Table I. Resonance frequencies and hyperfine fields at Ni^{61} nucleus at 77°K in pure nickel and for small concentrations of Ni^{61} in cobalt and iron using a moment 0.70 nm.

	ν (Mc/sec)	H_n (kilogauss)
Ni^{61} in nickel	28.3	80
Ni^{61} in cobalt	71.7	203
Ni^{61} in iron	89.1	252

cobalt[6] and iron[7] can be recalculated and are given in Table I, along with the resonance frequency, both at 77°K, which to within one percent is equal to the value at 0°K.

The hyperfine fields in Table I are seen to be readily understandable compared to those at Co^{59} and Fe^{57} nuclei in pure iron and pure cobalt and in the dilute alloys, if one uses the general idea that hyperfine fields are proportional to local moments. This idea has already been discussed in reference 7, where hyperfine fields (based on a moment 0.9 nm for nickel) are compared. The results are somewhat changed with the moment 0.70 nm, and this will be discussed at a later time. Also, the spin-echo method of observation permits the direct measurement of T_1 and T_2. Measurements of T_1 and T_2, together with the discussion of linewidths as a function of field, will also be discussed in greater detail at a later time.

The author wishes to thank Dr. L. H. Bennett for many helpful discussions concerning questions of hyperfine fields and the nuclear moment of nickel and for a critical reading of the manuscript. Also, the author is deeply indebted to Mr. D. E. Brown for help with various phases of the experimental work.

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THERMAL EXPANSION OF GERMANIUM[*]

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In many isotropic materials the thermal expansion coefficient is negative at low temperatures, e.g., vitreous silica[1] below 200°K, indium antimonide[1] below 55°K, silicon[1] below 120°K, germanium[1,2] below 40°K, and ice[3] below 60°K. These examples of an over-all lattice contraction are distinct from the metals plutonium, chromium, and Invar, where negative coefficients arise from magnetic interactions or from the electron gas, and are also distinct from highly anisotropic crystals such as cadmium or zinc in which the coefficient may be negative in one direction even though the volume coefficient, β, remains positive.

We define the average Grüneisen parameter by

$$\gamma = \beta V/\kappa_T C_V,$$

where C_V is the specific heat of volume V and κ_T is the isothermal compressibility. If C_i is the contribution of the ith mode to the specific heat, we may also write

$$\gamma = \sum \gamma_i C_i / \sum C_i,$$

where

$$\gamma_i = -d \ln \nu_i / d \ln V$$

is the logarithmic rate of change of lattice frequency with volume. Blackman[4] and Barron[5] have each discussed theoretical models for which γ_i is negative for certain transverse vibrational modes. If the relative contribution of such modes to the specific heat is sufficiently important at low temperatures, then the average γ or observed expansion coefficient may be negative.

Sheard[6] has shown how individual γ_i and the limiting averages at high and low temperatures, γ_∞ and γ_0, can be calculated from the pressure derivatives of the elastic constants. This procedure has given substantially correct results for

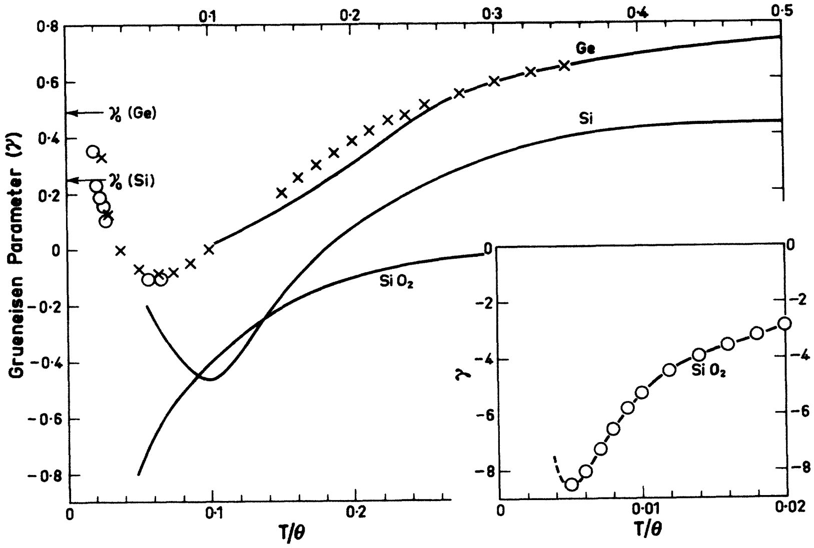

FIG. 1. Variation of the Grüneisen parameter γ with T/θ for germanium ($\theta \simeq 380$°K), silicon ($\theta \simeq 650$°K), and vitreous silica ($\theta \simeq 490$°K). Continuous curves are from data of Gibbons.[1] Points (circles, differential cell; crosses, absolute cell) are present work. Inset shows unpublished data for vitreous silica,[10] dashed curve for $T/\theta < 0.005$ being rather uncertain.

copper, silver, and alkali halides.[6,7] For germanium and silicon, Daniels[8] has calculated values of γ_0 from the pressure derivatives by a rather simpler procedure; this uses the relation

$$\gamma_0 = -d \ln\theta_0/d \ln V,$$

and de Launay's expression for the limiting value of the Debye temperature θ_0 as a function of the elastic constants. He obtained positive values of 0.49 (Ge) and 0.25 (Si) which indicate that the expansion coefficient must again become positive at sufficiently low temperatures (Fig. 1).

