NH_4^+ ions in the vicinity of λ transition is 0.74 eu, which is substantially less than the R ln2 = 1.38 eu for NH_4Cl. The result suggests that the change from complete disorder to complete order is spread out over a much wider temperature range than for the chloride and is consistent with the present low-frequency Raman data.

In conclusion, we point out that despite its close association with the λ transition, the low-frequency mode at 56 cm^{-1} is not, however, the "soft mode" for the order-disorder transition in its usual sense. While the peak frequency of this mode is insensitive to temperature (see Fig. 1), the spectral width is broadened considerably as the temperature is lowered below T_λ, along with the drastic decrease in scattering intensity. The anomalous broadening and the quantitative correlation of the temperature-weighted Raman intensity with the specific-heat data suggests that the mechanism of decaying short-range order below T_λ is correct. This mechanism, which has been shown to be responsible for both the specific-heat anomaly and the Raman scattering below T_λ, is likely also responsible for the correlated critical oscillations of NH_4^+ ions recently observed in the proton spin-lattice relaxation near the λ transition in NH_4Br.[10]

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Born-Oppenheimer Principle in Reverse: Electrons, Photons, and Plasmons in Solids—Singularities in Their Spectra*

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A novel application of the Born-Oppenheimer approximation is made which predicts the strength and nature of the singular threshold structure associated with plasmon satellites for a wide class of experiments involving the interactions of photons or fast electrons with solids.

I consider here the theory of plasmon singularities in a wide class of experiments in which a core electron is excited up into the continuum of unoccupied states. This excitation could be produced either by absorption of a photon or by a collision with a fast electron. It is measured either by detecting a change in the initial-state particle as in soft-x-ray absorption or high-energy-electron energy loss, or by detecting a final-state product as in x-ray photoemission, soft-x-ray emission, or appearance-potential spectroscopy.[1] Typically the spectra from such experiments have plasmon satellites and possibly threshold singularities.[2]

In experiments such as x-ray emission and absorption, the plasmon satellites tend to be much weaker than one might expect after estimating the coupling constant. There is, however, a strong cancelation[3] in second-order perturbation theory. In general, though, one knows that

second-order perturbation theory cannot be valid because it predicts neither the large number of weak satellites sometimes observed in insulators[4] nor the correct power-law form for the threshold singularities in metals,[2] which, as we will see, occur on the satellites as well. In contrast, in other types of experiments such as appearance-potential spectroscopy,[1] the plasmon singularities are large and dramatic,[5] and seem to follow rather closely my exact solution[6] to the core-hole model.

The point of view taken here is that the reason one can experimentally observe plasmon satellites at all on top of a structure broadened by the other effects of the electron-electron interaction is that at least for a limited region of phase space they are reasonably sharp, well-defined excitations. When the important interband transitions have much lower energies than the plasma energy, then the situation is like an electron gas and plasmons are long-lived at $q=0$, but their decay rate increases rapidly[7] with increasing q. In general, the situation is more complicated and each case must be treated separately. It is clear, however, that the region of q space where a plasmon is well defined (if any) must be such that energy and momentum cannot be conserved in a first-order direct process in which the plasmon decays into an electron-hole pair. Said another way, the electronic recoil energy must be smaller than the plasmon energy, and in fact it must be much smaller, or else the second-order matrix elements can be large. We assume for the examples given here that the region satisfying this criterion is centered at $q=0$ as in the electron gas.

The first stage of the approximation is then to treat the plasmon as a good excitation of the system. Plasmons which have significant decay rates will not be referred to as plasmons since they cannot produce sharp singularities in the spectrum. Therefore our Hamiltonian, and indeed much of our algebra,[8] will resemble that of Bohm and Pines although our philosophy will be quite different. Sharp plasmons cannot produce a substantial electronic recoil as discussed above but must be treated to all orders in perturbation theory.

The Born-Oppenheimer principle provides a time-honored and very accurate way to handle a similar problem in molecular spectra. Here the boson-like oscillator coordinates of the vibrational states are the "slow" variables because their recoil kinetic energy when the electronic state ("fast" variable) changes is negligible. The principle says that, to a very good approximation, one can solve the problem by holding the "slow" variables fixed, solving for the energy eigenvalues of the "fast" variables, and then using these eigenvalues as effective Hamiltonians for the "slow" variables—one for each state of the "fast" variables.

Here we use the Born-Oppenheimer principle in reverse. The boson-like oscillator coordinates of the plasmons are the "fast" variables, and the electrons are the "slow" variables. It is a good approximation for threshold singularities, because the electronic recoil must be a small fraction of the plasma energy, or else the plasmon would not be sharp and would not contribute to the singularity.

