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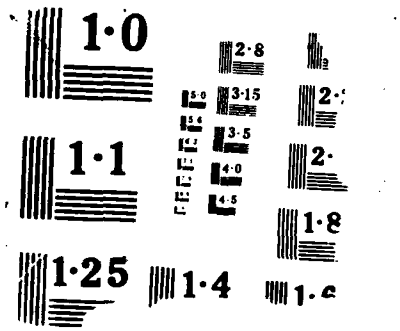
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Annual Letter Report

1987

I. Contract Information

-a) Title: "Far- and Mid-Infrared Properties of Metal-Insulator Composite Materials"

b) ONR Contract Number: N00014-85-K-0808

c) ONR Work Unit Number: 651-035

d) Principal Investigator: Dr. Robert P. Devaty

Personnel: Ralph E. Sherriff, Michael MacMillan, graduate students

e) ONR Scientific Officer: Dr. Wallace Smith

f) Period Covered: 87JAN01-87DEC31

II. Research Performed in 1987

A. Experiment

1. The Laboratory

Construction of the far infrared Fourier transform spectrometer was completed so that attention could now be focussed on experiments. Among the highlights are:

*SPECAC interferometer

-Design and construction of mylar beamsplitters, which can be used in place of the supplied free-standing wire grids to extend the high frequency cutoff of the instrument from $200/cm^{-1}$ to at least $350/cm^{-1}$.

-Design and construction of an output focussing mirror to replace the supplied TPX lens. Use of the mirror increases the throughput of the interferometer, especially at high frequencies.

-Design and construction of an optical chopper to modulate the Hg arc source for use with lock-in detection. The chopper can be used rather than phase modulation (vibrating the fixed mirror of the interferometer). Both methods have advantages and drawbacks, so it is desirable to have both.

*Software for data acquisition (about 3000 lines of Turbo Pascal) was written.

*Design and construction of a gas handling system for a bell jar vacuum evaporator so that it can be used to prepare small particles by inert gas evaporation.

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*Refurbishing an old leak checker, which now works.

*Electron Microscopy -- The principal investigator has been checked out on a JEM 2000 electron microscope in the Materials Science Department and has used it to characterize small Bi particles prepared by inert gas evaporation. The students are in training.

*The Nicolet System 740 FTIR spectrometer has just arrived and is under installation.

*Recent purchases include a vacuum oven, spare bolometer, digital plotter, and strip chart recorder.

2. Results

The principal experimental result is that we have observed the sphere plasma resonance in $\sim 1 \mu m$ Bi particles prepared by evaporation in argon and imbedded in paraffin. The particles were dispersed by repeated grinding in a freezer mill and pressing into pellets. The pellets were wedged or dimpled to avoid interference effects due to multiple reflections. Paraffin was chosen as the most transparent host up to 350 cm^{-1} from a number of candidates.

The frequency dependence of the absorption coefficient $\alpha(\omega)$ is shown on the plots. It was obtained by measuring transmission spectra for thick and thin pellets. Then

$$\alpha(\omega) = -\frac{1}{\Delta \ell} \quad \frac{T_{thick}(\omega)}{T_{thin}(\omega)}$$

where $\Delta \ell$ is the difference between the thicknesses of the pellets. Figure 1 shows the absorption coefficient due to paraffin alone and paraffin with added Bi. The parameter f is the volume fraction of Bi in the pellet. The paraffin shows two absorption lines (~ 80 cm^{-1} and ~ 240 cm^{-1}) as well as a background that increases with frequency. Although it is the most transparent host that we have found thus far, the paraffin makes a significant contribution to the absorption of the Bi-plus-paraffin pellets. To estimate the contribution of the Bi particles themselves, Figure 2 shows the absorption coefficient obtained by subtracting the paraffin curve from the Bi-plus-paraffin curve. The Bi sphere plasma resonance is clearly observed near 170 cm^{-1}. The position of the resonance is in at least qualitative agreement with the prediction of a simple model that treats the conduction electrons and holes in Bi using the Drude model. Use of subtraction to eliminate the contribution of paraffin to the absorption is not strictly valid. One consequence is that the paraffin lines are superimposed on the Bi absorption. The strong increase in absorption at the highest frequencies is not yet understood. It is not predicted by models based on free carriers and might be due to the onset of an interband transition.

Figure 3 shows the absorption coefficient divided by the volume fraction f for three samples with different values of f. The fact that the curves are not identical is evidence that clustering of the particles plays a role. The absorption coefficient is increasing at a greater-than-linear rate with volume fraction.

The origin of the linewidth of the resonance is not yet understood in detail. Possible contributions include: 1) the scattering time of carriers in bulk Bi, 2) scattering by the particle surface, 3) the superposition of multiple resonances due to the anisotropy of the carriers in Bi (We are in the process of performing an average over all orientations for Bi particles. For bisectrix-oriented particles, the only case we have worked out thus far, there are two resonances.), 4) fluctuations in the carrier density in the ensemble of particles due to confinement effects or surface states, and 5) interaction effects due to clustering of the particles.

Preliminary measurements show that the sphere resonance disappears for the smallest sizes. In one sample, a line sharper than the plasma resonance appeared near 190 cm^{-1}. We do not show these spectra because we wish to reproduce these interesting effects and investigate them thoroughly before making any claims.

The interest in size dependence can be motivated in at least two ways. If one takes the carrier densities for bulk Bi (3×10^{17} cm^{-3} for holes, 1×10^{17} c_m^{-3} for each of three electron pockets) and inverts them to estimate the volume per carrier, the result is that a sphere of about 200Å diameter is required for each electron-hole pair. Clearly, as the

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particle size is reduced from 1μm to below 100Å something should happen, whether it best be described as a metal-insulator transition or quantum size effect.

The question of discrete levels (quantum size effect) in small Bi particles can be examined qualitatively by the following simple estimate. The Kubo gap (mean energy level spacing at the Fermi energy, assuming no degeneracy of levels) is given by $\delta = 4E_F/3nV$ where E_F is the Fermi energy, n the carrier density, and V the volume of the particle. For Bi, $E_F = 0.028$ eV and $n = 1\times10^{17}$ cm^{-3} for each electron pocket, so

$$\delta(cm^{-1}) = \frac{5.75\times10^{9}}{(x[\text{Å}])^{3}} .$$

x is the particle diameter in Angstroms. Figure 4 is a plot of this equation. According to this estimate, the level spacing for 1μm particles is 5.75×10^{-3} cm^{-1}, much too small to be observed; whereas for 1000Å particles $\delta = 5.75$ cm^{-1}. For comparison, the level spacing for 50 Å Al particles is predicted to be 7.2 cm^{-1}. For particles below a few hundred Angstroms in diameter, δ becomes huge ($\delta = 5750$ cm^{-1} for x=100 Å). Once again, a simple argument leads to interesting size dependence.

