and negative Grüneisen constant.

In conclusion we observe that from an examination of a few substances having high Debye temperatures, it is found that the theory developed by Barron accounts well for the qualitative nature of the temperature variation of the Grüneisen constant in such diverse substances as copper, aluminium, vanadium, diamond and lithium fluoride. The behaviour of fluorspar also appears to follow this theory though experiments up to liquid hydrogen temperatures are needed to verify it unambiguously. Iron pyrites does not exhibit the variation of γ predicted by Barron till $0\cdot 167\ \theta_D$. Crystals of zinc sulphide exhibit the drop in γ at a much higher temperature than that predicted by Barron.

In Barron's theory the Grüneisen constants γ_j of different frequencies of the vibration spectrum are assumed to be independent of temperature. As mentioned previously evidence from the temperature variation of Raman spectrum in crystals does point to a dependence of γ_j on temperatures.

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