As an example let me consider a simple model of x-ray absorption and take the Hamiltonian to be

$$H=cc^{\dagger}[\epsilon_0-\textstyle\sum_q(4\pi e^2/q^2)\rho_q^{\dagger}-\sum_q V_q(a_q+a_{-q}^{\dagger})]+\sum_q\omega_q a_q^{\dagger}a_q+\sum_k(k^2/2m^*)c_k^{\dagger}c_k$$
$$+\textstyle\sum_q V_q\rho_q^{\dagger}(a_q+a_{-q}^{\dagger})+\sum_q(2\pi e^2/q^2)\rho_q^{\dagger}\rho_q. \qquad (1)$$

The operator c creates a deep core hole of energy ϵ_0, $c_k^{\dagger}$ creates a conduction electron of energy $k^2/2m^*$, and $a_q^{\dagger}$ creates a plasmon of energy ω_q; $\rho_q^{\dagger}$ is the density fluctuation operator for the conduction electrons: $\rho_q^{\dagger}=\sum_k c_{k+q}^{\dagger}c_k$. Note that we have assumed a unit form factor for the deep state so that its interaction V_q with the plasmons is the same as that of the conduction electrons. For simplicity we assume a simple dielectric function $\epsilon(q,\omega)=1-\omega_p^2/(\omega^2-\Delta_q^2)$ for small q. This corresponds to a plasmon energy given by $\omega_q^2=\omega_p^2+\Delta_q^2$, and $V_q=4\pi e^2\omega_p^2/2\omega_q q^2$. For an insulator, Δ is of the order of a typical interband transition and goes to a constant as $q\to 0$, while for a simple free-electron metal, $\Delta_q\to sq$ as $q\to 0$. The case of a metal is slightly more complicated because the plasmons themselves are composed at least partially of conduction-band particle-hole excitations; and if the Hamiltonian (1) were taken literally, we would be double counting. Thus one must be careful not to count the terms which renormalize the plasmon through its interaction with the Fermi sea, because we take the plasmon to be given *a priori;* alternatively one could use the Bohm-Pines[8] procedure.

The absorption coefficient for x rays of frequency ν is proportional to

$$\langle\psi_0|T\delta(\nu-H+E_0)T^\dagger|\psi_0\rangle=\sum_f|\langle\psi_f|T^\dagger|\psi_0\rangle|^2\delta(\nu-E_f+E_0), \tag{2}$$

where $|\psi_0\rangle$ and E_0 are the ground-state wave function and energy of the system containing no deep holes, no real plasmons, and the conduction electrons in their ground state (or no conduction electrons in the insulator case). The operator T is the transition operator given by $T^\dagger=(\sum_k f_k c_k^\dagger)c$, where f_k is the oscillator strength for the transition. What we do is to use the Born-Oppenheimer principle to calculate $|\psi_f\rangle$ and E_f. However, if the electron operators are held fixed, then (1) is easily diagonalized in the plasmon coordinates by the unitary transformation

$$U=\exp[\textstyle\sum_q(-V_q/\omega_q)(\rho_q-cc^\dagger)(a_{-q}-a_q^\dagger)]. \tag{3}$$

The transformed Hamiltonian $\tilde{H}_0$ is

$$\tilde{H}_0=\textstyle\sum_k(k^2/2m^*)c_k^\dagger c_k+\sum_q[2\pi e^2/q^2\epsilon(q,0)]\rho_q^\dagger\rho_q+\sum_q\omega_q a_q+a_q+\{\tilde{\epsilon}_0-\sum_q[4\pi e^2/q^2\epsilon(q,0)]\rho_q^\dagger\}cc^\dagger, \tag{4}$$

where we have noted that $V_q^2/\omega_q=[1-1/\epsilon(q,0)]2\pi e^2/q^2$.

Thus the Born-Oppenheimer Hamiltonian for the electronic states involves a screened Coulomb potential $\sum_q[4\pi e^2/q^2\epsilon(q,0)]e^{i\vec{q}\cdot\vec{r}}$ which is turned on at the time the x ray is absorbed and off again when it is re-emitted. For an insulator, the suddenness of the switching is irrelevant, and one has the ordinary excitonic solution. For a metal the solution is also known,[2] and we merely incorporate the results here; we assume that the second term in (4) can be neglected. One may also calculate the difference between (4) and the exact transformed Hamiltonian $U\tilde{H}U^\dagger$, which is

$$\tilde{H}_1=\sum_{qk}(V_q/\omega_q)c_{k+q}^\dagger c_k(\vec{q}\cdot\vec{k}/m^*)(a_q-a_{-q}^\dagger)$$
$$+\sum_{kqq'}(V_q/\omega_q)(V_{q'}/\omega_{q'})c_{k+q+q'}^\dagger c_k(\vec{q}\cdot\vec{q}'/2m^*)(a_{q'}-a_{-q'}^\dagger)(a_q-a_{-q}^\dagger). \tag{5}$$

In a metal one must be very careful not to count terms in (5) that renormalize the plasmon. Since $\sum(V_q/\omega_q)^2$ is the coupling constant for the problem, which is typically of the order of unity or less, and since the energy denominators in a perturbation expansion in powers of $\tilde{H}_1$ are of the order of ω_q, the deviations from (4) are clearly of the order of the electronic recoil energy divided by the plasma energy—a small quantity because q_{max} is small.

