Functions of Argon" (to be published).

[15] P. G. Mikolaj and C. J. Pings, "Direct Correlation Functions of Argon" (to be published).

[16] L. Jansen, Phil. Mag. 8, 1305 (1963).

[17] N. R. Kestner and O. Sinanoglu, J. Chem. Phys. 38, 1730 (1963).

[18] J. K. Percus, Phys. Rev. Letters 8, 462 (1962).

[19] L. Verlet, Physica 30, 95 (1964).

DIFFERENCES IN THE CHARACTERISTIC ELECTRON ENERGY-LOSS SPECTRA OF SOLID AND LIQUID BISMUTH*

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A number of types of experiments have been recently performed to determine the extent to which the electronic properties of solid metals may change on melting.[1-4] The results of some experiments indicate that for certain metals the valence electron-band structure of the solid does not appear to change significantly on melting while for other metals there may be appreciable changes. Knight, Berger, and Heine[4] conclude that where there is appreciable change in the short-range atomic structure on melting, such as is known to occur for Bi and Ga, changes in the electronic properties would be expected. A report is given in this Letter of measurements of the characteristic energy loss spectra of electrons scattered by solid and liquid Bi; differences in the loss spectra are indicative of differences in the band structure of Bi in the solid and liquid states.

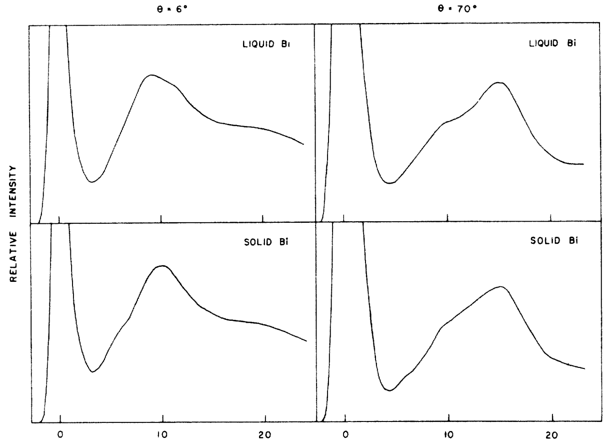

FIG. 1. Characteristic loss spectra of electrons scattered by solid and liquid Bi for total scattering angles θ of 6° and 70°.

A Bi specimen, typically 0.5 to 1 g, was supported by a graphite rod that could be heated by electron bombardment. After melting, the specimen was approximately spheroidal in shape. A platinum versus platinum-10% rhodium thermocouple was clamped to the graphite rod about $\frac{1}{16}$ inch below the specimen and could be used to monitor the specimen temperature.

The primary electron beam, of 8-keV energy, was incident on the specimen near a vertical region at an undetermined angle. Electrons scattered through a variable known angle were decelerated to a standard energy of about 45 eV, dispersed in a hemispherical electrostatic analyzer, and detected with an electron multiplier. Characteristic loss spectra were obtained on an *X*-*Y* recorder with the multiplier output pulse rate shown as a function of the sweep voltage applied to the primary gun cathode. The measured width at half-maximum intensity of the peak of electrons scattered without energy loss was 1.6 eV.

Characteristic loss spectra of solid and liquid Bi are shown in Fig. 1 for total electron scattering angles θ of 6° and 70°. As in a previous investigation of the energy-loss spectra of evaporated Bi films,[5] peaks at ≈10 and ≈15 eV loss are observed and interpreted as being due to excitation of surface[6] and volume[7] plasmons, respectively. In the present work, however, the excitation of the surface loss predominates in both solid and liquid at $\theta = 6°$ while the volume loss predominates at $\theta = 70°$, due to the varying electron penetration.[8] It was found necessary to heat the liquid Bi initially to about 400°C to dissolve or decompose the surface oxide or other contaminating layer and so to observe the structure that changed reversibly in character across the melting point.

The loss spectra of liquid and solid Bi differ in two related ways. Firstly, an additional peak is observed at 11.5 ± 0.3 eV loss in the spectrum of liquid Bi (and not in the solid), while a small loss peak is observed in the spectrum of solid

Bi at 5.3 ± 0.2 eV (and not in the liquid). Secondly, plots of the positions of the surface and volume plasmon losses as a function of temperature, shown in Fig. 2, reveal that while the volume loss increases in magnitude on melting (by 2.2 ± 0.7 %), the surface loss decreases in value on melting (by 5.6 ± 1.5 %).