B. Theory

1. Magnetic Field Dependence of Resonances in Small Bi Particles

The low carrier densities in Bi make it an ideal model system for the study of soid state plasmas. Cyclotron resonance lines provide information on the effective masses of carriers and the scattering times. Collective modes can also be observed, and the interaction of the cyclotron resonances with the collective excitations can be studied with magnetic fields that are attainable in the laboratory. The appropriate energies correspond to the far infrared region of the electromagnetic spectrum. For ordinary metals, this interaction is inaccessible experimentally.

The far infrared properties of bulk Bi have been studied in detail (1,2). Chin (2,3) applied far infrared magnetooptical spectroscopy to small particles of free standing Bi particles prepared by inert gas evaporation and other methods. The lamellar grating interferometer restricted the frequency coverage to 2-80 cm^{-1}. He observed a series of cyclotron resonance lines with unusual behavior: 1) The zero-field slopes of the lines could not be related to the effective masses of the carriers in bulk Bi. 2) At higher magnetic fields the dependence of the resonance frequencies on the field was nonlinear (Figure 5). Neither of these effects were explained.

In last year's letter report we described a simple model called "isotropic Bi," which was an attempt to explain Chin's data. The model was qualitatively successful, but did not take into account the anisotropy of the carriers in Bi. Over the past year we have improved the model to take the anisotropy into account. We describe the new results and predictions below. To develop the model, we benefitted greatly from published work on the interaction of electromagnetic radiation with a gyrotropic sphere (4,5). Much of the earlier interest was related to powdered semiconductors or electron-hole droplets in semiconductors.

We treat the carriers in Bi in the Drude model with a relaxation time. The conductivity tensor is calculated for each carrier separately using the appropriate effective mass tensor obtained from published work on bulk Bi (1). The frequency dependent complex conductivity tensor for Bi is obtained by summing the contribution of each carrier. The dielectric tensor is obtained from the conductivity tensor. In using the Drude model we have ignored many complications, including interband transitions, nonparabolic bands, field dependence of carrier concentrations, and size dependent corrections.

Absorption resonances are obtained from both the electric and magnetic dipole terms of the Mie series. We assume that the particles are sufficiently small that higher order terms can be neglected. The electric dipole absorption coefficient is

$$\alpha_{ED}(\omega) = \frac{9}{2}\sqrt{\varepsilon_0}f\frac{\omega}{c}\,\mathrm{Im}[\hat{E}_1^* \cdot \mathbf{B}^{-1} \cdot \hat{E}_1]$$

where ε_0 is the dielectric constant of the nonabsorbing host in which the particles are supported, f is the volume fraction of Bi particles imbedded in the host, ω is the angular frequency, c the speed of light, $\hat{E}_1$ a unit vector specifying the polarization of the electric field of the incident electromagnetic wave, and

$$\mathbf{B} = \mathbf{I} + 2\varepsilon_0 \, \boldsymbol{\varepsilon}^{-1}$$

where $\mathbf{I}$ is the identity matrix and $\boldsymbol{\varepsilon}$ is the dielectric tensor for Bi. For magnetic dipole absorption,

$$\alpha_{MD}(\omega) = \frac{1}{5}\sqrt{\varepsilon_0} f a^2 \left(\frac{\omega}{c}\right)^3 \mathrm{Im}[\hat{B}_1^* \cdot \overline{\boldsymbol{\varepsilon}^{-1}} \cdot \hat{B}_1]$$

where as is the particle radius, $\hat{B}_1$ a unit vector specifying the polarization of the magnetic field of the incident electromagnetic wave, and

$$\overline{\boldsymbol{\varepsilon}^{-1}} \equiv \mathrm{Tr}(\boldsymbol{\varepsilon}^{-1}) \, \mathbf{I} - (\boldsymbol{\varepsilon}^{-1})^T$$

where the superscript T denotes the transpose and Tr the trace of a matrix.

Figure 6 shows the field dependence of the electric dipole resonance frequencies for bisectrix oriented Bi particles. The Bi particles are assumed to be aligned so that the bisectrix axis is along the direction of the applied magnetic field, which is also the direction of propagation of the far infrared radiation (Faraday geometry). There is evidence that free standing Bi particles align in this fashion in a magnetic field (6). The behavior of the two resonances agrees very well with the data. Figure 7 shows the magnetic dipole resonances. One of these corresponds to the remaining resonance observed by Chin. The lowest three resonances (in frequency) are very weak, so it is no surprise that they were not observed. Figure 8 shows the magnetic field dependence of the resonances over a broader range of frequencies than studied by Chin. New field dependent resonances are predicted. At zero field these resonances extrapolate to the plasma sphere resonances. The complete picture shows the interaction between the cyclotron-like resonances with the collective plasma modes. We are interested in observing and studying these field dependent resonances. Since a magnetic field is required, we must travel to the far infrared lab at Cornell or to the High Field Facility at NRL. We plan to do so after sample preparation is under better control and the zero field behavior is well understood. At this time, we plan to publish this model after we have collected more data with which to compare.

2. Gyrotropic Sphere

Upon further investigation we learned that the magnetic dipole absorption as computed in the preceding section and for many similar models published in the literature is not correct (7,8). The problem arises because the quasistatic approximations in common use assume that the electric and magnetic multipole series of the Mie theory are separable. This assumption does not apply to the gyrotropic sphere, even in the long wavelength limit. As an example, consider electric dipole absorption, which corresponds to a collective oscillation of the carriers against a uniform compensating background (Here, we assume only one type of free carrier.). In a magnetic field, the motion of the oscillating charges will be deflected to produce eddy currents, which correspond to magnetic dipole absorption (to lowest order). The terms are no longer decoupied. The electric dipole term makes the largest contribution, but the magnetic dipole and electric quadrupole terms are of the same order. Thus, even in the long wavelength limit, the magnetic dipole and electric quadrupole absorption must be considered together. The result is not just a change in absorption strength, but the resonance frequencies are modified as well.

