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Infrared spectroscopic study of phonons coupled to charge excitations in FeSi

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From an investigation of the optical conductivity of FeSi single crystals using Fourier-transform infrared spectroscopy in the frequency range from 30 to 20 000 cm^{-1} we conclude that the transverse effective charge of the Fe and Si ions is approximately $4e$. Of the five optical phonons that are allowed by symmetry we observe only four, three of which have a Fano line shape presumably resulting from an interaction of these modes with the electronic continuum. We show that the large oscillator strength of the phonons results from a relatively weak coupling ($\lambda \approx 0.1$) of the lattice degrees of freedom to an electronic resonance above the semiconductor gap, which is also responsible for the large electronic polarizability ($\epsilon_\infty \approx 200$) of the medium. [S0163-1829(97)50208-6]

FeSi is a fascinating material that has been studied for many years for its unusual magnetic and thermodynamical properties.¹ To explain the anomalies in the magnetic susceptibility,¹ thermodynamic,² and spectroscopic properties^{3,4} several models have been proposed involving strong electron-electron correlations.⁵⁻⁸

In this paper we present a detailed analysis of the sharp absorption lines observed in the far-infrared region. First we solve an open question^{3,9} concerning the nature of these peaks by showing that they can be interpreted as optical phonons. Secondly we demonstrate that the large phonon oscillator strength of these modes results from a coupling of the lattice dynamical degrees of freedom to an electronic resonance above the semiconductor gap.¹⁰ Due to the fact that the gap closes at high temperatures, the FeSi system provides a unique opportunity to study this kind of coupling in detail while the gap can be swept continuously through the phonon frequencies. Our results indicate that the semiconductor gap has a strongly covalent character.

We investigated the optical reflectivity of FeSi single crystals (approximately $2 \times 7 \text{ mm}^2$ and thickness 1 mm) grown by the floating-zone method. The measurements were performed in near normal incidence configuration over a frequency range going from 30 to 20 000 cm^{-1} , using Fourier-transform spectrometers. The samples were mounted inside a liquid-helium flow cryostat with temperatures ranging from 4 to 300 K. The reflectivities were calibrated against a gold mirror from low frequency to 15 000 cm^{-1} and an aluminum mirror for higher frequencies.

In Fig. 1 the reflectivity data (R), the real part of the dielectric function (ϵ_1), and the dynamical conductivity (σ_1) obtained by Kramers-Kronig transform are shown up to 10 000 cm^{-1} for five different temperatures. There is a strong temperature dependence in the data up to 6000 cm^{-1} . Using the f -sum rule we estimate that at room temperature the free-carrier contribution corresponds to a charge-carrier density of the order of 10^{21} – 10^{22} cm^{-3} with a lifetime of 5 fs or less, which is rather untypical for clean semiconductors. The free-carrier contribution drops rapidly

upon reducing the temperature. This results in a strong depletion of the optical conductivity at low frequencies and in the onset of absorption at 570 cm^{-1} (70 meV), which we identify as a semiconducting gap in the particle-hole continuum, thus confirming earlier reports on the infrared properties.^{3,9}

Below the gap we observe a number of prominent absorption lines which were previously attributed to phonons³ and partly to excitons.⁹ FeSi has a cubic structure $B20$ [space group $P2_13$, factor-group $T(23)$, and site group C_3], with four Si and four Fe atoms per unit cell. Using the correlation method¹¹ we found for the irreducible representation of the FeSi optical vibrations $\Gamma = 2A + 2E + 5T$. From the factor group analysis it is possible to conclude that all these nine modes are Raman active. Contrary to what was reported in an earlier investigation,⁹ where only three infrared-active phonons were anticipated, in principle (i.e., based on symmetry selection rules) each of the five triply degenerate T symmetry modes can be infrared-active. The A and E modes are infrared forbidden. Using Raman spectroscopy Nyhus *et al.*¹² identified five T modes at 193, 260, 311, 333, and 436 cm^{-1} , two E modes at 180 and 315 cm^{-1} , and one A mode at 219 cm^{-1} . In our far-infrared spectra (Fig. 1) four of these peaks are clearly visible with resonance frequencies for the 300-K data at 198, 318, 338, and 445 cm^{-1} , while the 260- cm^{-1} mode apparently has a very small optical oscillator strength and is absent in our spectra. So far the 338- cm^{-1} mode had escaped detection in infrared spectroscopy,^{3,9} possibly due to inhomogeneous broadening of the lines. There is no evidence in our data for an optical phonon at 140 (Ref. 9) or at 820 cm^{-1} .³ Hence we conclude that all four strong absorption lines can be identified as optical phonons, while the oscillator strength of the optical phonon expected at 260 cm^{-1} is very small or zero.