One must also calculate the transformed transition operator

$$\tilde{T}^\dagger=\textstyle\sum_k\int d^3r f(r)\exp[\sum_q(V_q/\omega_q)(e^{i\vec{q}\cdot\vec{r}}-1)(a_q-a_{-q}^\dagger)]e^{i\vec{k}\cdot\vec{r}}c_k^\dagger c, \tag{6}$$

where $f(r)$ is the Fourier transform of the oscillator strength f_k. We note that $f(r)$ nearly vanishes unless r is less than the radius of the inner core state, so that $\vec{q}_{max}\cdot\vec{r}_{max}\ll 1$, and so to an extremely good approximation $\tilde{T}^\dagger\simeq T^\dagger$ and is independent of the plasmon coordinates. Thus in the Born-Oppenheimer approximation there are no satellites at all[8] in x-ray absorption (or emission). These are produced by treating (5) as a perturbation. For insulators one notes that unless the coupling constant is small, the two-plasmon term is just as important (that is, the same order in the electronic recoil divided by the plasma energy) as the one-plasmon term. Furthermore, the number of terms increases rapidly with the order of the perturbation theory because of the many different combinations produced by the two terms, so that the "convergence" is probably rather slow. This may explain why Brown's group[4] sees a long series of *weak* plasmon satellites. In a metal, however, the Fermi surface keeps the value of k large, so that unless the coupling constant is very large, the first term (one-plasmon term) of (5) will be much more important than the two-plasmon term. Thus the first plasmon satellite, although small itself, will be much larger than the second plasmon satellite. The calculation of the strength of, say, the first satellite in a metal is a straightforward application of perturbation theory in the first terms of $\tilde{H}_1$ of the same form encountered in the electron-phonon interaction, except that now the "bare" conduction Green's function is to be calculated in the presence of the transient shielded potential as in Ref. 2, and the final result is to be convoluted with the modified deep-hole Green's function again as in Ref. 2. Thus the Anderson orthogonality block affects all satellites equally. The divergence due to the transient electron-hole coupling[2] also occurs in the satellites, but the angular factors in $\tilde{H}_1$ cause

the exponents from a different combination of partial waves to survive. Detailed calculations like those of Ausman and Glick[9] will be necessary for each case. It would be quite possible, however, for the satellite to have a net positive exponent (divergence) while the main threshold does not. The place to look for this would probably be in emission spectra.

Let me now discuss an experiment in which the plasmon satellites are *strong*. Appearance-potential spectroscopy[1] provides such an example. Here one bombards the solid with electrons and plots the total soft-x-ray yield against the energy of these electrons. One in effect is measuring then the probability that one of these electrons excites a core hole and another conduction electron. This probability is proportional to an expression of the form (2), except now the transition operator T is

$$T^\dagger = \sum_{kk'} M_{kk'}(K) c_k^\dagger c_{k'}^\dagger c, \tag{7}$$

where $M_{kk'}(K)$ is the matrix element for an initial election of momentum K to scatter off the deep state into momentum state k while in the process producing another conduction electron of momentum k' and a deep hole. The point to note is that the initial fast electron interacts only weakly with plasmons, so that vertex corrections involving this electron can be neglected. However, the interaction is repeated, so that one does have to convolute the results (2) and (7) with the admittance function for the fast electron, which near plasmon thresholds can be shown to be of the form

$$\int dt\, e^{i\omega t}(1-\alpha e^{-i\omega_p t})^{-1}, \tag{8}$$

where α is the probability that in a collision the fast electron emits a sharp plasmon (as opposed to a broadened plasmon or an electron-hole pair). This is an annoyance, because (8) also produces plasmon satellites. Possibly the anisotropy of the plasmon coupling and propagation in graphite[10] can be used to separate these effects in a Houston and Park[5] type of experiment.