Furdyna et al. (7) and Goettig and Trzeciakowski (8) have computed the electromagnetic modes of a lossless gyrotropic sphere made up of a one-component plasma. Their results can easily be generalized to include multi-component plasmas, but loss mechanisms and anisotropic carrier masses have not been taken into account. However, this calculation does give the correct magnetic dipole-electric quadrupole frequencies in the long wavelength limit.

Ford and Werner (7) have given a complete solution for the interaction of electromagnetic radiation with a gyrotropic sphere for a specific form of the dielectric tensor in analogy with the Mie solution for the isotropic sphere. When they considered the long wavelength limit, their results did not agree with the calculation of Furdyna et al. (8). We have reexamined the calculation of Ford and Werner (7) and corrected errors in their approximations so that the two calculations now agree. However, our results based on the theory of Ford and Werner are more general because any dielectric tensor consistent with the assumed symmetry may be used. In particular, losses may be included. Our results also agree with Mie theory in the zero field limit. We do not present the equations here due to their complexity, but a manuscript is nearly ready for submission for publication.

Unfortunately, the calculation of Ford and Werner (7) and consequently our new results do not apply to Bi due to the anisotropy. However, the new results allow us to argue that the magnetic dipole term as computed using the old, incorrect approximation is not that bad for Bi. The reason is that a correction to the old model is a term proportional to the dielectric constant of the supporting host, which appears in the denominator and thus plays a role in determining the resonance frequencies. However, the frequency independent contribution to the dielectric tensor of Bi due to core polarizability, etc., is so large that the correction should be negligible.

III. Plans for 1988

We plan to continue experiments on small Bi particles and to initiate experimental work on the infrared properties of cermet films and other metal-insulator composite materials. The experimental work should continue to motivate development and refinement of theoretical models.

We plan to continue with far infrared studies of Bi particles imbedded in hosts such as paraffin in zero magnetic field. We shall focus on characterization of the material, particularly by electron microscopy, and improvements in sample preparation. If the particles are clustered and this presents a problem, we would modify the preparation procedures and perhaps replace paraffin with another substrate. The principal goal of the spectroscopic studies will be to measure and understand the dependence of the observed resonance on particle size. The interesting physics is the possibility of a semimetal-semiconductor transition and/or quantum size effects. We also want to understand the details of the sphere resonance, such as the origins of the linewidth. Theoretical models will be used to interpret the data. For example, we are in the process of taking an orientational average for Bi particles in zero applied field using the model described earlier in order to predict the shape of the resonance.

In this model, the measured bulk properties of Bi are used along with known data for, e.g., the volume fraction of particles. Only the scattering time is adjustable.

Once the Nicolet System 740 is installed and checked out, work will begin on the infrared properties of metal-insulator composites. The present philosophy is to study two or more selected systems in parallel in order to perform comparisons. The studies using the Nicolet will be performed at room temperature. In the far infrared, we can work at low temperatures and measure temperature dependence using the SPECAC and its associated cryostat, although a new insert must be designed and constructed. One system of interest is Pt/Al_2O_3 cermet films deposited on sapphire substrates. These samples are on hand and cover a broad range of volume fractions. A program to extract optical constants from measurements of transmission and reflection of these thin films is under development. A second system of interest is inert gas evaporated particles imbedded in an alkali halide host. A number of metals are strong candidates: Pt would provide the closest comparison wit the cermet films, Ag would provide a direct comparison with published work (10), while Au would provide new information on a relatively well understood simple metal. Pt has rather complicated optical properties, so it would be the most difficult metal to model.

Further interesting questions such as those discussed in the proposal will be examined as time permits.

IV. Index of Technical Reports: None, but there was an End-of-the-Fiscal-Year Letter.

V. Index of Publications and Presentations

1) "Far Infrared Magnetic Field Induced Absorption by Small Bismuth Particles," R.P. Devaty, A.K. Chin, and A.J. Sievers, Bull. Am. Phys. Soc. 32, 485 (1987).
2) "Extinction of Electromagnetic Waves by a Small Gyrotropic Sphere." R.P. Devaty, manuscript to be submitted for publication.
3) "Plasma Resonance in Small Bismuth Particles," R.E. Sherriff and R.P. Devaty, to be presented at the APS March Meeting, New Orleans, LA, March 21-25, 1988.

4) "Extinction Cross Section for a Small Gyrotropic Sphere," R.P. Devaty, to be presented at the APS March Meeting, New Orleans, LA, March 21-25, 1988.

VI. References

1. R.L. Blewitt and A.J. Sievers, J. Low Temp. Phys. 13. 617 (1973).
2. A.K. Chin, Ph.D. Thesis, Cornell University, 1977 (Materials Science Center Report No. 2823), unpublished.
3. R.P. Devaty, A.K. Chin, and A.J. Sievers, Bull. Am. Phys. Soc. 32, 485 (1987).
4. J.R. Dixon, Jr. and J.K. Furdyna, Phys. Rev. B18, 6770 (1978), and references therein.
5. R.S. Markiewicz, Phys. Rev. B18, 4260 (1978), and references therein.
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7. G.W. Ford and S.A. Werner, Phys. Rev. B18, 6752 (1978).
8. J.K. Furdyna, S. Goettig, J. Mycielski, and W. Trzeciakowski, Phys. Rev. B31, 7714 (1985).
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10. K.D. Cummings, J.C. Garland, and D.B. Tanner, Phys. Rev. B30, 4170 (1984).