At low temperature the value $\epsilon_\infty \approx 200$ (i.e., the dielectric constant at frequencies just above the last phonon resonance) indicates a high electronic polarizability for FeSi, mainly due to virtual transitions in a band from 700 to 1500 cm^{-1} , which becomes progressively masked by the negative free-

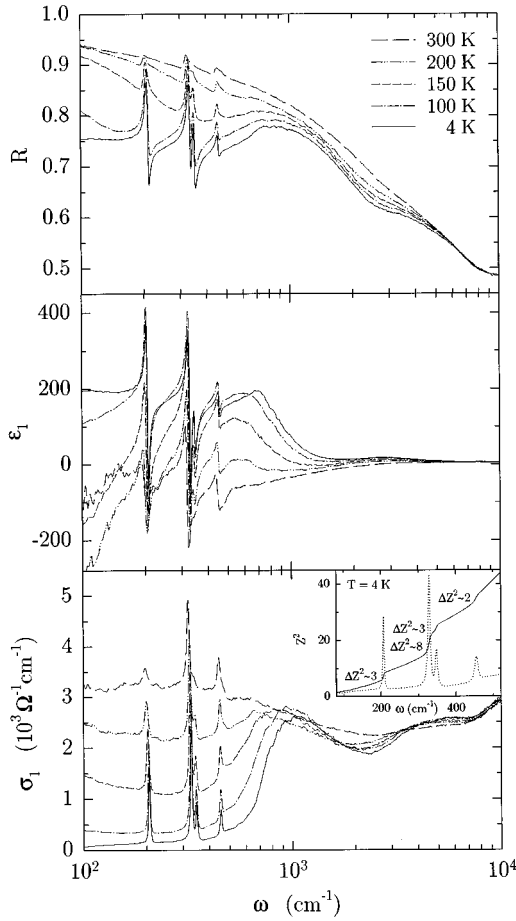


FIG. 1. Normal incidence reflectivity, real part of the dielectric function and optical conductivity of FeSi. In the inset we present an enlarged view of $\sigma_1(\omega)$ (dotted curve) and the function $Z^2(\omega) = 8\mu(4\pi n_i e^2)^{-1} \int_0^\omega \sigma(\omega') d\omega'$ for $T=4$ K.

carrier contribution upon increasing the temperature. We will discuss below that the optical phonons in the far-infrared region derive their optical oscillator strength from a coupling of the atomic coordinates to these charge degrees of freedom.

Previously the high intensity of these phonon lines has been indicated as evidence for a strong ionicity in this compound.³ The transverse effective charge e_T^* of the ions¹³ can be calculated directly by applying the f -sum rule to the vibrational component of $\sigma(\omega)$:

$$8 \int_0^\infty \sigma_1(\omega') d\omega' = 4\pi\mu^{-1} n_i e_T^{*2} = \sum_j S_j \omega_j^2, \quad (1)$$

where μ is the reduced mass of an Fe-Si pair, n_i is the number of Fe-Si pairs per unit volume (i.e., 4 per unit cell), S_j is the phonon strength, ω_j is the resonant frequency, and j is the index identifying the j th phonon. Throughout this paper we will use the dimensionless number $Z = e_T^*/e$ to indicate the total transverse effective charge summed over all phonons. In the inset of Fig. 1 we display for $T=4$ K the quantity $Z^2(\omega)$, obtained by integrating σ_1 in Eq. (1) up to a frequency ω . We observe, superimposed on a smooth remnant electronic background, four steps ΔZ^2 , one for each optical phonon. Adding up these steps we estimate for the total transverse effective charge at low temperature a value