To evaluate (2), we need the transformed transition operator (7):

$$\tilde{T}^\dagger = \sum_{kk'} \int\int d^3r\, d^3r'\, M(r,r') \left[\exp\sum_q (V_q/\omega_q)\{e^{i\vec{q}\cdot\vec{r}} + e^{i\vec{q}\cdot\vec{r}'} - 1\}(a_q - a_{-q}^\dagger)\right] \exp[i(\vec{k}\cdot\vec{r} + \vec{k}'\cdot\vec{r}')]\, c_k^\dagger c_{k'}^\dagger c$$
$$\simeq \left[\exp\textstyle\sum_q (V_q/\omega_q)(a_q - a_{-q}^\dagger)\right] T^\dagger. \tag{9}$$

The last equality follows because $r \sim k^{-1} \ll q^{-1}$ and $r' \sim r_{\text{core}} \ll q^{-1}$, so that one may, to a very good approximation, replace the curly brackets in the exponent of (9) by unity. Thus there are strong plasmon satellites without going to deviations from the Born-Oppenheimer approximation, and one can neglect $\tilde{H}_1$. Using (4) and (9) in (2), we see that the plasmon and electronic parts of the problem are separable. In a metal this means that each plasmon satellite has the same power-law singularity as the main threshold. The nature of this singularity is rather interesting, and different from Ref. 2 in that now one has two electrons in the transient potential, so there is greater likelihood of a positive exponent (divergence). The plasmon part of the problem is the same as the model core-hole problem I solved exactly earlier.[6] Therefore the strengths of the plasmon satellite edges follow a Poisson distribution, with the nth satellite proportional to $e^{-a}a^n/n!$, with $a = \sum_q (V_q/\omega_q)^2$.

After inspecting (6) and (9) it is clear how these results can be generalized to other types of experiment; if the number of "slow" electrons is conserved in the transition, then the plasmon singularities in the spectrum will be very weak, and for metals, the exponent of each satellite will be different from that of the main threshold; if the number of "slow" electrons is not conserved, then the satellite singularities will be strong, will follow a Poisson distribution, and for a metal will all have the same exponent as the main threshold. For the purposes of the above, a core electron, as well as conduction electrons with energies near threshold, is to be regarded as "slow."

A more complete experimental verification of these ideas would involve doing appearance-potential spectroscopy on one of the several materials for which x-ray absorption data is available and vice versa. X-ray photoemission (a strong satellite experiment) should be done on simple materials.

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Contribution of the Anomalous Term to the Nonlinear Electrical Conductivity of Superconducting Aluminum Films

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Experimental data on the nonlinear excess conductivity of Al films due to the fluctuation of the order parameter have been analyzed by taking account of the Aslamazov-Larkin term and the anomalous term proposed by Maki and Thompson. The analysis shows clearly the existence of a large contribution from the Maki-Thompson term to the nonlinear excess conductivity.

The anomalous term arising from the renormalization of the current vertex due to the fluctuation of the order parameter, which was proposed by Maki[1] and Thompson[2] (MT) and first observed by Crow *et al.*,[3] is regarded to be of major importance in the study of linear and nonlinear excess conductivity in superconducting systems.[4] In particular, quantitative analysis is required at present for the contribution of the MT term to the nonlinear excess conductivity.

Since Smith, Serin, and Abrahams[5] found a nonlinear excess current in Pb films above T_c, the nonlinearity has been studied theoretically[6-9] and experimentally.[10-13] Schmid[7] has given the expression of the nonlinear field dependence of the Aslamazov and Larkin (AL)[14] term for a thin film of thickness d based on the time-dependent Ginzburg-Landau (GL) equation with random force:

$$\sigma_{AL}'(T,E)=\sigma_{AL}'(T,0)\int_0^\infty dx\,\exp\{-x-[E/E_c(T)]^2x^3\}, \tag{1}$$

where

$$\sigma_{AL}'(T,0)=e^2/16\hbar d\epsilon, \tag{2}$$

$$E_c(T)=[16\sqrt{3}\,k_B T_c/\pi e\,\xi(0)]\epsilon^{3/2}\equiv E_{c0}\epsilon^{3/2}. \tag{3}$$

$\xi(0)$ is the GL coherence length at 0 K and $\epsilon=(T-T_c)/T_c$. At $E\gg E_c(T)$, Eq. (1) becomes

$$\sigma_{AL}'(T,E)=(e^2/16\hbar d)\Gamma(\tfrac{4}{3})(E_{c0}/E)^{2/3} \tag{4}$$

which is independent of temperature. Tsuzuki[8] later confirmed this result by a microscopic calculation using the temperature Green's function method. Experiments[10-13] on the nonlinear field dependence of the excess conductivity have been reported but the nonlinearity of the MT term has not been clarified in spite of its importance. Recently Maki[15] proposed that the electric field response of the MT term is given by

$$\sigma_{MT}'(T,E)=[\sigma'(T,0)/\ln(\epsilon/\delta)]\int_0^\infty (dx/x)[\exp(-\delta x/\epsilon)-\exp(-x)]\exp\{-[E/E_c(T)]^2x^3\}, \tag{5}$$