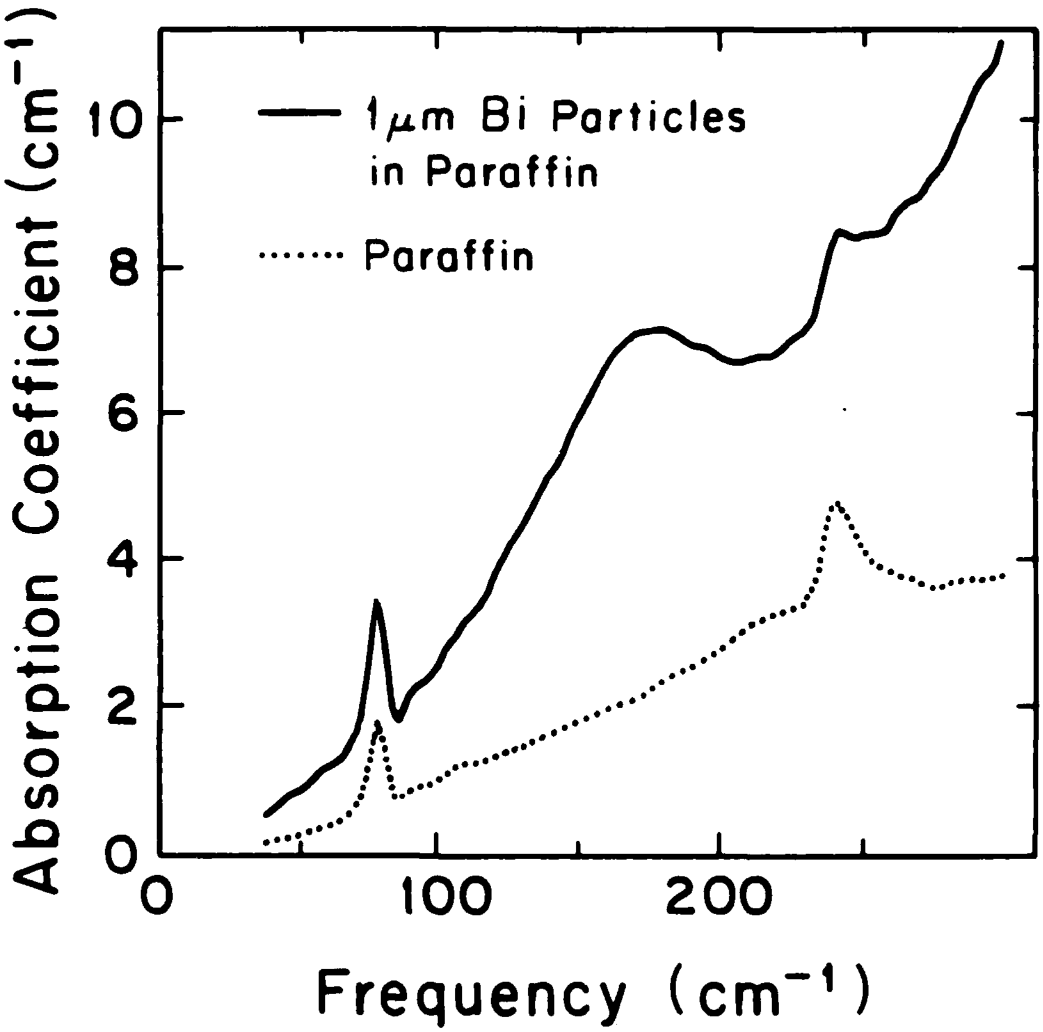

Figure 1: Far infrared absorption coefficient for ~1 μm diameter Bi particles dispersed in paraffin (solid line) and paraffin alone (dotted line).

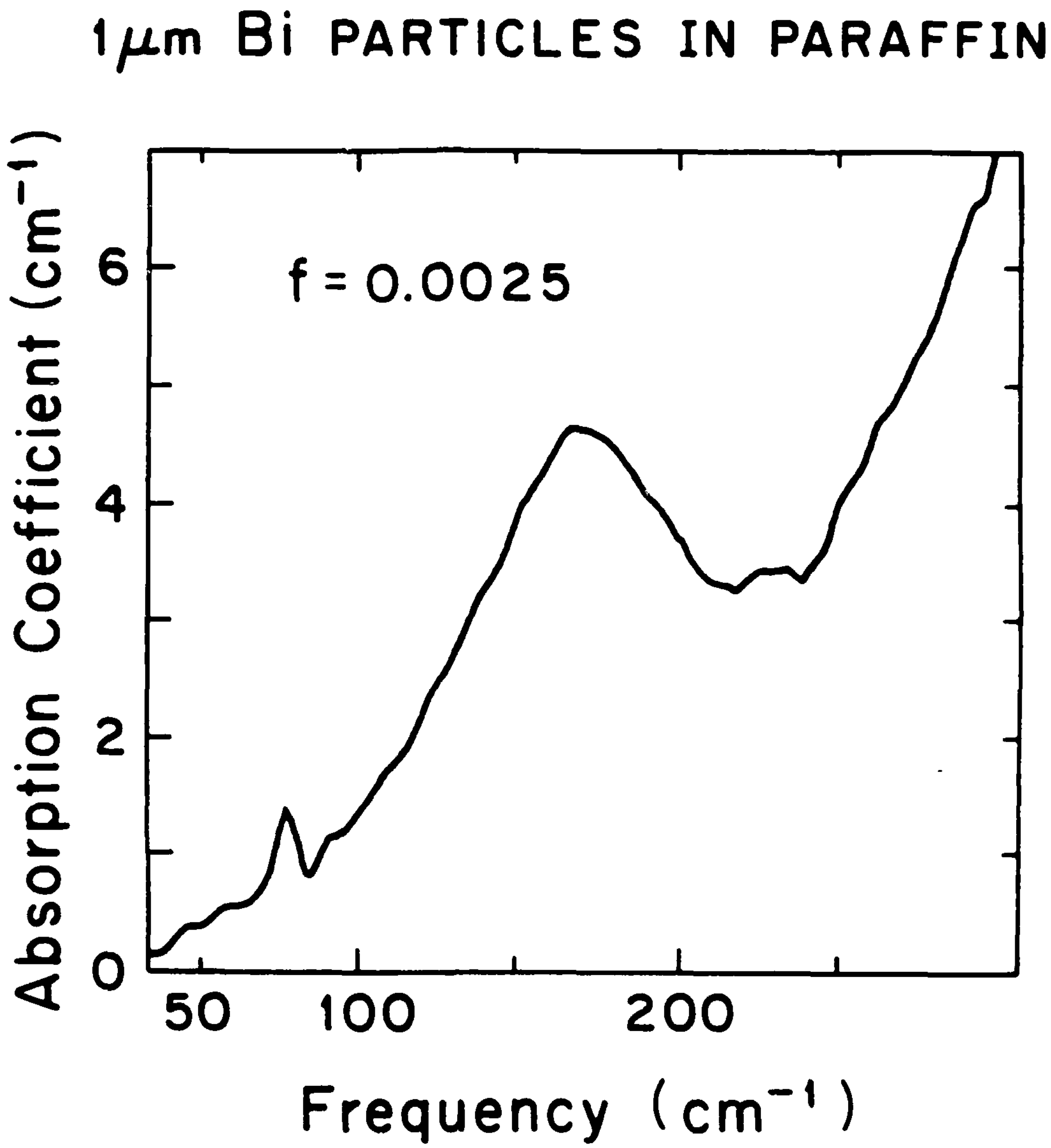

Figure 2: Far infrared absorption coefficient for ~1 μm Bi particles. This estimate of the absorption due to the particles alone was obtained by subtracting the paraffin absorption from the bismuth-plus-paraffin absorption (the curves shown in Fig. 1). The plasma sphere resonance appears at 170 cm^{-1}. The peaks at ~80 cm^{-1} and ~240 cm^{-1} are paraffin lines. The increase in absorption at the highest frequencies may be the onset of an interband transition.