The positions of characteristic energy-loss peaks can be described in terms of a frequency-dependent dielectric constant $\epsilon(\omega)$.[9] The condition for the volume-plasmon resonance[7] is $\epsilon(\omega = \omega_v) = 0$, and the condition for the surface-plasmon resonance[6] at a Bi-vacuum interface is $\epsilon(\omega = \omega_s) = -1$.[10] The dashed lines in Fig. 2 show the variation of position of the volume and surface losses with temperature expected using the simple free-electron dielectric constant $\epsilon(\omega) = 1 - \omega_p^2/\omega^2$, where $\omega_p = (4\pi N e^2/m)^{1/2}$ is the plasma frequency and N is the electron density.[11] It can be seen that this form of $\epsilon(\omega)$ is inadequate to describe either the positions of the plasmon losses in solid or liquid or the direction of change in the surface loss across the melting point. As there is no apparent change in the half-widths of the plasmon loss peaks on melting, the inclusion of a frequency-independent relaxation time in the free-electron $\epsilon(\omega)$ would be insufficient to interpret the data of Fig. 2.

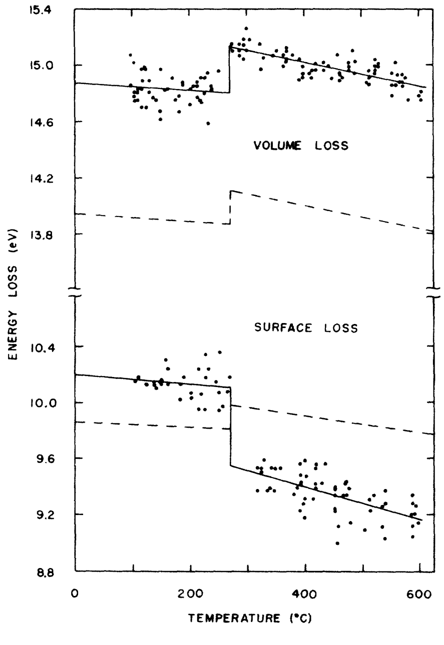

FIG. 2. Observed variation in the positions of the surface and volume plasmon losses in bismuth as a function of temperature. The solid lines are least-squares straight-line fits to the experimental points (scatter due mainly to random errors in locating the peak positions), and the dashed lines show the peak-position variation expected using free-electron theory for $\epsilon(\omega)$.

The contribution of interband transitions to $\epsilon(\omega)$ can be expressed in the form[12,13]

$$\epsilon(\omega) = 1 - \frac{f_0 \omega_p^2}{\omega^2} - \sum_{i=1}^{n} \frac{\omega_p^2 f_i}{\omega^2 - \omega_i^2}, \qquad (1)$$

where f_0 represents the free-electron oscillator strength, f_i represents the oscillator strength corresponding to the transition frequency ω_i, and where the effects of damping have again been ignored. It is apparent from Fig. 2 that the part of $\epsilon(\omega)$ due to the sum in Eq. (1) must be different in solid and liquid Bi. That is, there must be a different spectrum of optical transitions and hence a different band structure in the solid and liquid states.

Pines[12] has suggested using Eq. (1) with the resonance conditions for plasmon excitation to determine the position and oscillator strength of an interband transition in the case $n = 1$, should there be a single strong transition in the region of interest. Using the experimental values of ω_s and ω_v and also the oscillator-strength sum rule

$$\left(\sum_{i=0}^{n} f_i = 1 \right),$$

it can be shown that $\hbar\omega_1 = 13.4$ eV and $f_1 = 0.04$ for liquid Bi. An electron energy loss corresponding to this computed value of $\hbar\omega_1$ would be expected[13] at about 12.2 eV. This latter value agrees well, considering the assumption $n = 1$ and the neglect of damping, with the position of the structure observed at 11.5 eV. For solid Bi, it is necessary to assume $n \geq 2$; using the experimentally determined position $\hbar\omega_1 = 5.3$ eV, the resonance conditions can be satisfied by a small-oscillator-strength transition (undetectable in this experiment) if $\hbar\omega_2 \approx 14$ eV. The measurements of Cardona and Greenaway[14] show an optical absorption peak[15] in solid Bi at about 5.3 eV, though no structure in their reflectivity curve is apparent in the vicinity of 14 eV.

With more optical data, it would be possible to include damping terms in a more realistic version of Eq. (1). Nevertheless, it would be likely that there would be more than one significant contribution to $\epsilon(\omega)$ from interband transitions in both solid and liquid Bi; such contributions can be large even for small f_i when $\omega_i \approx \omega_v$ or $\omega_i \approx \omega_s$.