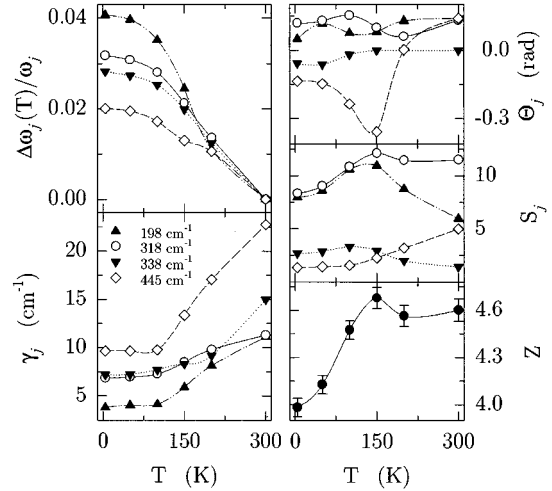


FIG. 2. Temperature dependence of the frequency shift [$\Delta\omega_j(T) = \omega_j(T) - \omega_j(300)$], decay rate (γ_j), Fano asymmetry parameter (Θ_j), and oscillator strength (S_j) of the four transverse optical phonons in FeSi. In the lowest section of the right-hand panel the transverse effective charge (Z) summed over all phonons is displayed.

$Z^2 \approx 16$. However, due to the fact that Fe and Si have practically the same electronegativity and electron affinity, strong ionicity is not expected from a chemical point of view, nor has it been inferred from *ab initio* calculations of the electron density distribution.^{6,14} This situation is reminiscent of the IV-VI narrow-gap semiconductors PbS, PbSe, PbTe, and SnTe, where Z values between 5 and 8 were found. For the latter systems this has been attributed to a resonance (or mesomeric) bonding effect.¹³ With this model the empirically found relation $Z^2 \sim (\epsilon_\infty - 1)$ was explained by the resonance aspect of the chemical bond^{13,15} in these compounds. Based on a similar concept a theory of infrared/optical spectra of coupled vibrational and charge transfer excitations was developed by Rice *et al.*¹⁰ in the context of dimerized organic linear-chain conductors.

The next step is the analysis of the phonon parameters for the different modes. Some of them exhibit an asymmetric line shape, probably deriving from an interaction between lattice vibrations and the electronic background. We were successful in fitting the phonon lines with a Fano profile. Fano theory¹⁶ describes the interaction of one or more discrete levels with a continuum of states resulting in asymmetric optical absorption peaks. After subtraction of the continuous electronic background the Fano profile is given by

$$\sigma(\omega) = i\sigma_0(q-i)^2(i+x)^{-1}, \quad (2)$$

where σ_0 is the background, $x = (\omega^2 - \omega_T^2)/\gamma\omega$ (γ and ω_T are the linewidth and the resonant frequency of the unperturbed vibrational state), and $q = -1/\tan(\Theta/2)$ is the dimensionless Fano parameter reflecting the degree of asymmetry of the peak (for $\Theta=0$ or, equivalently, $|q| \rightarrow \infty$ a Lorentz line shape is recovered). The following relation exists between the Fano parameters and the oscillator strength: $S = 4\pi\sigma_0(q^2 - 1)\gamma\omega_T^{-2}$. The Fano parameters obtained for all the peaks are summarized in Fig. 2, where we have plotted the phonon frequency shift $\Delta\omega(T)$, the linewidth γ , the

phonon strength S , and the asymmetry parameter Θ . We can see that $\Delta\omega(T)$ and γ show a very strong temperature dependence, in particular for $T > 100$ K. Clearly there is a strong decrease of the linewidth γ upon reducing the temperature. This dramatic loss of electronic relaxational channels, which comes with the opening of a gap in the electronic spectrum, suggests the presence of a coupling between electronic states and the lattice vibrations in FeSi.