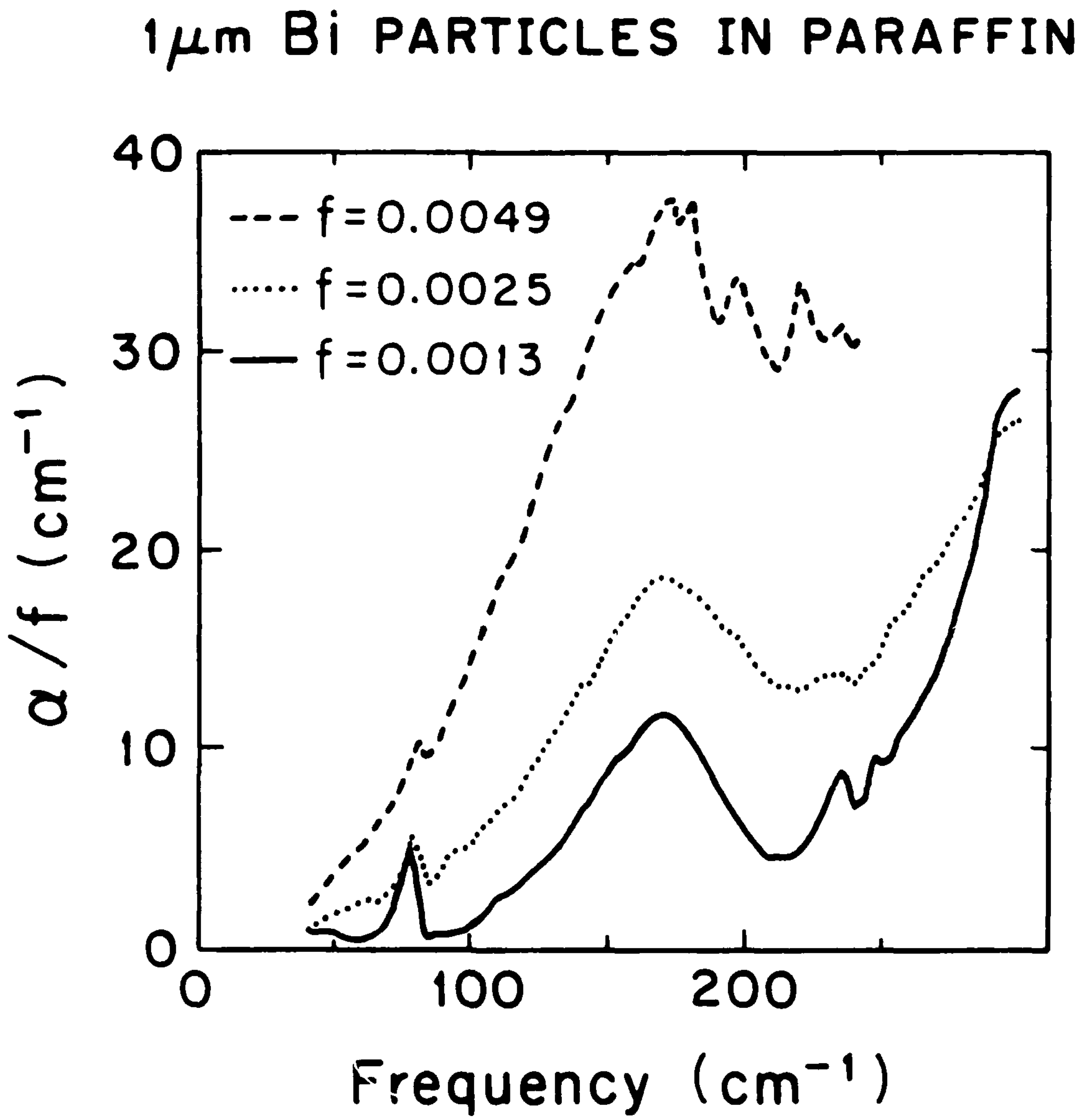

Figure 3: Volume fraction dependence of the absorption coefficient measured for Bi particles in paraffin. The absorption coefficient reduced by the volume fraction of Bi is shown for three values of f. α/f increases with f, which is evidence that interaction between the particles contributes to the measured absorption.