Two comparisons of electron energy-loss spectra in solid and liquid metals have been previously reported.[16] Boersch et al. show that the spectrum from liquid Hg is different than that from solid Hg, although there is a strong similarity in the spectra for the two states. Arifov and Kasymov, however, find no difference in the loss spectra of Sn and In when interchanged between the solid and liquid states.

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[1] N. E. Cusack, Repts. Progr. Phys. 26, 361 (1963).

[2] J. A. Catterall and J. Trotter, Phil. Mag. 8, 897 (1963).

[3] J. H. Kusmiss and A. T. Stewart, Bull. Am. Phys. Soc. 10, 482 (1965).

[4] W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. (N.Y.) 8, 173 (1959).

[5] C. J. Powell, Proc. Phys. Soc. (London) 76, 593 (1960).

[6] R. H. Ritchie, Phys. Rev. 106, 874 (1957); E. A. Stern and R. A. Ferrell, Phys. Rev. 120, 130 (1960).

[7] D. Pines, Rev. Mod. Phys. 28, 184 (1956).

[8] C. J. Powell, Bull. Am. Phys. Soc. 10, 433 (1965).

[9] L. Marton, L. B. Leder, and H. Mendlowitz, Advances in Electronics and Electron Physics, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 183; H. Frohlich and H. Pelzer, Proc. Phys. Soc. (London) A68, 529 (1955); J. Hubbard, Proc. Phys. Soc. (London) A68, 976 (1955).

[10] More precisely, volume and surface energy-loss peaks are observed for maxima in $\mathrm{Im}(1/\epsilon)$ and $\mathrm{Im}[1/(1+\epsilon)]$ at frequencies near $\epsilon = 0$ and $\epsilon = -1$, respectively. While the inclusion of finite damping terms in $\epsilon(\omega)$ would mean a difference of about 1 eV in the energies for which $\mathrm{Re}\epsilon = 0$ and $d[\mathrm{Im}(1/\epsilon)]/d\omega = 0$ [H. Mendlowitz, J. Opt. Soc. Am. 50, 739 (1960)], the exact resonance conditions are not used here as it is not feasible to improve the analysis without additional data.

[11] Data for the variation of Bi density with temperature were obtained from J. A. Cahill and A. D. Kirshenbaum, J. Inorg. Nucl. Chem. 25, 501 (1963).

[12] D. Pines, Physica, Suppl. 26, 103 (1960).

[13] C. B. Wilson, Proc. Phys. Soc. (London) 76, 481 (1960).

[14] M. Cardona and D. L. Greenaway, Phys. Rev. 133, A1685 (1964).

[15] There is zero optical transmittance in this region [W. C. Walker, O. P. Rustgi, and G. L. Weissler, J. Opt. Soc. Am. 49, 471 (1959), and O. P. Rustgi (private communication)].

[16] H. Boersch, J. Geiger, H. Hellwig, and H. Michel, Z. Physik 169, 252 (1962); U. A. Arifov and A. Kh. Kasymov, Dokl. Akad. Nauk SSSR 158, 82 (1964) [translation: Soviet Phys.—Doklady 9, 789 (1965)].

DETERMINATION OF THE LOCALIZED IMPURITY SPIN STATES IN FeCl$_2$

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Motions of magnetic impurities in ferromagnetic or antiferromagnetic materials are usually masked by the predominant spin-wave motions of host spins. However, it is possible to observe the separated motion of impurity spins or impurity-localized spin waves without exciting the host-spin system if magnetic characters of the host and impurity spins are considerably different from each other. In this communication we report the first observation of such an electron-spin resonance of Fe^{3+} impurity spins in the metamagnetic substance FeCl$_2$ at low temperatures, and determine the exchange coupling constants of the intralayer and interlayer interactions between Fe^{3+} and Fe^{2+} spins by investigating both the antiferromagnetic and ferromagnetic spin configurations of the host-spin system under external magnetic fields.

We investigated the magnetic resonance of a single crystal of FeCl$_2$ containing $\leq 1\%$ Fe^{3+} ions by microwaves of the 35-, 50-, and 70-Gc/sec regions between 4.2 and 1.5°K using pulsed magnetic fields up to 50 kOe.[1] Several resonance lines having systematic frequency dependences were observed, and a frequency-field diagram of the resonance points is shown in Fig. 1. Considering the frequency and angular dependences, absorption intensities, and the temperature variation of the resonance lines, we concluded that these resonances come from the substitutional Fe^{3+} impurity spins in FeCl$_2$.

The crystal structure of FeCl$_2$ is isomorphous with that of CdCl$_2$ having a layer structure along the c plane. There is a strong ferromagnetic exchange interaction among the intralayer ferrous ions, while the interlayer interaction is weak and antiferromagnetic. A strong uniax-