The behavior of the parameter Θ is also very important in establishing if such a coupling exists and whether it reflects the temperature dependence of the gap itself. While the 338-cm^{-1} line shows a slight asymmetry only at low temperature and this mode is well described by a classical Lorentz oscillator ($|\Theta| \approx 0$) for $T > 100$ K, the situation is rather different for the other phonons. All of them are characterized by considerable asymmetry, especially the one at 445-cm^{-1} . Significant in this analysis is also the sign of the parameter Θ . For the lines at 198 and 318-cm^{-1} we found $\Theta > 0$ at all temperatures, indicating a predominant interaction between these modes and electronic states higher in energy. On the other hand the 445-cm^{-1} peak exhibits a negative value of Θ (interaction with electronic states lower in energy), with a maximal degree of asymmetry (maximum in $|\Theta|$) at $T = 150$ K. One has to notice (Fig. 1) that it is approximately at this temperature that the gap edge crosses the phonon resonance frequency of 445-cm^{-1} . Moreover, for $T > 150$ K the asymmetry of this mode changes sign, i.e., $\Theta > 0$. At $T = 300$ K, having the gap already closed, the value of Θ is the same for all three phonons characterized by a considerable asymmetry.

These differences in the behavior of Θ can possibly be related to the way the gap disappears (Fig. 1). Increasing the temperature the conductivity increases within the gap as a result of two different processes. First the ‘‘closing in’’ of the gap: the movement of the gap edge from high to low frequency. Secondly the ‘‘filling in’’ of the gap: the increase with temperature of the background conductivity within the gap. Probably the 445-cm^{-1} phonon, as it is the closest one to the gap edge, is more strongly influenced by the closing in than by the filling in. In fact, as we pointed out, the asymmetry of the mode at 445-cm^{-1} changes sign when the gap edge has moved below the resonant frequency. The other phonons, whose Θ does not show such a strong temperature dependence, seem to be influenced predominantly by the filling in of the gap, a process smoother than the movement of the gap edge.

By summing over the contributions of the four phonons, using the values for S_j and ω_j displayed in Fig. 2, the temperature dependence of e_T^*/e was calculated. The total transverse charge shown in Fig. 2 increases with rising temperature and saturates at a value of $Z \approx 4.6$ for $T > 150$ K.

This value for Z , which, as mentioned, cannot be due to a real ionicity of the system, can be explained if we assume a coupling between the vibrational degrees of freedom and electron-hole excitations across the gap of 70 meV . These charge excitations have a large contribution of $E+T$ character and a weak contribution of A character, as measured in Raman spectroscopy.¹² Because of the lack of inversion symmetry for this crystal structure there are no charge or vibrational excitations of pure even/odd character. Therefore a coupling is allowed between all five infrared-active T

modes and the charge excitations of T character. As group theory does not provide a qualitative argument why one infrared mode is missing in our experimental spectra, we are led to the quantitative conclusion that its oscillator strength is below our detection limit.

Within this approach it is possible, considering a linear coupling between lattice vibrations and electronic oscillators, to account for the strong oscillator strength observed for the infrared-active phonons. For a phonon coupled to an electronic resonance the optical conductivity is:¹⁷

$$\sigma_j(\omega) = \frac{-i\omega n_e \mu^{-1} e_{T,j}^{*2}}{(1-\lambda_j)\omega_j^2 - \omega(\omega + i\gamma_j)}. \quad (3)$$