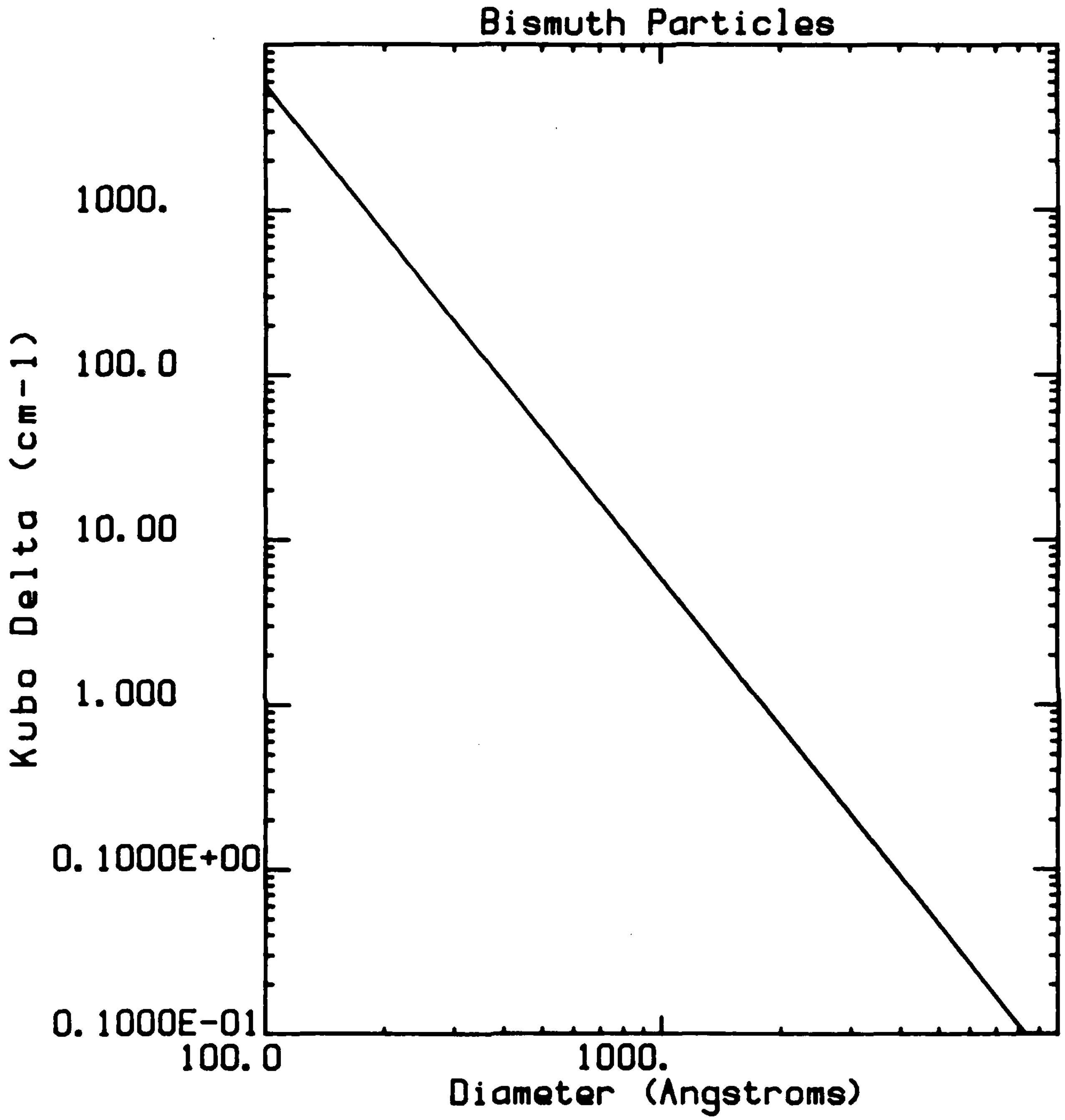

Figure 4: Theoretical estimate of the mean level spacing at the Fermi surface for small Bi particles versus particle diameter.

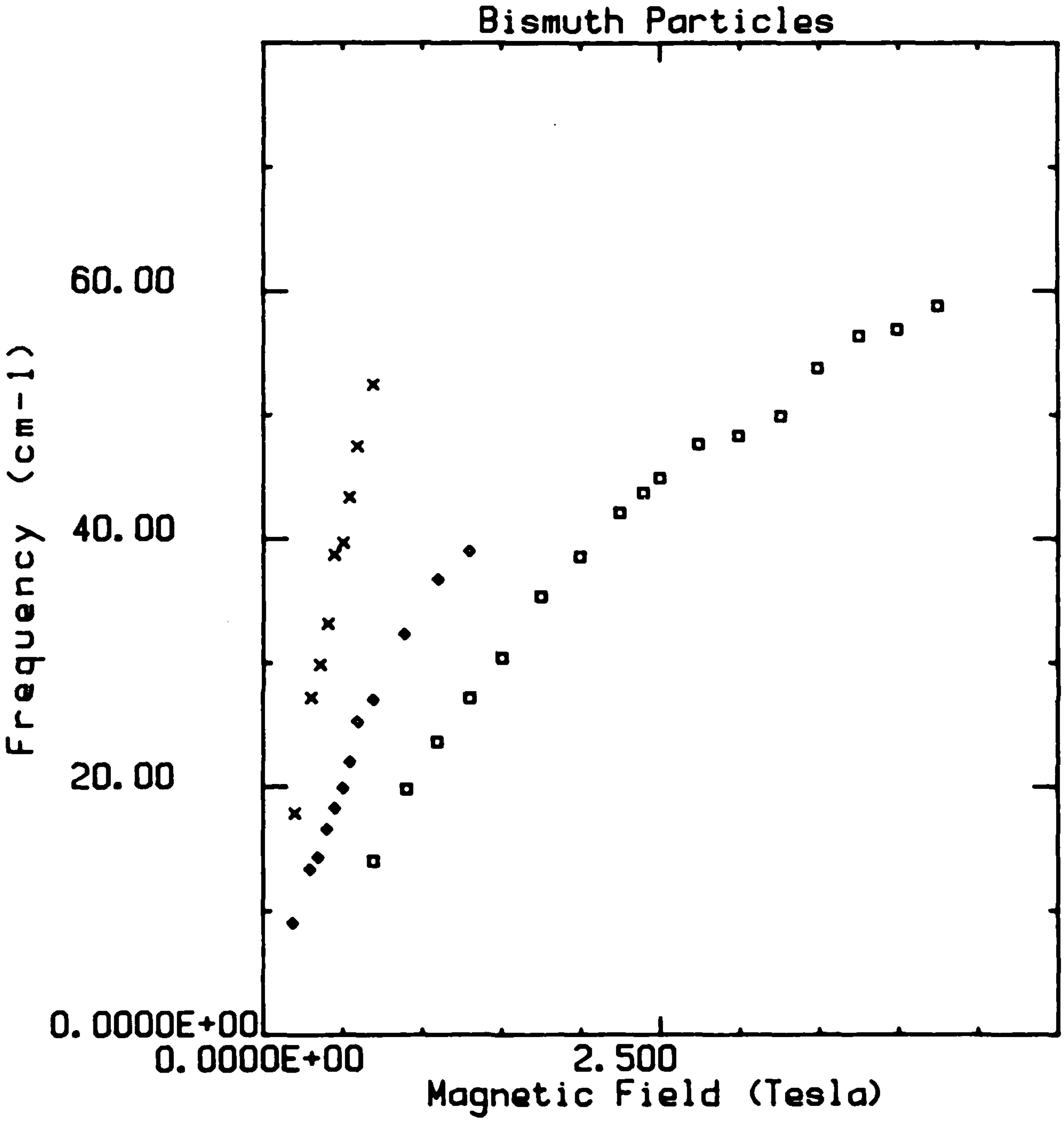

Figure 5: Magnetic field dependent resonances observed in 4000 Å diameter free-standing inert gas evaporated Bi particles by A.K. Chin (2).