We have now measured the expansion, down to liquid helium temperatures, of a cylinder of germanium (5 cm long × 2 cm diam), kindly given by The Amalgamated Wireless Valve Company of Sydney, Australia, through Dr. L. W. Davies. This cylinder was cut from a *GE1K* crystal, *n* type of about 1 Ω-cm with cylinder axis parallel to the (111) direction. Some rather tentative results, obtained in a differential expansion cell (relative to copper) by the 3-terminal capacitance method,[9] were mentioned briefly at a recent conference.[10] These indicated a small (positive) expansion when warming up to 14°K, the total length change being about 3 ± 1 in 10^8; then from 14°K to the limit of measurement at 30°K, the cylinder contracted.

More precise measurements have now been made on the same cylinder in an "absolute" capacitance cell; in this radial expansions as small as 1 in 10^9 were detected. From 2 to 15°K an expansion of about 5 parts in 10^8 occurred; from 16 to 42°K the germanium contracted about 100 parts in 10^8; above 42°K it expanded again. Figure 1 shows our values for the parameter γ for germanium compared with those of Gibbons.[1] It seems clear that γ is positive below 15°K ($T/\theta \simeq 0.04$) and approaches the value predicted from the pressure derivatives of the elastic constants. Much more sensitive measurements (to 1 in 10^{10}) will be required to establish the detailed behavior below 7 or 8°K ($T < \theta/50$).

These changes in the sign of γ or β imply that $(dS/dV)_T = \beta/\kappa_T$ changes its sign from positive, to negative, to positive. As Klein and Mountain[11] have pointed out, the negative sign means that an increase in pressure must increase the entropy and hence the number of low-frequency modes. In germanium, neutron scattering evidence[12] indicates a low-lying transverse acoustic branch of the frequency spectrum having a maximum frequency at about $\frac{1}{5}$ the cutoff frequency for the whole lattice spectrum. This branch is presumably important in determining the low-temperature behavior of the lattice. Expansion is positive near the continuum limit, but becomes negative as an appreciable fraction of the modes in this branch becomes excited.

It appears likely that other diamond structure elements (Si, InSb) will behave in a similar fashion,[13] but we wonder whether this will be true for glasses; for vitreous silica the expansion coefficient remains negative to below 3°K ($T < \theta/100$),[10] and comparison of elastic and heat capacity data[14] suggests the existence of a low-lying transverse optical mode of frequency near 10^{11} sec^{-1}. Only at temperatures well below 3°K would this mode be frozen out, which may be a required condition for elastic and thermal data to agree and for the sign of the expansion coefficient to become positive. It is interesting to conjecture about possible physical models that may give rise to these changes in expansion coefficient.

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SODIUM IRON FLUORIDE, A TRANSPARENT FERRIMAGNET

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The purpose of this Letter is to report new optical and magnetic observations, including a new giant anisotropy in sodium iron fluoride, $Na_5Fe_3F_{14}$, the first example of a ferrimagnetic material which is highly transparent in the bulk. This is in distinction to magnetic oxides such as yttrium iron garnet and the ferrites, as well as to other ferromagnets, which are only partially transparent for very much shorter optical path lengths. The measurements include the magnetization, microwave resonance, optical absorption, and optical Faraday rotation.

Knox and Geller reported[1] the discovery of sodium iron fluoride in 1958 along with a detailed analysis of its crystal structure. They showed that there are at least two forms: a high-temperature tetragonal form belonging to space group $D_{4h}{}^6$-$P4_22_12$ and having a structure closely related to that of chiolite,[2] $Na_5Al_3F_{14}$; and a low-temperature, monoclinic, pseudotrigonal form belonging to one of the three space groups $C_{2h}{}^3$-$A2/m$, $C_2{}^3$-$C2$, or $C_s{}^3$-C_m. The monoclinic cell has a very long a axis, 73.23 Å, and is quite complicated in structure. It is probable that the low-temperature form is the stable one at room temperature[3] and that both forms are ferrimagnetic.[1]

Recently we have grown several small single crystals of sodium iron fluoride whose sizes preclude the carrying out of some desired experiments. Therefore, the data presented should be considered in some respects to be qualitative. The magnetization measurements were made using a polycrystalline sphere approximately 1 mm in diameter. The microwave measurements were made using an oriented, polished, single-crystal sphere of approximately 0.3-mm diameter. The optical measurements were made using a flat crystal with natural faces 1 mm across and 0.25 mm thick. The light beam was 0.3 mm in cross section and was in a direction of twofold crystal symmetry.