Here $\lambda_j = g^2 m_e^{-1} \mu^{-1} \omega_j^{-2} \omega_{p,e}^{-2} \epsilon_e$ is a dimensionless electron-phonon coupling parameter and $\epsilon_e = \omega_{p,e}^2 [\omega_e^2 - \omega(\omega + i\gamma_e)]^{-1}$ is the contribution to the dielectric function due to an electronic oscillator coupled to the phonons. The indices e and j refer to the electronic oscillator and the j th phonon, respectively. The transverse effective charge in this model is

$$e_{T,j}^{*2} = \lambda_j \epsilon_e n_e^{-1} n_i (Z_i e)^2 \omega_j^2 \Omega_{\text{ph}}^{-2}. \quad (4)$$

The quantity $\Omega_{\text{ph}}^2 = 4\pi n_i \mu^{-1} Z_i^2 e^2$ is the square plasma frequency of the lattice, where Z_i is the formal valence of the ions. Using these experimental quantities of FeSi we obtain $\Omega_{\text{ph}}/(2\pi c Z_i) = 341\text{-cm}^{-1}$. From a detailed fit of our data to the generalization of Eq. (3) to several phonons coupled to the charge, which reproduces the intensities and the Fano line shapes of the four phonons, we obtained the coupling constants $\lambda_j = 0.063, 0.080, 0.096,$ and 0.036 for the four phonons at $198, 318, 338,$ and 445-cm^{-1} , respectively at 4 K. The Fano asymmetry parameter Θ in this model is $\Theta_j = 2 \text{Arg}[\epsilon_e(\omega_j)]$. To reproduce the positive and negative values of Θ for all phonons, we had to introduce in the model an electronic oscillator with a resonant frequency $\omega_e = 900\text{-cm}^{-1}$ as well as a Drude peak, both of them coupled to the phonons. If we insert these values of λ_j into Eq. (4), using the transverse effective charges of the inset of Fig. 1, we obtain $\epsilon_e \approx 80$ for the electronic resonance coupled to the phonons. This implies that about $1/3$ of the oscillator strength associated with the high electronic dielectric constant ($\epsilon_\infty \approx 200$) is coupled to the phonons. We conclude from this analysis that the high transverse effective charge results from a moderate coupling of the optical phonons to an electronic resonance with a large oscillator strength.

An important question concerns the relation of this resonance to the unusual magnetic properties in FeSi. Each Si atom is coordinated by six Si neighbors at a distance of 2.78 \AA , while the transition-metal atom has seven Si neighbors with distances varying from 2.27 to 2.52 \AA . As the same structure is formed for CrSi, MnSi, FeSi, CoSi, NiSi, RuSi, RhSi, ReSi, and OsSi it appears that the backbone of these compounds is formed by the Si and transition-metal outer shells. The localized $3d$ electrons on the transition-metal sites would have a magnetic moment [e.g., $S = 1$ for Fe (Ref. 15)]. These local moments can then be compensated by the conduction electrons of the backbone. The many-body ground state built from a superposition of such singlets centered at every Fe site then corresponds to a state that could be described as a Kondo insulator.⁵ Alternatively one can pos-

tulate that an even number of $3d$ electrons resides on every Fe atom in a singlet ground state,⁸ while thermal excitations to a high spin (e.g., triplet) state would be responsible for the Curie-like magnetic susceptibility at elevated temperatures. However, neither of these two scenarios results in a resonance hybrid¹⁵ of bonds between Fe and Si. Hence our experimental evidence for such resonant behavior may indicate that a different theoretical approach is required.

In conclusion we have investigated the optical conductivity of FeSi. We observed the opening of a gap of the order of 70 meV upon reducing the temperature below 100 K. On the basis of a group theoretical analysis all the sharp absorption peaks observed in the gap region have been assigned to particular lattice excitations. The position, oscillator strength, and asymmetry of the phonons were analyzed using the Fano

model. The large value of the transverse effective charge ($e_T^* \approx 4e$) along with the observed resonance behavior of the phonon parameters when the gap sweeps through the phonon-frequency provides strong evidence for a moderate coupling ($\lambda \approx 0.1$) between the vibrational degrees of freedom and low energy electron-hole excitations in this compound.

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