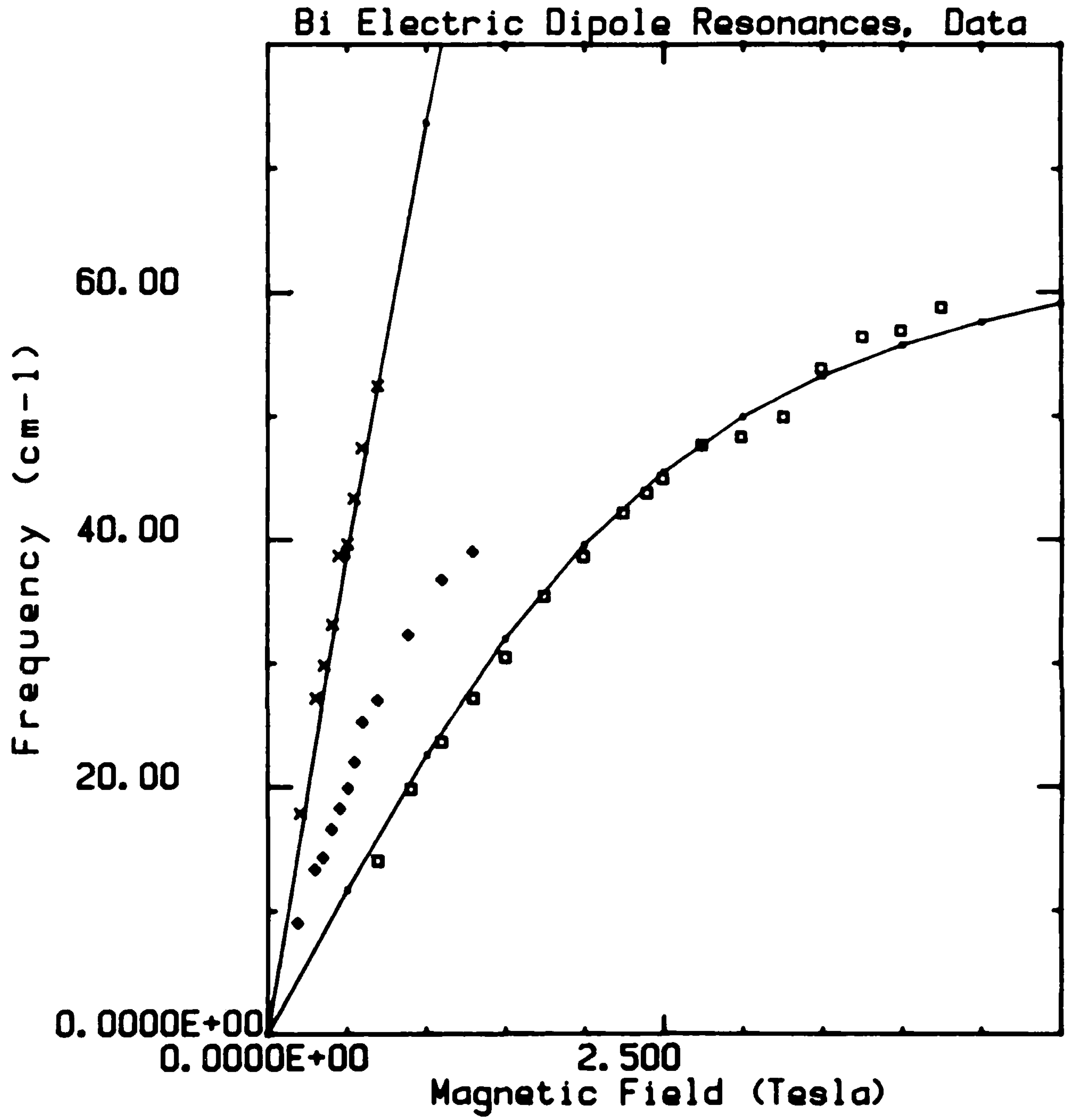

Figure 6: Comparison of magnetic field dependence of computed electric dipole resonances (dots connected by solid lines) with Chin's (2) data. No parameters were adjusted. Parameters used were those for bulk Bi given by Blewitt and Sievers (1). The agreement is good.

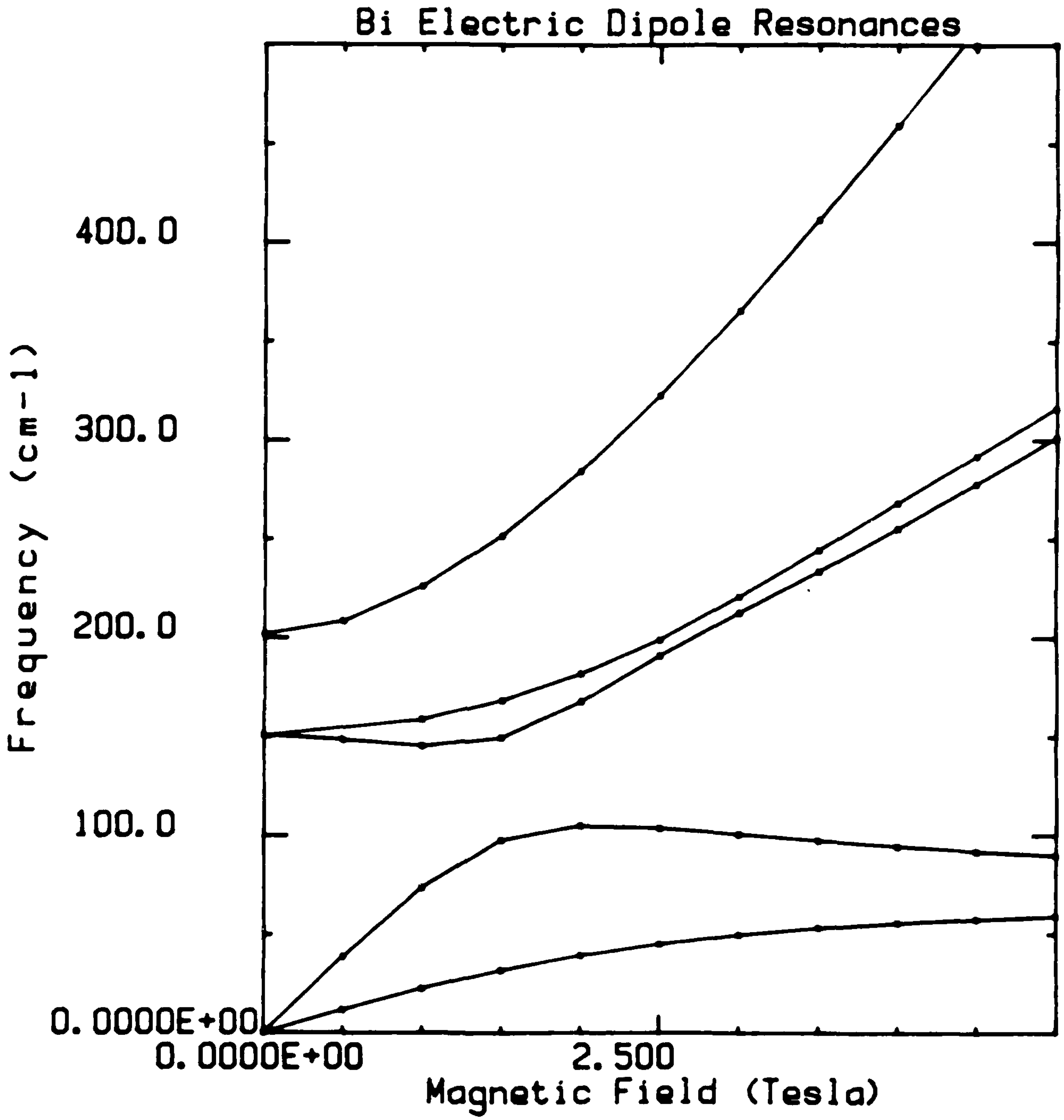

Figure 7: Predicted magnetic field dependence of electric dipole resonances in small Bi particles. The zero field resonances between 150 and 200 cm^{-1} are the plasma sphere resonances currently under investigation. This model treats free carriers only, but includes the anisotropy of the effective mass tensors of the electrons and holes in Bi.

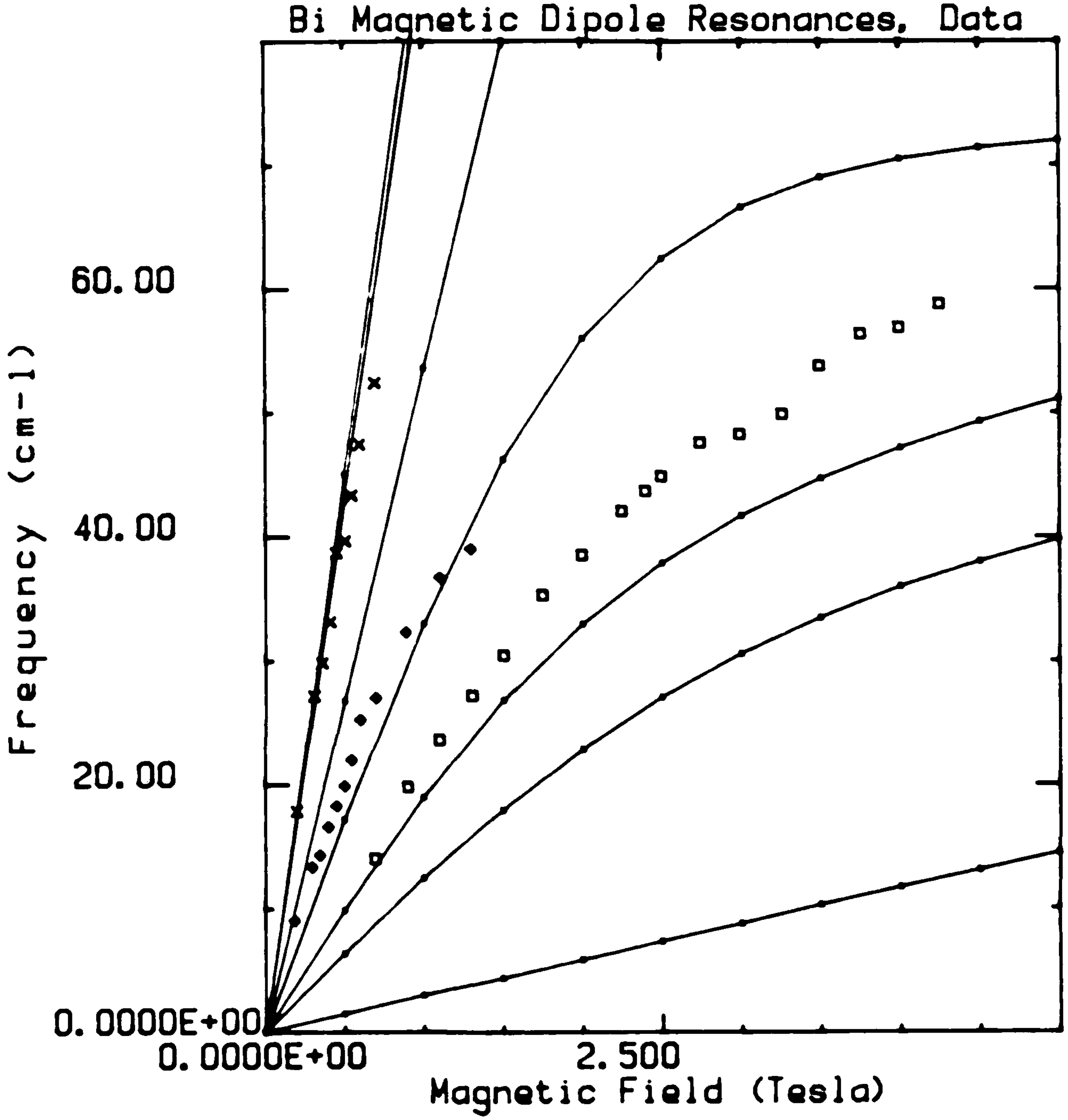

Figure 8: Comparison of the predicted magnetic field dependence of magnetic dipole resonances (dots connected by lines) with the data of A.K. Chin (2). The remaining resonance is consistent with one of the magnetic dipole resonances. The strengths of the three computed resonances having the lowest frequencies are so small that it is not expected that they would have been observed in the experiment. The model for magnetic dipole absorption is not rigorously correct.

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